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Xanthate-Mediated Radical Polymerization of *N*-Vinylpyrrolidone in Fluoroalcohols for Simultaneous Control of Molecular Weight and Tacticity

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ABSTRACT: The simultaneous control of the tacticity and molecular weight of poly(*N*-vinylpyrrolidone) during radical polymerization is reported for the first time. For molecular weight control, xanthates of (*O*-ethylxanthylmethyl)benzene and [1-(*O*-ethylxanthyl)ethyl]benzene were used as RAFT/MADIX chain transfer agents (CTAs) for the radical polymerization of *N*-vinylpyrrolidone (NVP). Both led to a controlled/living radical polymerization, and the latter showed higher chain transfer ability under the optimal conditions; the molecular weight distribution was 1.36 when the molecular weight was up to 26 700. The polymerization was studied between 20 and 120 °C and at various concentrations of CTA. All the polymerizations showed an induction period and rate retardation dependent on both the concentration of CTA and temperature. For tacticity control, the polymerization was carried out in fluoroalcohols via a conventional radical process without CTAs to give syndiotactic polymers. The polymer tacticity was dependent on the amount of the fluoroalcohol, and a more acidic and bulkier fluoroalcohol led to a higher syndiotacticity. Especially with $(CF_3)_3COH$, the *r* dyad increased to 62.6% from 53.5% for the atactic poly(NVP) obtained in the usual solvents. The ^1H NMR analysis of the mixture of NVP and the fluoroalcohols indicated that a 1:1 hydrogen-bonding complex was formed, suggesting that the complex was responsible for the tacticity control of the polymer. When the CTA was used in the fluoroalcohols, the living and syndiospecific polymerization proceeded to enable the simultaneous control of the molecular weight and the tacticity.

Introduction

N-Vinylpyrrolidone or *N*-vinyl-2-pyrrolidinone (NVP) is representative of the unconjugated monomers that can be polymerized into high molecular weight polymers only by a radical mechanism similar to vinyl acetate.[1−3] Although the monomer contains an amide group on the substituents similar to acrylamides, the nitrogen is directly attached to the vinyl group, and thus the vinyl group is not conjugated with the carbonyl group unlike acrylamides. This characteristic monomer structure most probably provides the unique feature of its polymer, which has been attracting much attention in the chemical, medical, and material fields because of a unique combination of properties, including the solubility in water and in organic solvents, very low toxicity, high complexing ability, good film-forming characteristics, and the ability to adhere to a number of substrates since its discovery in the 1930s. These physical properties may definitely depend on the polymer structures, such as molecular weight and tacticity, and thus the control of the polymerization will contribute to the development of more sophisticated materials based on the polymers.

These past 10 years have witnessed tremendous developments in the living or controlled radical polymerizations, most of which can be categorized into three processes, such as the nitroxide-mediated polymerization (NMP),[4,5] metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),[6−10] and polymerization controlled by reversible addition−fragmentation chain transfer (RAFT) or macromolecular design via the interchange of xanthates (MADIX).[11,12] These systems are most frequently employed because they can produce polymers with well-controlled molecular weights, narrow molecular weight distributions, and desired architecture such as block, graft, and star polymers from a wide range of conjugated vinyl monomers.

In contrast, as for the nonconjugated monomers, such as vinyl acetate (VAc) and vinyl chloride (VC), the molecular weight control had been quite difficult due to the highly reactive radical species derived from them and to the lack of suitable reagents or catalysts that can induce a fast interconversion between the highly reactive radical and the dormant species. However, in recent years, there appeared effective systems for VAc based on the MADIX/RAFT,[13−18] iron-catalyzed,[19] degenerative iodine-transfer,[20,21] and cobalt-mediated[22] processes and for VC with the copper-catalyzed[23] and nonmetal-catalyzed[24] ones. Another novel effective process with organotellium[25] or organostibine[26] proved highly effective for a wide range of monomers from conjugated to nonconjugated monomers such as VAc and NVP. Apart from the antimony-based system,[26] there were no relevant and effective systems for NVP. A patent referred to the living radical polymerization of NVP by RAFT, but no details were available.[11e] A xanthate with a poly(ethylene glycol) segment was employed for the polymerization of *N*-vinylformamide

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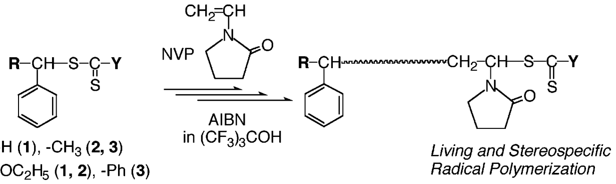
Scheme 1



that produced block copolymers with relatively broad molecular weight distributions.[27] Thus, the living or controlled radical polymerization of NVP has not yet been completely established.

On the other hand, tacticity control during radical polymerizations has become possible[28] for commercially available vinyl monomers such as vinyl esters,[29] methacrylates,[30] and (meth)acrylamides[31,32] using fluoroalcohols or hexamethylphosphoramide as solvents or Lewis acids as additives. For example, the syndiospecific radical polymerization of VAc proceeds in a bulky fluoroalcohol, which most probably interacts with the carbonyl group of the monomer and/or the growing chain end via hydrogen bonding. In contrast, the tacticity control of poly(NVP) has not been investigated and not yet attained. The conventional radical polymerization of NVP led to almost atactic polymers ($r \sim 53.5\%$), and the triad composition remained virtually unchanged independently of the polymerization temperature from −78 to 100 °C ($mm/mr/rr = 24/43/33$).[33] Among a variety of solvents, only water had a little effect on the tacticity of the polymers ($r \sim 55\%$).[34]

In this study, we thus investigated the living radical polymerization of NVP in the presence of xanthates (**1** and **2**) or dithioesters (**3**) and the syndiospecific radical polymerization of NVP in fluoroalcohols (Scheme 1). By combining the two polymerizations, we further studied the simultaneous control of the molecular weights and the tacticity using the MADIX agents in fluoroalcohols for the NVP polymerization. The stereospecific living/controlled radical polymerization is still one of the unattained targets in controlled radical polymerization and has been reported quite recently for some monomers such as acrylamides,[35−37] methacrylates,[37b,38] and VC[24e] with a combination of the living and stereospecific radical processes. However, there have been no such examples for combining the RAFT/MADIX systems with the fluoroalcohol-mediated stereospecific processes even for other monomers.

