Stereospecific Free Radical Polymerization of Vinyl Esters Using Fluoroalcohols as Solvents

Kazunobu Yamada,[†,§] Tamaki Nakano,[‡] and Yoshio Okamoto*[,‡]

Joint Research Center for Precision Polymerization (JRCPP)−Japan Chemical Innovation Institute (JCII) and the Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Received June 4, 1998; Revised Manuscript Received August 17, 1998

ABSTRACT: Solvent effects on the stereochemistry of free radical polymerization of vinyl acetate (VAc) and vinyl pivalate (VPi) were investigated. In the polymerization of VAc, an alcoholic solvent with a smaller pK_a and higher bulkiness afforded a polymer having a higher syndiotacticity. The polymerization of VAc in perfluoro-*tert*-butyl alcohol ($(CF_3)_3COH$) at −78 °C led to a diad syndiotacticity *r* of 72%, which is the highest for the radical polymerization of vinyl esters. On the other hand, the polymerization of VPi in fluoroalcohol at a low temperature afforded a polymer rich in heterotacticity (up to $mr = 61\%$). Synthesis of a heterotactic homopolymer by the free radical polymerization of monosubstituted vinyl monomers is unprecedented. The stereochemical effects observed in this study may be due to hydrogen-bond interaction between the fluoroalcohol molecules and the ester groups of the vinyl ester monomer and the side chain of the growing polymer. Mechanisms of stereoregulation were proposed.

Introduction

Poly(vinyl alcohol) (PVA) is commercially produced by free radical polymerization of vinyl acetate (VAc) followed by saponification (hydrolysis) of the obtained polymers and finds wide applications including fibers, films, adhesives, and substitutes for asbestos. Although conventional PVA is atactic, much attention has been paid to the synthesis of stereoregular PVA having a syndiotactic main chain. This is because the thermal and mechanical properties of PVA such as heat resistance, hot-water resistance, tensile strength, and elastic modulus are greatly influenced by a slight change in main-chain tacticity and increasing syndiotacticity of PVA improves the above properties.[1] Polymerizations of bulky vinyl esters such as vinyl trifluoroacetate,[2−4] vinyl pivalate (VPi),[4−6] vinyl diphenylacetate,[7] and vinyl 2,2-bis(trifluoromethyl)propionate (**1**)[8] are known to give polymers rich in syndiotacticity which can be converted to PVA. However, these methods lack versatility and require expensive monomers. It is therefore important to find an effective method in which VAc can be used as a monomer. For this purpose, here we investigated solvent effects on the stereochemistry of vinyl ester polymerization.

Although solvent effects on the stereochemistry of free radical polymerization of VAc are generally very small,[9−11] the polymerization in phenol has been reported to afford a polymer exceptionally rich in syndiotacticity (diad, $r = 56.5\%$),[9] and on one hand, this effect has been ascribed to the increased bulkiness of the monomer's side group because of hydrogen-bond formation between the solvent and the acetyl group. On the other hand, we recently found that a bulky fluorine-containing monomer **1** affords a polymer with a high syndiotacticity.[8] On the basis of these results, we became interested in the free radical polymerization of VAc and VPi in various protic solvents, particularly fluoroalcohols, that would efficiently interact with the ester group of the monomer and the side chain of the growing species through hydrogen bonding. The solvents that we used for the polymerization in this study include 1,1,1-trifluoroethanol (CF_3CH_2OH), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol ($(CF_3)_2C(CH_3)OH$), 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$), and perfluoro-*tert*-butyl alcohol ($(CF_3)_3COH$). These solvents are reported to interact strongly with proton acceptors such as dimethyl ether and acetonitrile.[12,13] This paper describes the full details of the radical polymerization of VAc and VPi using these solvents and the stereochemical analysis of the obtained polymers.[14]

Experimental Section

Materials. VAc (Wako) and VPi (Wako) were washed with 2% aqueous NaOH and distilled immediately before use. $(CF_3)_3COH$ (Aldrich; purity >99%), CF_3CH_2OH (Aldrich; purity >99%), $(CF_3)_2C(CH_3)OH$ (P.C.R.; purity >97%), and $(CF_3)_2CHOH$ (Wako; purity >99%) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Tri-*n*-butylborane (*n*-Bu_3B) was obtained as a tetrahydrofuran (THF) solution (1.0 M) (Aldrich) and used after removal of the solvent. The other reagents were purified by the usual methods.

Procedures. Polymerization was carried out under dry nitrogen in a dried glass tube equipped with a three-way stopcock. The reaction at 60 °C was performed using AIBN by thermal initiation and those at 0 and 20 °C under UV light irradiation (400-W high-pressure mercury lamp). Polymerization at −40 and −78 °C was conducted using *n*-Bu_3B as follows.[4,15] A tetrahydrofuran solution of *n*-Bu_3B (0.40 mL) was placed in a glass ampule under nitrogen, and the solvent was removed under vacuum. A polymerization solvent was added and the solution was cooled to the reaction temperature. Then a monomer was added (total volume = 2 mL) and polymerization was initiated by introducing air (5 mL) with a syringe. Monomer conversion was determined by ^{1}H NMR analysis of the reaction mixture in acetone-d_6 at room temperature. Reaction products of VAc polymerization were diluted with acetone, precipitated in diethyl ether, filtered, and dried under vacuum at 60 °C. The reaction products of VPi

* To whom correspondence should be addressed.
† JRCPP−JCII.
‡ Department of Applied Chemistry.
§ On leave from R & D Center, Unitika Ltd., 23 Kozakura, Uji, Kyoto 611-0021, Japan.

10.1021/ma980889s CCC: $15.00
Published on Web 10/16/1998

Table 1. Radical Polymerization of VAc Using AIBN in Protic Solvents[a]