Experimental Section

Materials. *N*-Vinylpyrrolidone (Kishida, >98%) was distilled twice under reduced pressure to remove the inhibitors. α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. Di-*tert*-butyl peroxide (tBP) (Kishida, 98%), 2,2,2-trifluoroethanol (Aldrich, 99%), 1,1,1,3,3,3-hexafluoro-2-propanol (Wako, >99%), and perfluoro-*tert*-butyl alcohol (Aldrich, 99%) were used as received. *n*-Bu_3B (1 M solution in THF, Aldrich) was used after removal of the THF under reduced pressure. 1-Phenylethyl phenyldithioacetate (**3**) was prepared according to the literature.[39] All other reagents were purified by usual methods.

[(*O*-Ethylxanthyl)methyl]benzene (1).[12] The synthesis was conducted by stirring ethanol (40 mL) and KOH (5.6 g, 0.1 mol) until a clear solution was formed. CS_2 (20 mL) was added into the solution slowly, and the mixture was stirred for 10 h at room temperature before excessive CS_2 was distilled off at 70 °C. Benzyl chloride (9.5 mL) in 20 mL of ethanol was added to the residual solution, and the mixture was further stirred at 55−65 °C for 5 h. After removal of the inorganic salt and most of the ethanol, 50 mL of water was added and the solution was extracted with diethyl ether (3 × 40 mL); the combined organic layer was dried over $MgSO_4$. Removal of the inorganic salt and evaporation of the solvent afforded a yellow oil product: 13.5 g, 64%. ^1H NMR (ppm, $CDCl_3$), δ: 1.42 (t, 3H, CH_3), 4.64 (tetra, 2H, CH_2), 4.38 (s, 2H, CH_2Ph), 7.2−7.4 (m, 5H, Ph).

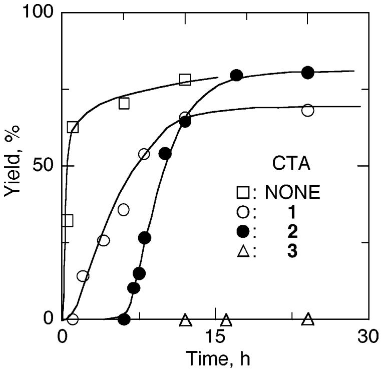


Figure 1. AIBN-induced bulk radical polymerization of NVP in the absence and the presence of chain transfer agents at 60 °C: $[NVP]_0 = 9.46$ M (bulk); $[NVP]_0/[\text{chain transfer agents}]_0/[AIBN]_0 = 150/1/0.2$. Chain transfer agents: (○) **1**, (●) **2**, (△) **3**, (□) none.

[1-(*O*-Ethylxanthyl)ethyl]benzene (2).[12] The synthesis was conducted similar to the synthesis of **1** by replacing benzyl chloride with (1-bromoethyl)benzene. Yield yellow oil: 62.5%. ^1H NMR (ppm, $CDCl_3$), δ: 1.26 (t, 3H, CH_3), 1.58 (d, 3H, CH_3), 4.49 (tetra, 2H, CH_2), 4.77 (tetra, 1H, *CH*Ph), 7.1−7.4 (m, 5H, Ph).

Measurements. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz) and a Varian INOVA 500 spectrometer (125 MHz), respectively. The triad tacticity of the polymer was determined on the area of the methine carbon of the backbone, and the measurement was carried out at 84 °C in D_2O with proton decoupling. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of poly(NVP) were determined by size-exclusion chromatography (SEC) in DMF containing 100 mM LiCl at 40 °C on two polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-980 precision pump and a Jasco 930-RI detector. The columns were calibrated against seven standard poly(MMA) samples (Shodex; $M_p = 1990{-}1\,950\,000$; $M_w/M_n = 1.02{-}1.09$). Glass transition temperature (T_g) of the polymer was recorded on SSC-5200 differential scanning calorimetry (Seiko Instruments Inc.). Samples were first heated to 220 °C at 15 °C/min, equilibrated at this temperature for 5 min, and cooled to 40 °C at 5 °C/min. After being held at this temperature for 5 min, the samples were then reheated to 220 °C at 10 °C/min. All T_g values were obtained from the second scan, after removing the thermal history.

Polymerization. Typically, a mixture of NVP (6.66 g, 60 mmol), **1** (84.8 mg, 0.4 mmol), and AIBN (13 mg, 0.08 mmol) was degassed by three cycles of freeze−vacuum−thaw; then the solution was evenly charged in six glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. After the desired time, the solution was diluted with methanol before dropping into a large amount of diethyl ether and collected by centrifugation, purification was carried out by repeating dissolution in methanol and precipitation from ether, and finally dried under vacuum at 60 °C for 12 h. Polymer yields were measured gravimetrically. Polymerization at 20 and 0 °C was carried out under UV irradiation (500 W high-pressure mercury lamp) in the presence of AIBN; polymerization at −40 °C was carried out with *n*-Bu_3B in the presence of a small amount of air. The polymerization procedure in the presence of fluoroalcohols was carried out similarly.

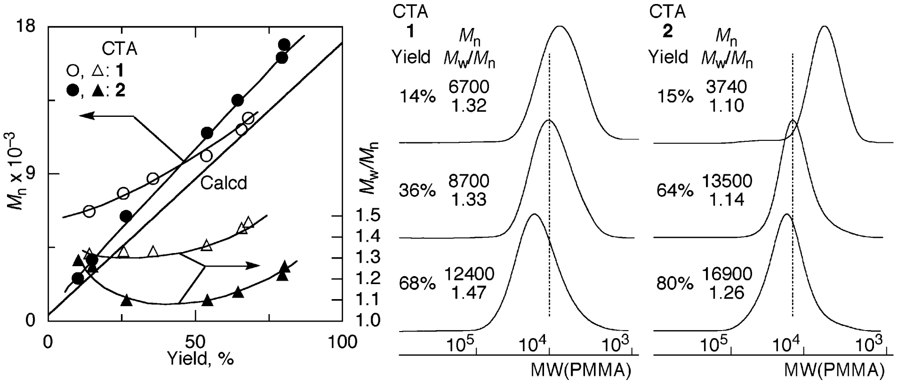


Figure 2. M_n, M_w/M_n, and SEC curves of poly(NVP) obtained with AIBN/**1** (○, △) or **2** (●, ▲) in bulk at 60 °C: $[NVP]_0$ = 9.46 M (bulk); $[NVP]_0$/[chain transfer agents]$_0$/$[AIBN]_0$ = 150/1/0.2.

Results and Discussion

1. Living Radical Polymerization of NVP: Control of Molecular Weight. (a) Effects of the Structure of the RAFT or MADIX Agents. The bulk radical polymerizations of NVP were carried out with AIBN at 60 °C in the absence and the presence of RAFT (**3**; 1-phenylethyl phenyldithioacetate) or MADIX (**1** and **2**) agents. Figure 1 shows the kinetic data along with the fitted curves. The polymerizations were retarded upon the addition of **1** and **2** similar to the other radical polymerizations in the presence of chain transfer agents (CTAs).[11,12] All the CTAs gave more or less induction period, i.e., about 1 h with **1** and 6 h with **2**, while no polymerization occurred with **3** at least for 108 h under the conditions. The reason for the induction period often observed in RAFT/MADIX polymerizations[11−18] has been discussed in several papers but is still not completely understood.[40−44] The behavior of these CTAs is similar to the radical polymerization of vinyl acetate in the presence of these CTAs.[13−18]

Figure 2 shows the M_n, M_w/M_n, and SEC traces of the obtained polymers with the xanthates (**1** and **2**) during the bulk polymerizations with AIBN at 60 °C. The M_n of the polymers obtained with **2** increased in direct proportion to the monomer conversion and agreed with the calculated values assuming that one molecule of CTA generates one polymer chain though based on the poly(MMA) calibration. The M_ns with **1** were slightly higher than the calculated values at low conversion of monomer. A similar phenomenon was observed in other RAFT systems[42] and was explained in terms of chain transfer ability of the CTAs. CTA with a lower transfer ability led to a higher deviation of molecular weight from the theoretical one during the initial stage of polymerization. Both CTAs gave narrow molecular weight distributions (MWDs), and especially **2** produced narrower MWDs, even at low monomer conversion. This is most probably because the 1-phenylethyl radical, a secondary carbon radical, derived from **2** is more easily formed than the benzyl radical, a primary one, from **1**, which results in a faster consumption of the chain transfer agents and narrower MWDs.[11e]

We further examined a series of polymerizations by using xanthate **1** and **2** at four different concentrations of these chain transfer agents ($[NVP]_0$ = 9.46 M (bulk); $[AIBN]_0$ = 15.4 mM; $[CTA]_0$ = 63, 38, 27, 17 mM) (see Supporting Information). These results indicated again that the xanthate **2** is more effective than **1** in terms of the molecular weight control of poly(NVP) under all the conditions. The M_n obtained with **2** increased in direct proportion to monomer conversion over whole range of conversions at all the concentrations of **2** (Figure S1). Furthermore, the molecular weight control can be attained up to 60 000 though slightly broader molecular weight distribution was observed (M_w/M_n = 1.75). In contrast, xanthate **1** gave higher molecular weights at low conversions, and linear increase of the molecular weights was not observed in this case (Figure S5).

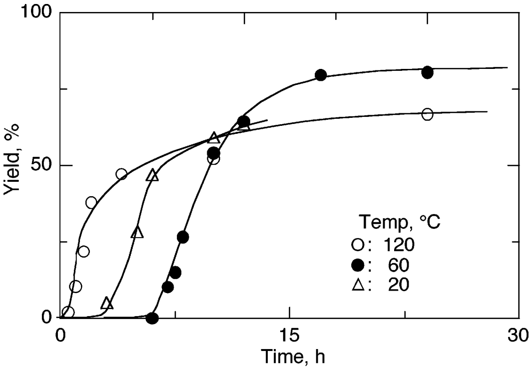


Figure 3. Effects of temperature on xanthate-mediated radical polymerization of NVP with AIBN/**2** in bulk at 20−120 °C: $[NVP]_0$ = 9.46 M (bulk); $[NVP]_0/[\mathbf{2}]_0/[AIBN]_0$ = 150/1/0.2. Temperature: (△) 20, (●) 60, (○) 120 °C. UV was irradiated in the polymerization at 20 °C.

These results indicate that the xanthates are effective CTAs in controlling the molecular weights of poly(NVP) and that **2** is more suitable than **1**.

(b) Effects of Temperature. The bulk polymerization with **2** was then carried out at various polymerization temperatures between 20 and 120 °C, with UV irradiated at 20 °C. Although the UV irradiation was directed to accelerating the decomposition of AIBN at a low temperature, it may give some effects on the cleavage of the C−S bond at the MADIX agent and/or at the dormant polymer terminal.[45] Figure 3 shows the conversion dependence vs time at the various temperatures. At 120 °C under the same conditions, a faster polymerization proceeded with a much shorter induction period (<0.25 h) than that at 60 °C.