run	solvent	pK_a[b] of solvent	temp. (°C)	time (h)	conv.[c] (%)	yield[d] (%)	$\bar{M}_n \times 10^{-4}$ [e]	$\bar{M}_w/\bar{M}_n$[e]	triad tacticity[f] *mm*	*mr*	*rr*	diad syndiotacticity[g] *r* (%)
1	CF_3COOH	0.23	60	24	*h*	*h*						
2	CH_3COOH	4.8	60	6	88	76	1.90	2.14	22.9	48.4	28.6	52.8
3	$(CH_3)_3CCOOH$	5.0	60	4		83	4.09	1.83	20.3	50.2	29.5	54.6
4	$CH_3CONHCH_3$	12	60	6		49	1.63	1.56	22.0	50.0	27.9	52.9
5	PhOH	9.8	60	24	15	1	0.33	1.26				
6	$(CH_3)_3COH$	19	60	6	93	88	3.18	1.97	21.3	49.4	29.3	54.0
7	$(CH_3)_3COH$	19	20	24	77	73	6.38	1.64	20.9	49.5	29.5	54.3
8	CH_3OH	16	60	6	80	68	1.14	2.02	22.1	49.6	28.4	53.2
9	CH_3OH	16	20	24	66	58	1.05	1.85	22.2	49.2	28.6	53.2
10	CF_3CH_2OH	12.4	60	2	82	81	2.58	1.92	21.1	49.2	29.7	54.3
11	CF_3CH_2OH	12.4	20	24	72	62	1.31	1.91	19.8	49.9	30.3	55.2
12	$(CF_3)_2C(CH_3)OH$	9.6	60	3	87	78	4.38	1.83	18.4	50.2	31.4	56.5
13	$(CF_3)_2C(CH_3)OH$	9.6	20	24	75	64	1.88	2.67	17.9	50.0	32.1	57.1
14	$(CF_3)_2CHOH$	9.3	60	2	80	74	2.81	1.71	18.7	49.7	31.6	56.4
15	$(CF_3)_2CHOH$	9.3	20	24	76	81	1.66	2.03	17.2	50.3	32.5	57.7
16	$(CF_3)_3COH$	5.2	20	24	87	94	6.15	1.78	13.0	49.4	37.6	62.3
17	none		60	0.1	78	73	5.44	1.64	21.8	49.6	28.6	53.4[i]
18	none		20	1		71	5.54	1.85	22.6	48.9	28.5	52.9

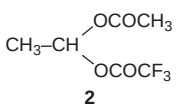
[a] $[VAc]_0 = 2.2$ M (20 vol %). $[AIBN]_0 = 0.15$ M. Reaction at 20 °C was initiated with UV irradiation. [b] Reference 19. [c] Determined by ^1H NMR in acetone-d_6. [d] Et_2O-insoluble part. [e] Determined by GPC of original polymers using polystyrene standard in THF. [f] Determined by ^1H NMR of PVA in DMSO-d_6. [g] Calculated based on triad tacticity ($r = rr + mr/2$). [h] Solvent reacted with VAc to give adduct **2**. [i] Bulk polymerization was repeated five times under the identical condition in order to confirm the reproducibility of the reaction and to estimate the dispersion in tacticity determination. The range of errors was ±0.5%.

polymerization were diluted with acetone, precipitated in methanol/water (=4/1), and recovered in the same way. Poly(VAc) was saponified as follows. To a solution of poly(VAc) (0.2 g) in methanol (9 mL), a 10% methanol solution of NaOH (1 mL) was added, and the mixture was stirred for 2 h at 40 °C to give methanol-insoluble products (PVA). Poly(VPi) was saponified as reported.[5] The obtained PVA was collected by filtration, washed well with methanol containing a small amount of acetic acid and with acetone, and then dried under vacuum.

Measurements. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of poly(VAc) and poly(VPi) were determined by size-exclusion chromatography (SEC) calibrated with standard polystyrenes using a Jasco PU-980 pump equipped with a Jasco RI-930 detector and TSKgel GMH_{HR}-H and $G3000H_{HR}$ columns (eluent, THF; temperature, 40 °C). The tacticity of PVA was determined by ^1H NMR or ^{13}C NMR spectra recorded on a Varian Gemmini 2000 spectrometer (400 MHz for ^1H) or UNITY−INOVA (500 MHz for ^1H) in dimethyl sulfoxide-d_6 (DMSO-d_6) at room temperature (^1H) or at 100 °C (^{13}C). The melting point of PVA was measured using a Seiko SSC5200 differential scanning calorimeter at a heating rate of 10 °C/min.

Results and Discussion

Polymerization of VAc. Polymerization of VAc was carried out in various protic solvents using AIBN at 60 or 20 °C and the stereochemistry of polymerization was investigated (Table 1). Among the polymerizations, that in CF_3COOH resulted only in an adduct (**2**) of VAc and



2

the solvent which was identified by ^1H NMR spectroscopy.[16] A highly acidic solvent with a pK_a below 4.8 may have a possibility of adding the vinyl group of VAc and not giving a polymer. Though phenol is known to give a syndiotactic-rich polymer (r = 56.5%) at low solvent content (10∼50 wt %, $[VAc]_0 = 5.8$∼9.9 M),[9] the present polymerization at a higher solvent content (80 vol %, $[VAc]_0 = 2.2$ M) gave only a small amount of oligomeric products. This may be attributed to the

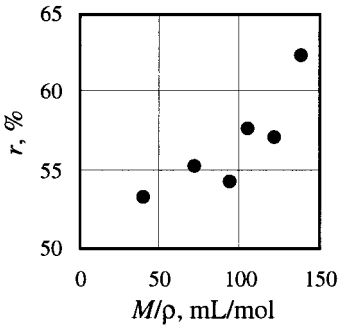


Figure 1. Relationship between molecular volume (M/ρ) of the alcoholic solvents and diad syndiotacticity (r) of PVA obtained through the polymerization of VAc in the solvents at 20 °C. The data points correspond to CH_3OH, CF_3CH_2OH, $(CH_3)_3COH$, $(CF_3)_2CHOH$, $(CF_3)_2C(CH_3)OH$, and $(CF_3)_3COH$ (from left to right).

π-complex formation[17] between the growing radical and the solvent and to chain transfer to the solvent.[18] Most reactions using the other solvents afforded polymers with higher M_n's in higher yields compared with those in methanol which is generally used as a solvent for the industrial production of PVA. Although the stereochemistry of polymerization in CH_3COOH, $CH_3CONHCH_3$, and CH_3OH was similar to that of bulk polymerization, the polymerization in the other solvents resulted in higher syndiotacticity of the products compared with the bulk polymerization. Among the solvents, $(CF_3)_3COH$ appeared to be especially effective in enhancing the syndiotactic specificity, and a polymer with a diad r of over 62% was obtained under the reaction conditions of run 16 in Table 1.

One of the solvent properties which affect the stereochemistry of polymerization seems to be bulkiness of the solvents. Bulkiness of a solvent can be evaluated as molecular volume (mL/mol) which is defined as the ratio of the molecular weight (M) to the density (ρ). Figure 1 shows the relationship between the syndiotactic specificity and M/ρ. The plots indicate a rough tendency in which a solvent with a higher M/ρ leads to a higher syndiotacticity. Another solvent property which affects the stereochemistry appeared to be pK_a.

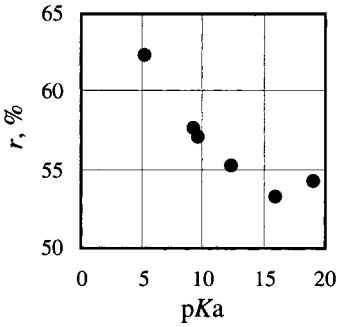


Figure 2. Relationship between the pK_a of the alcoholic solvents and diad syndiotacticity (r) of PVA obtained through the polymerization of VAc in the solvents at 20 °C.