The molecular weights increased with the monomer conversion irrespective of the temperatures, as shown in Figure 4. The MWDs were broader for the polymers obtained at the higher temperature, 120 °C, which suggests the uncontrolled nature of the polymerizations at such a high temperature due to side reaction at a high concentration of the radical species. In contrast, lowering temperature decreases the concentration of the radical species to minimize the side reactions and

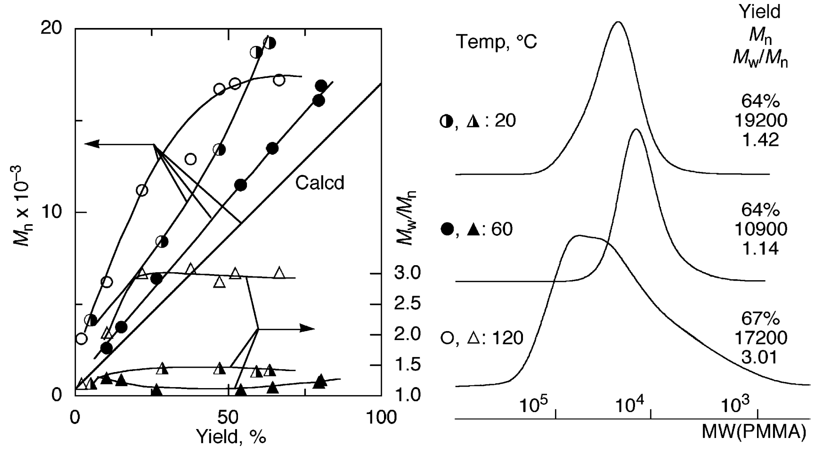


Figure 4. M_n and SEC curves of poly(NVP) obtained with AIBN/**2** in bulk at 20−120 °C: $[NVP]_0$ = 9.46 M (bulk); $[NVP]_0/[\mathbf{2}]_0/[AIBN]_0$ = 150/1/0.2. Temperature: (◑, ▲) 20, (●, ▲) 60, (○, △) 120 °C. UV was irradiated in the polymerization at 20 °C.

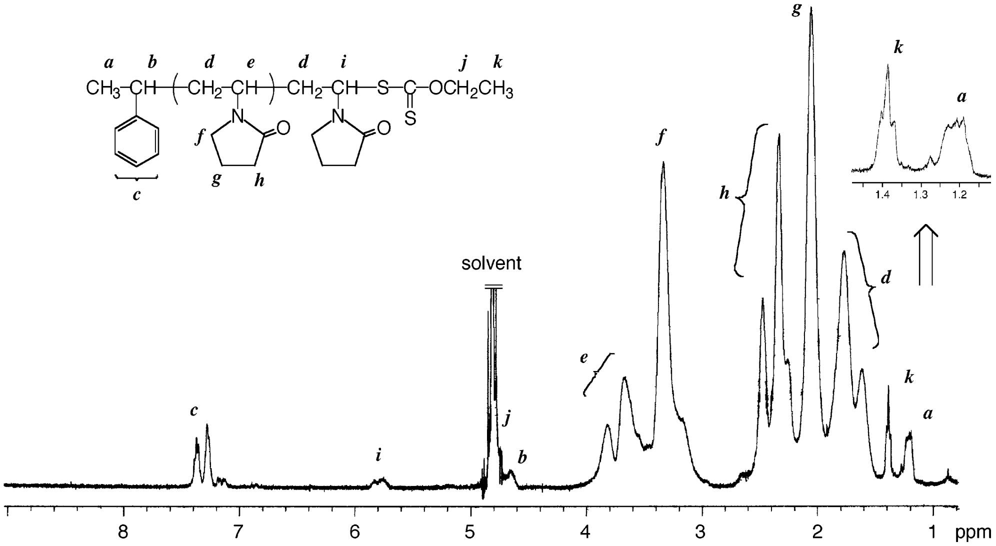


Figure 5. ^{1}H NMR spectrum (400 MHz, D_2O) of poly(NVP) prepared with AIBN/**2** in bulk at 60 °C.

Table 1. Dependence of Tacticity of Poly(NVP) on Solvent and Polymerization Temperature[a]

entry	*T*, °C	solvent	yield, %	M_n[b]	M_w/M_n[b]	*mm*/*mr*/*rr*, %[c]	*r*, %[c]
1	60	bulk	58	135 200	3.11	30.8/29.4/38.8	53.5
2	60	CF_3CH_2OH	59	116 200	2.96	28.3/34.4/37.3	54.5
3	60	$(CF_3)_2CHOH$	57	149 500	3.05	27.3/34.4/38.3	55.6
4	60	$(CF_3)_3COH$	36	121 200	2.89	23/38/39	58.0
5	20	bulk	58	126 900	4.79	30.8/29.4/38.8	53.5
6	20	CF_3CH_2OH	65	130 000	3.11	28.3/34.3/37.4	54.6
7	20	$(CF_3)_2CHOH$	73	164 000	2.30	26.5/35.3/38.2	55.8
8	20	$(CF_3)_3COH$	83	92 400	3.36	22.5/37.1/40.4	59.0

[a] Polymerization conditions: fluoroalcohol/NVP = 1.65/1 v/v, in the presence of 1% (based on monomer) AIBN, reaction at 20 °C was under UV irradiation. [b] Determined by SEC. [c] Determined by the methine carbon in ^{13}C NMR. Calculated by the equation $r = rr + mr/2$. For example, see Figure 7.

results in better molecular weight control in most cases. We also investigated the polymerization at 0 °C with UV irradiation under the same conditions in bulk, while solidification of the monomer occurred (mp of NVP: 13.5 °C) to give less reproducible results. Thus, the most suitable polymerization temperatures in controlling the molecular weights should be 20−60 °C.