Figure 2 shows the relationship between the pK_a[19] of the alcoholic solvents and the syndiotacticity of the polymers obtained in the solvents at 20 °C. The plots indicate that a solvent with a smaller pK_a (higher acidity) yields a polymer with a higher syndiotacticity. However, a solvent with an exeedingly small pK_a (strong acid) such as CF_3COOH reacts with the monomer as mentioned earlier.

Because $(CF_3)_3COH$ has the largest effect in enhancing the syndiotactic specificity of VAc polymerization, the polymerization in $(CF_3)_3COH$ at various temperatures and solvent concentrations was examined in search of reaction conditions giving higher stereospecificity (Table 2). The results indicate that a lower monomer concentration (a higher solvent concentration) and a lower reaction temperature lead to higher syndiotactic specificity. The polymerization in $(CF_3)_3COH$ (80 vol %) at −78 °C gave a polymer with a diad syndiotacticity of 72% (run 11) which is the highest syndiotacticity observed for the free radical polymerization of vinyl esters. Figure 3 shows ^{13}C NMR (methine carbon) spectra of PVAs obtained through the bulk polymerization of VAc and the polymerization in $(CF_3)_3COH$ at −78 °C (runs 3 and 11 in Table 2, respectively). The spectra show the high syndiotacticity of the latter PVA.

Figure 4 shows the temperature dependence of tacticty in the polymerization of VAc in $(CF_3)_3COH$ (Fordham plots[21]). The difference in activation enthalpy ($\Delta H^{\ddagger}$) and that in activation entropy ($\Delta S^{\ddagger}$) between isotactic and syndiotactic-specific propagation can be determined by the plot according to the following eq 1:[20]

$$\ln\left(\frac{Pi}{Ps}\right) = \frac{\Delta Si^{\ddagger} - \Delta Ss^{\ddagger}}{R} - \frac{\Delta Hi^{\ddagger} - \Delta Hs^{\ddagger}}{RT} \qquad (1)$$

where P_i and P_s are the mole fractions of isotactic and syndiotactic diads, respectively, R is a gas constant (1.987 cal/mol·K), and T is the polymerization temperature (K). The obtained values of $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ for the polymerizations of VAc are summarized in Table 3 along with the data for the VAc polymerization in PhOH and the bulk polymerization of **1**. The positive values of $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ in all cases of the solution polymerization of VAc indicate that syndiotactic propagation is favored by enthalpy in the solvents. Syndiotactic propagation appears to be favored also by entropy in the VAc polymerization in PhOH and CH_3OH, whereas it is disfavored by entropy when CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$ are used as solvents.

We recently reported the syndiotactic-specific polymerization of bulky vinyl ester **1**[8] in which the stereochemistry was ascribed to steric and electrostatic repulsion based on the bulky monomer and polymer structure. In the bulk polymerization of **1**, the syndiotactic-specific propagation was favored by enthalpy and disfavored by entropy similar to the polymerizations of VAc in CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$. This suggests that a similar stereochemical mechanism is responsible for the stereochemistry of the polymerization of VAc in bulky fluoroalcohols; that is, steric repulsion caused by the VAc hydrogen-bound by bulky solvents has a role in stereoregulation.

Polymerization of VPi. Polymerization of VPi was also examined using the fluoroalcohols as solvents. Table 4 shows the conditions and results of polymerizations of VPi in alcohols under various conditions. In contrast to the syndiotacticity-enhancing effect of the fluoroalcohols in the VAc polymerization, the solvents appear to be effective in increasing the heterotactic triad (*mr*) of the polymers. The effect was more pronounced when a solvent with a smaller pK_a and higher bulkiness was used and $(CF_3)_3COH$ exhibited the largest stereoeffect. The stereochemistry of the VPi polymerization was affected by polymerization temperature and its effect was varied depending on the solvents. By lowering the temperature, the *rr* fraction in CH_3OH, both *mr* and *rr* fractions in CF_3CH_2OH, and the *mr* fraction in $(CF_3)_3COH$ were increased. In $(CF_3)_2CHOH$, *rr* increased with a decrease in temperature but the change in *mr* was not simple. The solvent effects were also dependent on the monomer concentration as found for the polymerization of VAc in $(CF_3)_3COH$; a lower monomer concentration gave a higher *mr* content. The highest heterotacticity (*mr* triad = 61%) was attained by the polymerization of VPi under the conditions of run 18 in Table 4. Figure 5 shows ^{13}C NMR (methine carbon) spectra of the PVAs derived from the polymers obtained in runs 3 and 18, respectively, in Table 4.

A heterotactic polymer has been defined as a polymer having more than 50% heterotactic triads.[21] Heterotactic-specific polymerization needs higher-order stereoregulation than isotactic- and syndiotactic-specific polymerizations, and only limited numbers of examples of the heterotactic polymer synthesis are known. Heterotactic homopolymers have been obtained mainly by ionic polymerization including cationic polymerization of acetaldehyde[22] and vinyl ethers bearing bulky substituents[23] or anionic polymerization of α-substituted acrylates,[21] methacrylates[24] and *N*,*N*-diethylacrylamide.[25] However, the heterotactic fraction usually does not exeed 50% in free radical polymerization with the exception of methyl α-aryloxymethacrylate polymerization[26] and the copolymerization of methyl methacrylate and styrene in the presence of boron trichloride.[27] Thus, the synthesis of a heterotactic polymer from monosubstituted vinyl monomers having an *mr* of 61% by a free radical mechanism is unprecedented.

Configurational Statistics of Polymer and Stereoregulation Mechanism. (a) VAc Polymerization. To gain information on the stereoregulation mechanism in the free radical polymerization of vinyl esters in fluoroalcohol, the configurational statistics of the polymers were investigated using the stereostructual information obtained from ^{13}C NMR spectra of the PVAs. With the triad and the pentad stereochemical information obtained from the ^{13}C NMR spectra (Figure 3),[28] a Bernoulli model and a first-order Markov model were tested.[29] As shown in Table 5, the tacticity of