(c) End-Group Analysis by ^{1}H NMR. The end-group structures of the poly(NVP) obtained with AIBN/**2** at 60 °C were analyzed by ^{1}H NMR spectroscopy (Figure 5). Besides the large absorptions (*d*−*h*) attributed to the repeat units of NVP at 1.5−4.0 ppm, there are several characteristic signals originating from **2**. The 2-phenylethyl-protons at the α-end, *a*, *b*, and *c*, were seen at 1.2, 4.7, and 7.2−7.4 ppm, respectively. In addition to these small peaks, the methyl protons (*k*) of the *O*-ethylxanthyl groups at the ω-end were observed at 1.4 ppm. The methine protons (*i*) of the ω-terminal NVP unit adjacent to the ethylxanthyl group also appeared at 5.8 ppm.

The number-average degree of polymerization (DP_n) for the polymers with the assumed structure can be determined from the peak intensity ratio $[(e + f)/k]$ of the methyl protons (*k*) at the ω-terminal to the sum of the methine (*e*) and methylene (*f*) protons adjacent to the nitrogen atom of the NVP units. The M_n(NMR, ω-end) calculated from the DP_n(NMR, ω-end) was 2090, which was close to the calculated value [M_n(calcd) = 2050] assuming that one molecule of **2** generates one

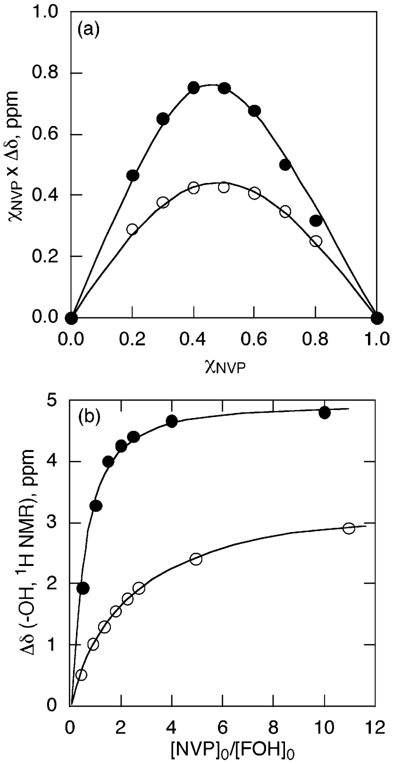


Figure 6. (A) Job plots for the association of a fluoroalcohol with NVP evaluated from the changes in chemical shift (ppm) of the carbonyl carbon of NVP ($[NVP]_0 + [FOH]_0 = 1.0$ M, 125 MHz, $CDCl_3$, 25 °C). FOH: (●) $(CF_3)_3COH$, (○) CF_3CH_2OH; χ_{NVP}: molar fraction of NVP. (B) Change in the chemical shift on the hydroxy proton of the fluoroalcohols in the presence of NVP ($[FOH]_0 = 100$ mM, 400 MHz, $CDCl_3$, 25 °C). FOH: (●) $(CF_3)_3COH$, (○) CF_3CH_2OH.

living polymer chain. The M_n obtained from the α-end peak [M_n(NMR, α-end)] was 1940, also close to the calculated value. This means that one polymer chain of NVP was generated from one molecule of **2** and that the xanthyl groups remained at the ω-ends for almost all of the polymer chains without loss during the polymerization.

Thus, the xanthate, like **2,** proved effective for controlling the molecular weights and the terminal groups for the radical polymerization of NVP.

2. Stereospecific Radical Polymerization of NVP: Control of Tacticity. (a) Effects of Fluoroalcohols. The tacticity control of poly(NVP) has been only slightly successful during radical polymerization, and there were almost no significant effects of the solvents on the tacticity of poly(NVP).[33,34] Although the control of tacticity during the radical polymerization of VAc had also been difficult, recent dramatic progress has been achieved with the use of bulky fluoroalcohols as the solvent, which induced the syndiospecific radical polymerization of VAc.[29] Several fluoroalcohols [CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$] were then employed for the AIBN-induced conventional radical polymerization of NVP.

Table 1 shows the M_n, M_w/M_n, and racemo (r) dyads of the polymers. The tacticity was measured from the methine carbon of poly(NVP) by ^{13}C NMR spectroscopy.[33,34] The use of fluoroalcohols increased the r dyads, and upon increasing the number of trifluoromethyl groups and the bulkiness, the syndiotacticity was further enhanced. In bulky fluoroalcohols, lowering the polymerization temperature enhanced the syndiotacticity. Especially with perfluoro-*tert*-butyl alcohol, the highest syndiotacticity was achieved at 20 °C ($r = 59.0\%$). The special role of $(CF_3)_3COH$ might be related to its bulkiness, as it has been shown that fluoroalcohol with a bulkier group and a higher acidity significantly enhanced the syndiotacticity of poly(VAc).[29] On the other hand, the temperature might influence the polymer tacticity through two independent routes: (1) low temperature favored hydrogen-bonding association with monomers, and (2) low temperature more favored isotactic or syndiotactic radical addition of monomer during polymerization, which arose from the enthalpy difference between the two addition routes.

Table 2. Saturated Chemical Shift of OH ($\Delta\delta_c$), Equilibrium Constant (K), and Degree of Association (α) of NVP for Interaction between NVP and Fluoroalcohols[a]

solvent	pK_a	$\Delta\delta_c$,[b] ppm	K, L/mol	α[c]
CF_3CH_2OH	12.4	3.37	6.23	0.92
$(CF_3)_3COH$	5.2	4.90	61.4	0.98

[a] Conditions of the NMR titration: [FOH] = 0.1 mol/L, $CDCl_3$, at room temperature. [b] $\Delta\delta_c = \delta$(saturated solution) − δ(free fluoroalcohol), obtained by fitting the data based on the nonlinear least-squares method so that the plot for eq 3 should be a straight line passing through the origin. [c] Calculated based on the conditions in Table 1: $[NVP]_0 = 3.57$ M, $[CF_3CH_2OH]_0 = 5.15$ M, $[(CF_3)_3COH]_0 = 4.46$ M.