Table 2. Radical Polymerization of VAc in $(CF_3)_3COH$ at Various Temperatures[a]

run	$[VAc]_0$ (mol/L)	$[solvent]_0$ (vol %)	temp. (°C)	time (h)	conv.[b] (%)	yield[c] (%)	$\bar{M}_n \times 10^{-4}$ [d]	$\bar{M}_w/\bar{M}_n$ [d]	triad tacticity[e] *mm*	*mr*	*rr*	diad syndiotacticity[f] *r* (%)
1	10.9	0	60	0.1	78	73	5.44	1.64	21.8	49.6	28.6	53.4
2	10.9	0	20	1		71	5.54	1.85	22.6	48.9	28.5	52.9
3	10.9	0	−78	600	10	8	7.35	1.55	22.5	48.8	28.7	53.1
4	5.4	50	60	0.5	82	72	6.85	1.97	18.9	50.4	30.7	55.9
5	5.4	50	20	4	69	75	11.9	1.76	16.5	49.3	34.2	58.9
6	5.4	50	−78	240	16	12	9.77	1.91	10.0	45.0	45.0	67.5
7	2.2	80	40	3	65	68	14.3	1.59	15.3	50.3	34.3	59.5
8	2.2	80	20	24	87	94	6.15	1.78	13.0	49.4	37.6	62.3
9	2.2	80	0	48	55	43	11.5	1.79	11.5	49.0	39.4	64.0
10	2.2	80	−40	24	89	81	5.83	1.47	8.2	47.5	44.3	68.0
11	2.2	80	−78	168	69	50	8.30	1.52	5.4	44.9	49.8	72.2

[a] Polymerizations at 0∼60 °C were carried out with AIBN (0.15 M). Reactions at 0 and 20 °C were initiatied by UV irradiation. Polymerizations at −40 and −78 °C were carried out with *n*-Bu_3B (0.20 M) in the presence of a small amount of air. [b] Determined by ^1H NMR in acetone-d_6. [c] Et_2O-insoluble part. [d] Determined by GPC of original polymers using polystyrene standard in THF. [e] Determined by ^1H or ^{13}C NMR of PVA in DMSO-d_6. [f] Calculated based on triad tacticity ($r = rr + mr/2$).

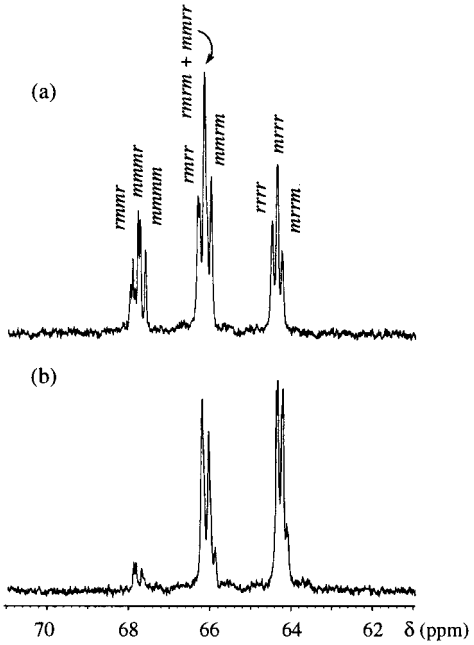


Figure 3. ^{13}C NMR spectra (methine region) of PVA obtained in run 3 (a) and run 11 (b), respectively, in Table 2 (DMSO-d_6).

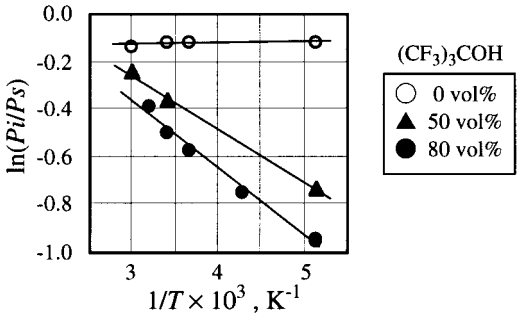


Figure 4. Temperature dependence of tacticity in the polymerization of VAc in $(CF_3)_3COH$.

atactic PVA obtained through the bulk polymerization at −78 °C was well-described by a Bernoulli model with $P(m) = 0.47$ as well as the free radical bulk polymerization of various vinyl esters.[4] However, the tacticity of syndiotactic PVA with $r = 72\%$ was better described by a first-order Markov model with $P(m/r) = 0.81$ and $P(r/m) = 0.31$ than a Bernoulli model with $P(m) = 0.28$, where $P(m/r)$ means the probability that a monomer adds in *r* fashion to an *m* chain end.

The Markov model indicates that the stereochemistry of monomer addition is affected by the configuration of the penpenultimate monomeric unit. In the polymerization of VAc in $(CF_3)_3COH$ at −78 °C, the polymerization stereochemistry is affected by the configuration of the second and the third monomeric units from the chain end (penultimate and penpenultimate units). This suggests that the steric repulsion between the entering VAc and the chain-end monomeric units bound by the solvent molecules through hydrogen bonding influences the stereochemistry of the polymerization.

Interaction between VAc and the solvents (CH_3OH, CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$) was studied in $CDCl_3$ at 20 °C by means of ^1H and ^{13}C NMR spectroscopy. In the presence of an alcohol, the signal of the carbonyl carbon of VAc in ^{13}C NMR shifted downfield, and in the presence of VAc, the OH signal of an alcohol in ^1H NMR also showed a downfield shift. These results indicate that the interaction between VAc and an alcohol is caused by the hydrogen bonding between the carbonyl oxygen of VAc and the hydroxyl group of an alcohol.

Stoichiometry of the interaction was evaluated by Job's method[30] (Figure 6) using a $CDCl_3$ solution containing VAc and an alcohol by means of ^{13}C NMR spectroscopy. Complex concentration in the plots was calculated according to eq 2:

$$[ROH{-}VAc] = \frac{\delta(C{=}O) - \delta(C{=}O)_f}{\delta(C{=}O)_c - \delta(C{=}O)_f}[VAc]_0 \qquad (2)$$

where $\delta(C{=}O)$, $\delta(C{=}O)_f$, and $\delta(C{=}O)_c$ are the C=O signal chemical shifts of a sample mixture, VAc in the absence of an alcohol, and a saturated mixture, respectively. Although the magnitude of error is rather large because of the relatively small equilibrium constant (vide infra), the plots indicate that the stoichiometry of the interaction between VAc and CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$ is roughly 1:1 while that between VAc and CH_3OH may be VAc/MeOH > 1/1.

$$ROH + VAc \overset{K}{\rightleftharpoons} ROH\cdots VAc \qquad (3)$$

The equilibrium constant (*K*) of the VAc−ROH interaction (eq 3) was determined by a ^1H NMR titration experiment. Figure 7 shows the changes in the ^1H NMR chemical shift of the hydroxyl group of the alcohols according to the change in the concentration of VAc. The downfield shift of the OH signal due to hydrogen

Table 3. Activation Parameters for the Polymerization of VAc and Vinyl 2,2-Bis(trifluoromethyl)propionate (1)

monomer	solvent	$[solvent]_0$ (vol %)	$\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ [a] (cal/mol)	$\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ [a] (cal/mol·K)	ref
VAc	none	0	−10 ± 40	−0.3 ± 0.2	this work
	PhOH	10[b]	28	−0.35	9
	CH_3OH	80	80 ± 70	0.0 ± 0.3	this work
	CF_3CH_2OH	80	200 ± 70	0.3 ± 0.3	this work
	$(CF_3)_2CHOH$	80	520 ± 70	1.1 ± 0.3	this work
	$(CF_3)_3COH$	80	550 ± 50	0.9 ± 0.2	this work
1	none	0	460	0.2	8

[a] The ranges of errors were estimated based on the errors in tacticity determination (±0.5%; see Table 1). [b] wt %.