(b) Interaction between Fluoroalcohol and NVP. To determine the stereocontrol mechanism of our system, the interaction between NVP and the fluoroalcohols was studied by ^1H and ^{13}C NMR. Upon the addition of fluoroalcohols to the $CDCl_3$ solution of NVP, the carbonyl carbon shifted to a lower field (for example, from 173.3 to 175.6 ppm at molar ratio of $(CF_3)_3COH$/NVP = 0/1 to 4/1, respectively), while the hydroxyl proton of the fluoroalcohols also significantly shifted to a lower field [for example, from 4.23 to 9.04 ppm at concentration ratio of NVP/$(CF_3)_3COH$ = 0.05/0.1 to 1/0.1 (mol/L)/(mol/L), respectively]. These results indicate that a hydrogen bond was formed between the two components. Further investigation by Job's method[46] showed that a 1:1 complex formed between the fluoroalcohol and NVP, as shown in eq 1 (Figure 6).

The equilibrium constant of the complex between NVP and CF_3CH_2OH or $(CF_3)_3COH$ was best fit to 6.23 and 61.4 L/mol, respectively, by eqs 2 and 3. The higher the acidity [pK_a = 12.4 for CF_3CH_2OH and 5.2 for $(CF_3)_3COH$],[47] the larger the equilibrium constant (K). On the basis of these values, the degree of association (α) of the monomer could be calculated for each fluoroalcohol under the conditions in Table 1 [α = 0.92 for CF_3CH_2OH and 0.98 for $(CF_3)_3COH$] (Table 2). There is not so much of a difference between these two values. Thus, the difference in the syndiotacticity derived from the two fluoroalcohols might be caused mainly by the difference in their bulkiness, and it can be safely concluded that the bulkiness of the fluoroalcohol played a critical role in enhancing the polymer syndiotacticity.

$$\mathrm{FOH} + \mathrm{NVP} \overset{K}{\rightleftharpoons} \mathrm{FOH{-}NVP} \qquad (1)$$

$$[\mathrm{FOH{-}NVP}] = [\mathrm{NVP}]_0 \Delta\delta / \Delta\delta_c \qquad (2)$$

$$[\mathrm{FOH{-}NVP}] = K([\mathrm{NVP}]_0 - [\mathrm{FOH{-}NVP}])([\mathrm{FOH}]_0 - [\mathrm{FOH{-}NVP}]) \qquad (3)$$

where FOH represents the fluoroalcohol, K is the

Table 3. Effect of Polymerization and Concentration of $(CF_3)_3COH$ (FOH) on Tacticity and T_g of Poly(NVP)[a]

entry	T, °C	FOH/NVP, mL/mL	α[b]	yield, %	M_n[c]	M_w/M_n[c]	$mm/mr/rr$, %[d]	r, %[d]	T_g, °C[e]
1	60	0/0.25	0	36	121 200	2.89	30.8/29.4/38.8	53.5	180
2	20	0/0.25	0	83	92 400	3.36	30.8/29.4/38.8	53.5	180
3	20	0.05/0.25	0.15	65	247 300	2.48	28/31.8/40.2	56.1	180
4	20	0.45/0.25	0.99	32	326 800	2.23	22.5/36.5/41.5	59.8	176
5	−40	0.45/0.25		37	56 300	2.56	18.9/37.1/44	62.6	171

[a] Polymerization conditions: in the presence of 1% (based on monomer) AIBN, reaction at 20 °C was under UV irradiation and at −40 °C was initiated by air and n-Bu_3B. [b] Degree of Association of NVP. [c] Determined by SEC. [d] Determined by the methine carbon in ^{13}C NMR. Calculated by the equation $r = rr + mr/2$. [e] Measured by DSC at heating rate of 10 °C/min.

equilibrium constant, $\Delta\delta$ is the difference in the observed OH chemical shift of FOH between the absence and the presence of a certain amount of NVP, $\Delta\delta_c$ is the difference in the chemical shift of OH between the absence of NVP and that saturated with NVP, and $[NVP]_0$ and $[FOH]_0$ represent the initial concentration of the corresponding component, respectively.

(c) Synthesis of Syndiotactic Poly(NVP). To further increase the syndiotacticity of the polymers, the polymerization temperature and the fluoroalcohol concentration were changed during the free radical polymerizations of NVP with $(CF_3)_3COH$. As shown in Table 3, with the increasing concentration of the fluoroalcohol and the decreasing polymerization temperature, the syndiotactic content of the polymer was enhanced and finally reached $r = 62.6\%$ using an almost double volume of $(CF_3)_3COH$ to that of NVP at −40 °C. Additionally, when the volume ratio of $(CF_3)_3COH$/NVP reached 0.45/0.25, up to 99% of the monomer existed as the hydrogen-bonded complex. Under this condition, a lower temperature still slightly increased the syndiotacticity (entries 4 and 5 in Table 3). This suggests that the activation enthalpies of the isotactic and syndiotactic additions during the polymerization were somewhat different, whereas no difference was observed in the absence of the fluoroalcohol, indicating that the difference in the enthalpy was due to the presence of the hydrogen-bonding complex.