Table 4. Radical Polymerization of VPi in Fluoroalcohols[a]

									tacticity[e]		
run	$[VPi]_0$ (mol/L)	solvent	temp. (°C)	time (h)	conv.[b] (%)	yield[c] (%)	$\bar{M}_n \times 10^{-4}$ [d]	$\bar{M}_w/\bar{M}_n$[d]	*mm*	*mr*	*rr*
1	6.8	None	60	0.2	82	77	2.21	4.69	15.2	49.7	35.2
2	6.8	None	20	1	65	64	7.12	1.63	13.7	49.2	37.1
3	6.8	None	−40	24	52	52	15.3	2.05	11.1	47.9	41.0
4	1.4	CH_3OH	60	4	74	67	1.54	1.84	14.2	49.2	36.6
5	1.4	CH_3OH	20	24	61	58	1.65	1.84	12.7	48.3	39.0
6	1.4	CH_3OH	−40	24		35	3.05	1.56	9.4	45.5	45.1
7	1.4	CF_3CH_2OH	60	4	87	81	2.33	2.01	16.4	50.7	32.9
8	1.4	CF_3CH_2OH	20	24	77	69	2.74	2.09	15.0	51.3	33.7
9	1.4	CF_3CH_2OH	−40	24	70	62	2.90	1.62	12.7	52.0	35.3
10	1.4	$(CF_3)_2CHOH$	60	4	85	61	1.47	1.57	18.6	53.9	27.5
11	1.4	$(CF_3)_2CHOH$	20	24	72	38	1.62	1.83	17.2	55.0	27.9
12	1.4	$(CF_3)_2CHOH$	−40	24	72	58	2.58	2.14	12.9	51.3	35.9
13	3.4	$(CF_3)_3COH$	60	0.5		85	7.16	2.37	17.2	51.8	31.0
14	3.4	$(CF_3)_3COH$	20	4	72	73	3.82	1.86	17.7	55.1	27.2
15	3.4	$(CF_3)_3COH$	−78	168		59	9.52	1.51	19.1	57.7	23.2
16	1.4	$(CF_3)_3COH$	60	2	80	80	3.88	1.66	20.1	57.5	22.4
17	1.4	$(CF_3)_3COH$	20	24	73	69	2.40	1.97	20.7	57.5	21.8
18	1.4	$(CF_3)_3COH$	−40	24	84	83	4.17	1.84	21.3	61.0	17.7

[a] Polymerizations at 20 and 60 °C were carried out with AIBN (0.15 M). Reaction at 20 °C was initiatied by UV irradiation. Polymerizations at −40 and −78 °C were carried out with the *n*-Bu_3B (0.20 M) in the presence of a small amount of air. [b] Determined by ^1H NMR in acetone-d_6. [c] MeOH/H_2O(=4/1)-insoluble part. [d] Determined by GPC of poly(VPi) using polystyrene standard in THF. [e] Determined by ^1H or ^{13}C NMR or PVA in DMSO-d_6.

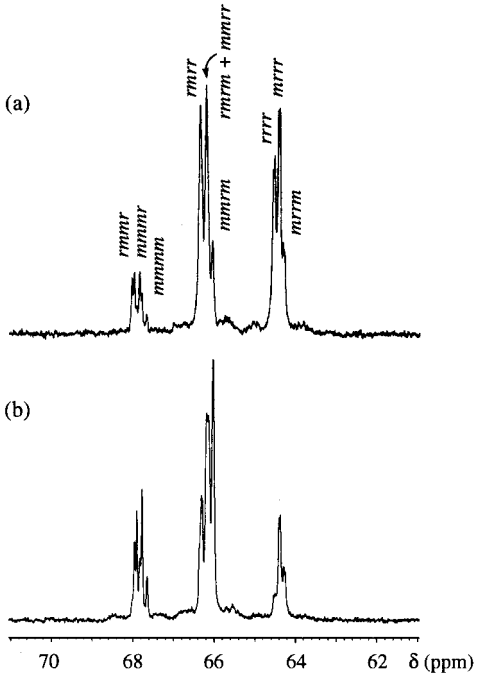


Figure 5. ^{13}C NMR spectra (methine region) of PVA obtained in run 3 (a) and run 18 (b), respectively, in Table 4 (DMSO-d_6).

bonding was found in the presence of VAc, and its magnitude was larger when an alcohol with a smaller pK_a was used for the experiment. The equilibrium constants (*K*) (Table 6) were determined by the analysis of the data in Figure 7 by nonlinear least-squares

Table 5. Stereochemical Statistics of the Polymerization of VAc at − 78 °C

	bulk polymerization[a]		polymerization in $(CF_3)_3COH$[b]		
		Bernoulli $P(m) = 0.47$		Bernoulli $P(m) = 0.28$	1st-order Markov[c] $P(m/r) = 0.81$
pentad	observed	$P(r) = 0.53$	observed	$P(r) = 0.72$	$P(r/m) = 0.31$
mmmm	0.05	0.05	∼0	0.01	∼0
mmmr	0.11	0.11	0.02	0.03	0.02
rmmr	0.07	0.06	0.03	0.04	0.04
(*mm*)	(0.22)	(0.22)	(0.05)	(0.08)	(0.05)
mmrm	0.11	0.11	0.03	0.03	0.03
rmrm } *mmrr* }	0.25	0.25	0.18	0.16	0.17
rmrr	0.15	0.14	0.24	0.21	0.25
(*mr*)	(0.50)	(0.50)	(0.45)	(0.40)	(0.45)
mrrm	0.06	0.06	0.06	0.04	0.05
mrrr	0.13	0.14	0.20	0.21	0.21
rrrr	0.09	0.08	0.24	0.27	0.24
(*rr*)	(0.28)	(0.28)	(0.50)	(0.52)	(0.50)

[a] $[VAc]_0 = 10.9$ M (run 3 in Table 2). [b] $[VAc]_0 = 2.2$ M (run 11 in Table 2). [c] Calculated using the following equations:[28] $P(m/r) = (mr)/[2(mm) + (mr)]$, $P(r/m) = (mr)/[2(rr) + (mr)]$.

fitting[31] to a 1:1 isotherm (4):[30]

$$\frac{[VAc]_0}{\Delta\delta(OH)} = \frac{1}{K}\frac{1}{\Delta\delta(OH)_c} + \left([VAc]_0 + [ROH]_0 - \frac{\Delta\delta(OH)}{\Delta\delta(OH)_c}[ROH]_0\right)\frac{1}{\Delta\delta(OH)_c} \quad (4)$$

where $\Delta\delta(OH)$ and $\Delta\delta(OH)_c$ are the changes in the OH signal chemical shift for a given solution and a saturated solution, respectively. *K* was larger when an alcohol

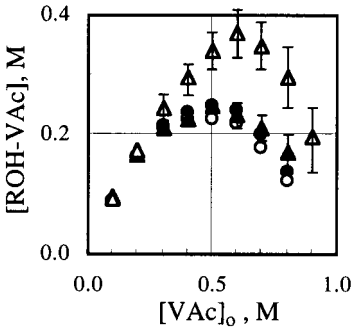


Figure 6. Job plots for the association of an alcohol with VAc evaluated from the changes in the chemical shift (ppm) of the carbonyl carbon of VAc in the presence of alcohols ($[VAc]_0 + [ROH]_0 = 1.0$ M, 100 MHz, $CDCl_3$, 20 ± 1 °C). Alcohols: $(CF_3)_3COH$ (●), $(CF_3)_2CHOH$ (○), CF_3CH_2OH (▲), and CH_3OH (△). Errors based on the chemical shift change within 0.01 ppm are omitted.

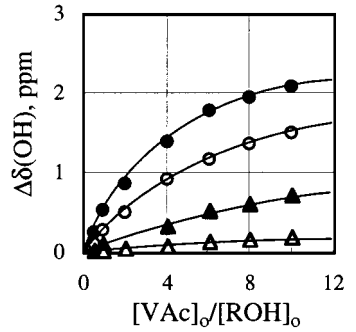


Figure 7. The changes in the chemical shift of the hydroxy proton of the alcohols in the presence of VAc ($[ROH]_0 = 50$ mM, 400 MHz, $CDCl_3$, 20 ± 1 °C). Alcohols: $(CF_3)_3COH$ (●), $(CF_3)_2CHOH$ (○), CF_3CH_2OH (▲), and CH_3OH (△).

Table 6. Equilibrium Constants (*K*) for the Association of an Alcohol with VAc and the Degrees of Association (α) in the Polymerization Systems[a]

alcohol	pK_a	$\Delta\delta(OH)_c$ (ppm)[b]	K (M^{-1})[c]	α[d]
CH_3OH	16			
CF_3CH_2OH	12.4	2.1	1.1	0.91
$(CF_3)_2CHOH$	9.3	2.6	3.3	0.95
$(CF_3)_3COH$	5.2	3.0	5.1	0.95

[a] Based on the changes in the chemical shift of the hydroxy proton of the alcohol in the presence of VAc. $[Alcohol]_0 = 50$ mM, $CDCl_3$, 20 ± 1 °C. [b] $\Delta\delta(OH)_c = \delta$(saturated solution) − δ(free alcohol). [c] Calculated according to eq 4 using a nonlinear least-squares method (see text). [d] Values for the polymerization system of runs 11, 15, and 16 in Table 1.

with a smaller pK_a was used and the VAc−$(CF_3)_3COH$ system had the largest K. By applying the K values to the monomer solution in pure fluoroalcohols corresponding to the polymerization conditions of runs 11, 15, and 16 in Table 1, 91%, 95%, and 95% of VAc are assumed to be bound by solvent molecules in CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$, respectively (Table 6). The close values of the degree of association (α) for the systems using CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$ as solvents indicate that the different stereospecificities observed in the solvents are mainly due to the bulkiness of the solvents.

These results suggest that for syndiotactic-specific propagation, the side chains of the monomer and the growing species acquire the apparent bulkiness bound by the bulky solvent molecules through hydrogen bonding and the steric repulsion between the apparently bulky incoming monomer and the apparently bulky side chains of the growing polymer in the vicinity of the active end. This explanation is consistent with the fact that the bulky vinyl esters yield polymers with higher syndiotacticity compared with VAc.

(b) VPi Polymerization. The configurational statistics of the VPi polymerization (runs 3 and 18 in Table 4) were investigated (Table 7). The stereochemistry of the bulk polymerization giving a syndiotactic polymer (run 3) could be described by a Bernoulli model with $P(m) = 0.35$ or a first-order Markov model with $P(m/r) = 0.68$ and $P(r/m) = 0.37$. However, the stereochemistry of the polymerization in $(CF_3)_3COH$ giving a heterotactic polymer (run 18) could not be described by either a Bernoullian or a first-order Markov model or even by a second-order Markov model, indicating that the heterotactic-specific propagation is caused by a more complexed mechanism than the syndiotactic-specific propagation.

Recently, a stereochemical mechanism was proposed for the highly heterotactic-specific anionic polymerization of methacrylates using bulky aluminum compounds.[25] The mechanism involves coordination of an aluminum complex to a monomer and the monomeric units in the vicinity of the growing end. The heterotactic-specific propagation found in the present study may be explained by a similar mechanism (Figure 8). Two kinds of growing species, ~~~*m*M• and ~~~*r*M•, having *m* and *r* chain-end configurations, respectively, are proposed and the former adds the monomer preferentially in *r*-fashion and the latter in *m*-fashion, leading to a heterotactic triad. The different stereoselectivities of the two species are assumed to be related to different strengths of the interaction between monomeric units of the growing species and the alcohol molecules: a racemo sequence may have stronger interaction than a meso sequence because of steric reasons. According to this explanation, the ~~~*r*M• species may have the alcohol molecules bound to both the chain-terminal and the penultimate unit (Figure 8B), and the ~~~*m*M• species may not have an alcohol molecule at the penultimate unit (Figure 8A). Steric repulsion between the entering VPi bound by an alcohol and the chain-terminal unit of ~~~*m*M• which is also bound by an alcohol may explain the monomer addtion in *r*-fashion. The monomer addition of ~~~*r*M• in *m*-fashion may be attributed to the higher crowdedness in the vicinity of the chain end of the species compared with ~~~*m*M•. Similar to the bulky triarylmethyl methacrylate polymerization giving isotactic polymers because of the helical conformation of the growing chain,[32] the growing species of VPi polymerization may assume a temporary conformation (partial helix) leading to *m*-monomer addition induced by the steric repulsion.