Figure 7 shows the methine and methylene signals of the ^{13}C NMR spectra of the syndiotactic ($r = 62.6\%$) and atactic ($r = 53.5\%$) poly(NVP), prepared in the presence and absence of $(CF_3)_3COH$, respectively. From the triad content of the methine carbon, the decrease in the isotacticity (*mm*) and the corresponding increase in the syndiotacticity (*rr*) in the presence of the fluoroalcohol were obvious. The methylene carbon gave the tetrad tacticity structure, but only five peaks were well-resolved. Although the calculation of the higher degree of tacticity is not yet available, the increase in the *rrr* content was obvious for the polymer prepared in the presence of $(CF_3)_3COH$.

The glass transition temperature (T_g) of the atactic poly(NVP) obtained in this study was 180 °C, almost the same as those in recent literature.[48,49] On increasing the syndiotacticity, T_g became lower and finally to 171 °C for the sample with $r = 62.6\%$. The effects of the tacticity on T_g were further investigated below for the polymers with different tacticities but with almost the same molecular weights because T_g also depends on the molecular weight of the polymers.

3. Living Stereospecific Radical Polymerization of NVP: Simultaneous Control of Molecular Weight and Tacticity. For the simultaneous control of the molecular weight and steric structure, the radical polymerization of NVP was conducted in perfluoro-*tert*-butyl alcohol at 20 °C with AIBN and xanthate (**2**) under UV irradiation. The polymerization occurred with an induction period (<0.5 h) and reached at 70% conversion in 24 h. As shown in Figure 8, the M_n increased in direct proportion to the monomer conversion and the MWDs remained narrow throughout the reactions. Thus, the living/controlled radical polymerization of NVP was feasible even in $(CF_3)_3COH$. The polymers had a high syndiotacticity ($r = 59.8\%$) similar to those obtained without xanthates at the same temperature in the presence of the same amount of $(CF_3)_3COH$.

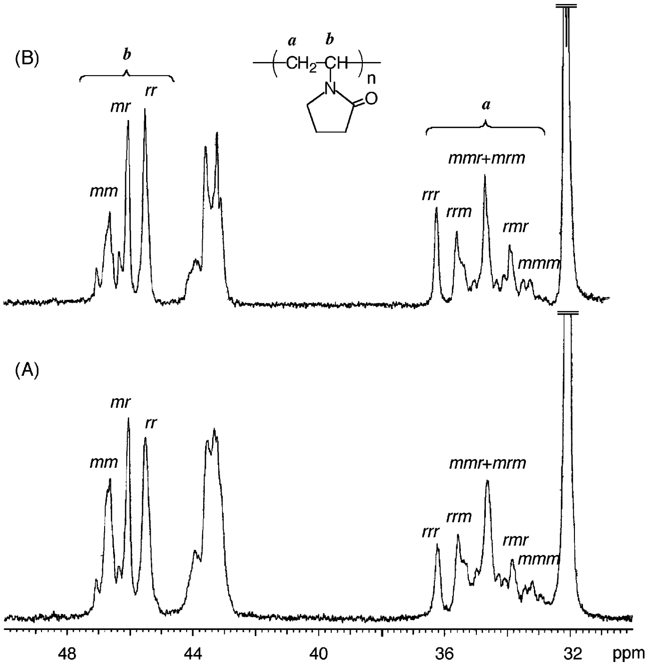


Figure 7. ^{13}C NMR spectra (125 MHz, D_2O, 84 °C) of poly(NVP) prepared in the absence (A) and the presence (B) of $(CF_3)_3COH$.

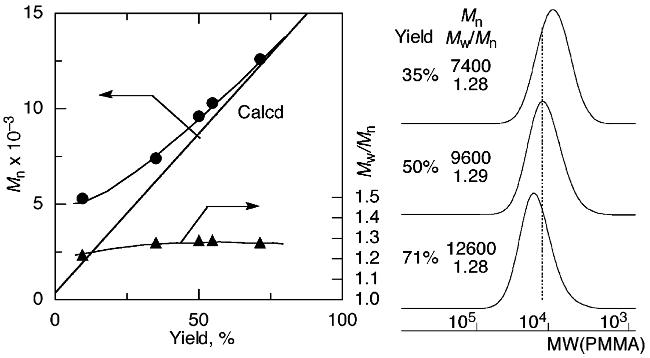


Figure 8. M_n (●), M_w/M_n (▲), and SEC curves of poly(NVP) obtained with AIBN/**2** in $(CF_3)_3COH$ at 20 °C under UV irradiation: $[NVP]_0 = 4.73$ M; NVP/$(CF_3)_3COH$ = 1/1 v/v; $[NVP]_0/[\mathbf{2}]_0/[AIBN]_0 = 150/1/0.28$.

Table 4. Xanthate-Mediated Radical Polymerization of NVP in Various Alcohols or Fluoroalcohols[a]

entry	solvent	T, °C	yield, %	M_n(calcd)[b]	M_n[c]	M_w/M_n[c]	*mm/mr/rr*, %[d]	*r*, %[d]
1	CH_3CH_2OH	60	20	3400	6400	1.19	26.7/36.7/36.6	55.0
2	$(CH_3)_2CHOH$	60	17	2900	6500	1.13	27.4/35.9/36.7	54.7
3	$(CH_3)_3COH$	60	18	3100	6700	1.13	27.3/34.4/38.3	55.5
4	CF_3CH_2OH	60	35	5900	9600	1.20	25.5/39.5/35	54.8
5	$(CF_3)_2CHOH$	60	27	4600	6600	1.14	22/42.4/35.6	56.3
6	$(CF_3)_3COH$	60	30	5000	8900	1.20	22.5/38/39.5	58.5
7	CH_3CH_2OH	20	20	3400	9800	1.49	26.8/35.8/37.4	55.3
8	$(CH_3)_2CHOH$	20	18	3100	9600	1.40	28.2/33.3/38.5	55.2
9	$(CH_3)_3COH$	20	45	7500	13600	1.28	29.2/30.4/40.4	55.6
10	CF_3CH_2OH	20	18	3000	8400	1.23	25/40/35	55.0
11	$(CF_3)_2CHOH$	20	46	7700	11600	1.31	23/41.5/35.5	56.3
12	$(CF_3)_3COH$	20	48	8100	13400	1.33	22/36.5/41.5	59.8

[a] Polymerization conditions: $[NVP]_0/[\mathbf{2}]_0/[AIBN]_0 = 150/1/0.2$; NVP/solvent = 1/1.65 v/v, 60 °C for 18 h; 20 °C under UV irradiation for 36 h. [b] $M_n(\text{calcd}) = MW(NVP) \times [NVP]_0/[\mathbf{2}]_0 \times \text{yield} + MW(\mathbf{2})$. [c] Determined by SEC. [d] Determined by the methine carbon in ^{13}C NMR. Calculated by the equation $r = rr + mr/2$.