Melting Point of PVA. Stereoregular PVA is expected to have superior thermal and mechanical properties, and the melting point (T_m) can be a criterion for the heat-resistance property of PVA. Recently, it was reported that the polymerization of VPi in *n*-hexane and saponification of the obtained polymer afforded a PVA with $r = 69\%$ and T_m of 258 °C.[6] Figure 9 shows the relationship between syndiotacticity and T_m of the PVAs obtained through the polymerization of VAc and VPi in $(CF_3)_3COH$ in the present study along with those obtained by VPi polymerization in *n*-hexane.[6,33,34] With an increase in syndiotacticity, T_m increased and the PVA with $r = 72\%$ showed a T_m of 269 °C. This value is higher than that of the PVA with $r = 69\%$ obtained

Table 7. Stereochemical Statistics for the Polymerization of VPi at − 40 °C

	bulk polymerization[a]			polymerization in $(CF_3)_3COH$[b]			
pentad	observed	Bernoulli $P(m) = 0.35$ $P(r) = 0.65$	1st-order Markov $P(m/r) = 0.68$ $P(r/m) = 0.37$	observed	Bernoulli $P(m) = 0.52$ $P(r) = 0.48$	1st-order Markov $P(m/r) = 0.59$ $P(r/m) = 0.63$	2nd-order Markov[c] $\alpha = 0.14$, $\beta = 0.83$ $\gamma = 0.60$, $\delta = 0.30$
mmmm	0.01	0.02	0.01	0.03	0.07	0.04	∼0
mmmr	0.05	0.06	0.05	0.09	0.13	0.10	0.05
rmmr	0.06	0.05	0.05	0.10	0.06	0.07	0.16
(*mm*)	(0.11)	(0.12)	(0.11)	(0.21)	(0.27)	(0.21)	(0.21)
mmrm	0.06	0.06	0.06	0.21	0.13	0.16	0.30
rmrm } *mmrr* }	0.21	0.21	0.22	0.27	0.25	0.32	0.27
rmrr	0.21	0.19	0.21	0.13	0.12	0.13	0.04
(*mr*)	(0.48)	(0.46)	(0.48)	(0.61)	(0.50)	(0.61)	(0.61)
mrrm	0.07	0.05	0.06	0.05	0.06	0.07	0.02
mrrr	0.18	0.19	0.19	0.11	0.12	0.08	0.07
rrrr	0.17	0.18	0.17	0.02	0.05	0.02	0.09
(*rr*)	(0.41)	(0.42)	(0.41)	(0.18)	(0.23)	(0.18)	(0.18)

[a] $[VPi]_0 = 6.8$ M (run 3 in Table 4). [b] $[VPi]_0 = 1.4$ M (run 18 in Table 4). [c] Calculated from the triad and tetrad according to the following equations:[28] $\beta = 2(mrm)/(mr)$, $1 - \beta = (mrr)/(mr)$, $\gamma = (mmr)/(mr)$, $1 - \gamma = 2(rmr)/(mr)$, $(rr)/(mr) = (1 - \beta)/2\delta$, $(mm)/(mr) = \gamma/2(1 - \alpha)$. Tetrad tacticity was determined based on methylene signals in ^{13}C NMR spectrum: $(rrr) = (0.079)$, $(mrr) + (mrm) = 0.358$, $(rmr) + (mmr) = 0.486$, $(mmm) = (0.077)$.

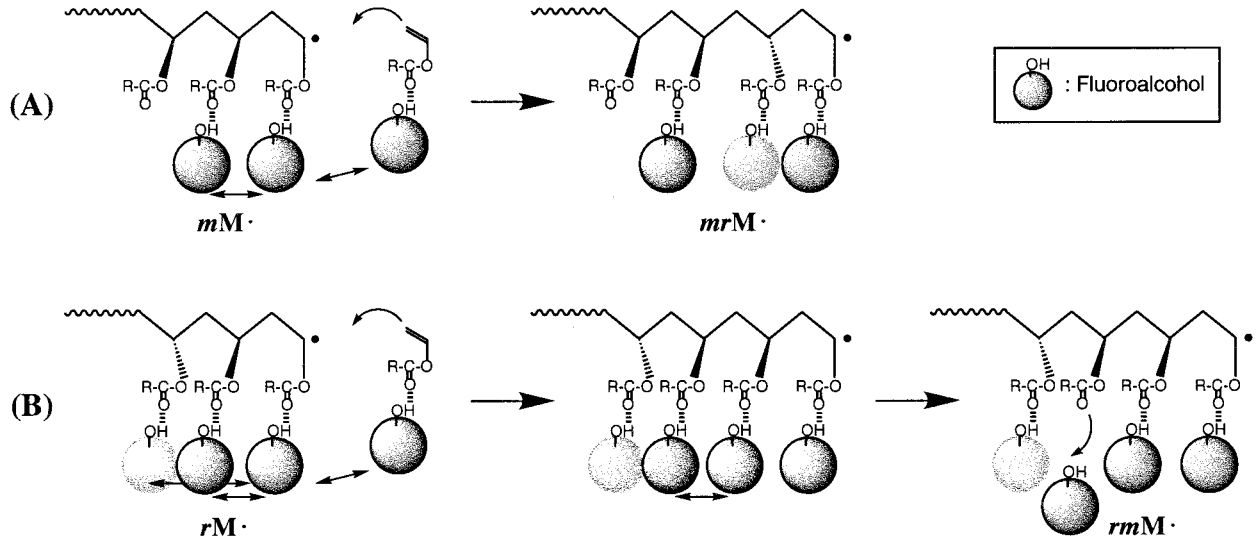


Figure 8. Stereoregulation mechanism in the heterotactic-specific free radical polymerization of VPi in fluoroalcohols.

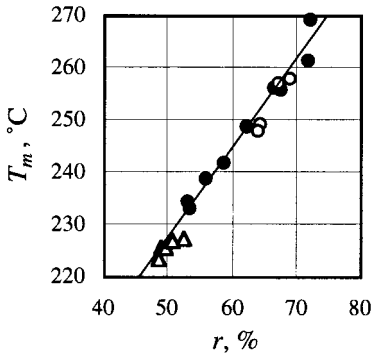


Figure 9. Relationship between diad syndiotacticity (*r*) and melting point of PVA obtained through the polymerization of VAc in $(CF_3)_3COH$ (●), VPi in $(CF_3)_3COH$ (△), and VPi in *n*-hexane (○).[6,33,34]

through the polymerization of VPi.[6] On the other hand, T_m of the heterotactic PVA obtained through the VPi polymerization in $(CF_3)_3COH$ is lower than that of an atactic PVA. This may be attributed to the decrease in syndiotactic sequences which may contribute to enhancement of the melting point through the intermolecular hydrogen bonding of PVA.