Table 5. Influence of Concentration of $(CF_3)_3COH$ (FOH) on Tacticity of Poly(NVP)[a]

entry	FOH/NVP, mL/mL	yield, %	α[b]	M_n(calcd)[c]	M_n[d]	M_w/M_n[d]	*mm/mr/rr*, %[d]	*r*, %[e]	T_g, °C[f]
1	0/0.25	53	0	9 000	15 700	1.43	30.8/29.4/38.8	53.5	174
2	0.25/0.25	71	0.75	12 000	15 200	1.51	22.5/37.2/40.3	58.9	171
3	0.45/0.25	72	0.99	12 100	15 600	1.56	22/36.5/41.5	59.8	165

[a] Polymerization conditions: $[NVP]_0/[\mathbf{2}]_0/[AIBN]_0 = 150/1/0.2$; 20 °C under UV irradiation for 42 h. [b] Degree of association of NVP. [c] $M_n(\text{calcd}) = MW(NVP) \times [NVP]_0/[\mathbf{2}]_0 \times \text{yield} + MW(\mathbf{2})$. [d] Determined by SEC. [e] Determined by the methine carbon in ^{13}C NMR. Calculated by the equation $r = rr + mr/2$. [f] Measured by DSC at heating rate of 10 °C/min.

We further examined a series of polymerizations by changing the concentrations of **2** in $(CF_3)_3COH$ ($[NVP]_0 = 4.6$ M; $[AIBN]_0 = 10.2$ mM; $[\mathbf{2}]_0 = 32, 19, 14$ mM) (see Supporting Information). The M_n increased in direct proportion to monomer conversion and can be increased at least up to 35 600 though slightly broader molecular weight distribution was observed ($M_w/M_n = 1.84$) (Figure S8).

These results indicate that living and stereospecific radical polymerization of NVP was achieved with **2** in the fluoroalcohol.

Table 4 summarizes the further investigation of the xanthate-mediated radical polymerization of NVP in various alcohols with and without the fluoro substituents at 60 and 20 °C. In all the alcoholic solvents, controlled molecular weights and narrow MWDs were attained. The polymers obtained in nonfluorinated alcohols showed the syndiotacticity around 55%, slightly higher than that in the bulk (53.5%; see Table 1). A similar tacticity was also obtained in CF_3CH_2OH ($r \sim 55\%$). Upon increasing the number of CF_3 substitutens and the bulkiness, a higher syndiotacticity was obtained similar to the radical polymerization without chain transfer agents.

To observe the effects of the tacticity on T_g of poly(NVP), a series of polymers with almost the same molecular weights but with different tacticities were synthesized by varying the amount of $(CF_3)_3COH$ in the presence of **2** at 20 °C (Table 5). The T_g of poly(NVP) with $M_n = 15\,700$ ($M_w = 22\,500$) and $r = 53.5\%$ was 173.6 °C, slightly lower than the polymers with a higher molecular weight and with the same tacticity ($T_g = 180$ °C; for example, $M_n = 92\,400$, $M_w = 310\,000$, $r = 53.5\%$ in Table 3). This is due to the molecular weight effects. Upon increasing the syndiotacticity to $r = 58.9\%$ and 59.8% while keeping the molecular weight nearly the same ($M_n = 15\,000-16\,000$; $M_w = 22\,000-24\,000$), the T_g decreased to 171.3 and 165.2 °C, respectively. Figure 9 is a plot of the T_g values vs the M_w for various samples with different tacticities. These results indicate that the T_g value decreased with the increasing syndiotacticity at least between $r = 53\%$ and 63%.

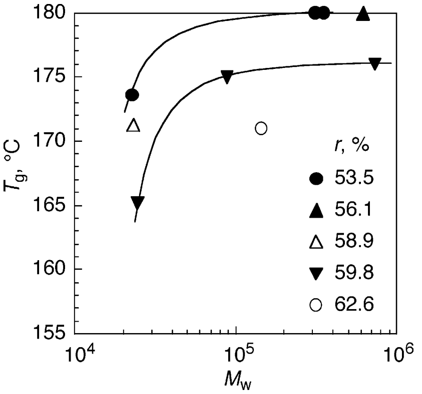


Figure 9. Glass transition temperature (T_g) dependence on M_w for the poly(NVP) with different tacticities ($r = 53-63\%$).

Conclusion. The controlled/living radical polymerization of NVP proceeds in the presence of xanthates; meanwhile, fluoroalcohols enhance the syndiotacticity of the polymer. The higher acidity and bulkiness of the fluoroalcohols led to the higher syndiotacticity. The polymer tacticity was dependent on the amount of fluoroalcohols, but low temperature hardly favored the syndiotacticity except for the bulky fluoroalcohols. The hydrogen-bonding interaction between the monomer/propagating radical and fluoroalcohol might be responsible for the stereocontrol. This system can be used for the synthesis of functional polymers based on poly(NVP) in the future.

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Supporting Information Available: Plots for xanthate-mediated radical polymerization at varying the concentrations of **1** and **2** in bulk and $(CF_3)_3COH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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