Conclusions

Syndiotactic PVA with a diad syndiotacticity of 72% and a melting point of 269 °C was obtained by the polymerization of VAc in $(CF_3)_3COH$ at −78 °C. $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ in this polymerization system were estimated to be 550 ± 50 cal/mol and 0.9 ± 0.2 cal/mol·K, respectively. The stereochemistry of the polymerization was well-described by a first-order Markov model. However, the polymerization of VPi in $(CF_3)_3COH$ at −40 °C gave a heterotactic polymer with an *mr* of 61%. The stereochemistry of the polymerization was not well-described by either a first-order Markov model or a second-order Markov model. The stereospecificity of the polymerizations of vinyl esters may be ascribed to (a) hydrogen-bond interaction between the fluoroalcohol molecules and the ester groups of the monomer and the growing species and (b) steric repulsion between these apparently bulky side groups. The unique solvent effects of fluoroalcohols on the stereochemistry of the vinyl ester polymerizations may be applicable to the radical polymerization of other monomers.

Acknowledgment. We acknowledge Professor M. Sawada and Dr. Y. Takai (Osaka University) for their

kind cession of their fitting programs for ^{1}H NMR titrations. This work was supported by NEDO for the project on Technology for the Novel High-Functional Materials in Industrial Science and Technology Frontier Program, AIST.

References and Notes

(1) For reviews, see: (a) Finch, C. A., Ed. *Polyvinyl Alcohol—Developments*; Wiley: Chichester, 1992. (b) Fujii, K. *J. Polym. Sci., Macromol. Rev.* **1971**, *5*, 431. (c) *PVA no Sekai (The World of PVA)*; Kobunshi Kankokai: Kyoto, 1992.
(2) Matsuzawa, S.; Yamaura, K.; Noguchi, H.; Hayashi, H. *Makromol. Chem.* **1973** *165*, 217.
(3) Matsuzawa, S.; Yamaura, K.; Noguchi, H. *Makromol. Chem.* **1973**, *168*, 27.
(4) Nozakura, S.; Sumi, M.; Uoi, M.; Okamoto, T.; Murahashi, S. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 279.
(5) Fukae, R.; Kawakami, K.; Yamamoto, T.; Sangen, O.; Kato, T.; Kamachi, M. *Polym. J.* **1995**, *27*, 1257.
(6) Fukae, R.; Yamamoto, T.; Fujita, Y.; Kawatsuki, N.; Sangen, O.; Kamachi, M. *Polym. J.* **1997**, *29*, 293.
(7) Nakano, T.; Makita, K.; Okamoto, Y. *Polym. J.* **1998**, *30*, 681.
(8) Yamada, K.; Nakano, T.; Okamoto, Y. *Polym. J.* **1998**, *30*, 641.
(9) Imai, K.; Shiomi, T.; Oda, N.; Otsuka, H. *J. Polym. Sci., Part A* **1986**, *24*, 3225.
(10) Yamamoto, T.; Yamamoto, T.; Minamizawa, T.; Hirota, M. *Kobunshi Ronbunshu* **1979**, *36*, 557; *Chem. Abstr.* **1991**, 158200.
(11) Kador, U.; Mehnert, P. *Makromol. Chem.* **1971**, *144*, 29.
(12) Schrems, O.; Oberhoffer, H. M.; Luck, W. A. P. *J. Phys. Chem.* **1984**, *88*, 4335.
(13) Luck, W. A. P.; Peil, S. *J. Mol. Struct.* **1990**, *224*, 185.
(14) The preliminary results of VAc polymerization have been reported (Yamada, K.; Nakano, T.; Okamoto, Y. *Proc. Jpn. Acad.* **1998**, *74* (*B*), 46).
(15) Zutty, N. L.; Welch, F. J. *J. Polym. Sci.* **1960**, *43*, 445.
(16) d 1.63 (d, 3H), 2.19 (s, 3H), 6.98 (q, 1H) ($CDCl_3$, room temperature). (CAS registry no. 25432-06-8).
(17) Kamachi, M.; Liaw, D. J.; Nozakura, S. *Polym. J.* **1979**, *11*, 921.
(18) Clarke, J. T.; Howard, R. O.; Stockmayer, W. H. *Makromol. Chem.* **1961**, *44/46*, 427.
(19) Filler, R.; Schure, R. M. *J. Org. Chem.* **1967**, *32*, 1217.
(20) Fordham, J. W. L. *J. Polym. Sci.* **1959**, *39*, 321.
(21) Hatada, K.; Sugino, H.; Ise, H.; Kitayama, T.; Okamoto, Y.; Yuki, H. *Polym. J.* **1980**, *12*, 55.
(22) (a) Goodman, M.; Brandrup, J. *J. Polym. Sci., Part A* **1965**, *3*, 327. (b) Brame, E. G., Jr.; Vogl, O. *J. Macromol. Sci.* **1967**, *A1*, 277.
(23) Nozakura, S.; Ishihara, S.; Inaba, Y.; Matsumura, K.; Murahashi, S. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1053.
(24) (a) Kitayama, T.; Zhang, Y.; Hatada, K. *Polym. J.* **1994**, *26*, 868. (b) Kitayama, T.; Hirano, T.; Hatada, K. *Tetrahedron* **1997**, *53*, 15263.
(25) Kobayashi, M.; Ishizone, T.; Hirao, A.; Nakahama, S.; Kobayashi, M. *Polym. Prepr. Jpn.* **1997**, *46* (2), 183.
(26) Balakrishnan, T.; Devarajan, R.; Santappa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1909.
(27) Gotoh, Y.; Iihara, T.; Kanai, N.; Hirai, H. *Chem. Lett.* **1990**, 2157.
(28) (a) Wu, T. K.; Sheer, M. L. *Macromolecules* **1977**, *10*, 529. (b) Ovenall, D. W. *Macromolecules* **1984**, *17*, 1458. (c) Hikichi, K.; Yasuda, M. *Polym. J.* **1987**, *19*, 1003.
(29) Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: San Diego, CA, 1996; p 133.
(30) (a) Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley: New York, 1987; p 24—28. (b) Gil, V. M. S.; Oliveira, N. C. *J. Chem. Educ.* **1990**, *67*, 473. (c) Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375.
(31) The data fitting was performed using a BASIC program written by Professor M. Sawada and Dr. Y. Takai (Osaka University).
(32) Yuki, H.; Hatada, K.; Niimori, T.; Kikuchi, Y. *Polym. J.* **1970**, *1*, 36.
(33) Fukae, R.; Yamamoto, T.; Sangen, O.; Saso, T.; Kato, T.; Kamachi, M. *Polym. J.* **1990**, *22*, 636.
(34) Lyoo, W. S.; Ha, W. S. *J. Polym. Sci., Part A* **1997**, *35*, 55.

MA980889S