Stereospecific Polymerization of Vinyl Acetate in Fluoroalcohols and Synthesis of Syndiotactic Poly(vinyl alcohol)

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ABSTRACT: The free-radical polymerization of vinyl acetate (VAc) was carried out in various alcoholic solvents in connection with our recent publication in which we reported that the radical polymerization of VAc in $(CF_3)_3COH$ as a solvent results in a polymer having a high syndiotacticity ($r = 72.2\%$) [K. Yamada, T. Nakano, and Y. Okamoto, *Macromolecules*, **31**, 7598 (1998)]. In this study, $(CF_3)_2CHOH$, a fluoroalcohol much less expensive than $(CF_3)_3COH$, was found to have an r-enhancing effect similar to $(CF_3)_3COH$. The syndiotacticity achieved in this system was up to 70.3% , which is comparable to that during the radical polymerization of vinyl esters in $(CF_3)_3COH$. Through the large-scale polymerization using $(CF_3)_2CHOH$ as a solvent, syndiotactic PVA ($r = 69.2\%$) was obtained for the characterization of its physical properties. It is noteworthy that the polymerization in $(CF_3)_2CHOH$ at $-78°C$ smoothly proceeded in spite of the fact that the reaction system was apparently solid.
KEY WORDS Vinyl Acetate / Radical / Polymerization / Fluoroalcohol / Tacticity / Poly(vinyl alcohol) /

Stereochemical control during the radical polymerization of vinyl monomers is one of the most important topics in synthetic polymer chemistry because the stereostructure of the main chain often significantly affects the properties of the polymers. Poly(vinyl alcohol) (PVA) is a typical polymer whose physical properties are sensitive even to a slight change in the main-chain stereostructure.[1] PVA is industrially produced by the radical polymerization of VAc and the hydrolysis of the obtained polymer. Therefore, it is important to regulate the stereochemistry of the radical polymerization of VAc in order to obtain the PVA with controlled properties. It is known that a higher syndiotactic content in PVA improves its properties such as heat resistance, tensile strength, and elastic modulus.

An effective method for obtaining a poly(vinyl ester) rich in syndiotacticity is to polymerize a bulky monomer.[2—8] Although a properly designed monomer leads to effective stereoregulation, this method inherently lacks versatility and an economic advantage. We have recently introduced a new, more versatile method of stereoregulation that is based on the solvent effects of some fluoroalcohols and is effective not only for the radical polymerization of vinyl esters[9] but also

methacrylates.[10] Among the fluoroalcohols examined so far, perfluoro-*tert*-butyl alcohol ($(CF_3)_3COH$) exhibits the largest stereoeffect. During the polymerization of VAc using $(CF_3)_3COH$ as a solvent, a diad syndiotactic specificity of up to 72.2% has been achieved; this is the highest r value for the radical polymerization of vinyl esters reported so far.[9] However, from the view point of the practical synthesis of syndiotactic PVA for the characterization of its physical properties, the polymerization in $(CF_3)_3COH$ is not recommended because of the high cost of the alcohol. On the other hand, Imai reported that syndiotactic-specifity in VAc polymerization was enhanced using phenol as solvent at 60°C.[11] However, the effect of phenol was only slight.

In the present study, we explored other fluoroalcohol solvents which have a stereoeffect comparable to $(CF_3)_3COH$ during VAc polymerization, and found a more economical solvent, 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$), has a syndiotactic enhancing effect similar to that of $(CF_3)_3COH$.[12] In this paper, the details of the radical polymerization of VAc in $(CF_3)_2CHOH$ are presented.

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Table I. Polymerization of VAc in various solvents[a]

Run	Solvent	Temp. °C	Time h	Yield[b] %	M_n^c ×10^{-3}	M_w/M_n^c	Tacticity[d] mm	mr	rr	r
1[e]	None	60	0.1	73	54	1.6	21.8	49.6	28.6	53.4[f]
2[e]	None	20	1	71	55	1.9	22.6	48.9	28.5	52.9
3[e]	None	−78	600	8	74	1.6	22.5	48.8	28.7	53.1
4	C_6H_5OH	−78	144	0						
5	$t\text{-}C_4H_9OH$	−78	144	44	50	2.0	22.8	49.9	27.3	52.3
6	CH_3COOH	−78	144	0						
7	$(CH_3)_3CCOOH$	−78	144	24	118	4.2	21.7	50.0	28.3	53.3
8[e]	CF_3CH_2OH	60	2	81	26	1.9	21.1	49.2	29.7	54.3
9[e]	CF_3CH_2OH	20	24	62	13	1.9	19.8	49.9	30.3	55.2
10	CF_3CH_2OH	−78	144	6	62	1.8	17.4	48.7	33.9	58.2
11	$(CF_3)_2CHOH$	−78	144	73	71	2.0	7.9	43.6	48.5	70.3
12[e]	$(CF_3)_3COH$	20	24	94	62	1.8	13.0	49.4	37.6	62.3
13[e]	$(CF_3)_3COH$	−78	168	50	83	1.5	5.3	44.9	49.8	72.2

[a] $[VAc]_o$ = 10.8 mol L^{-1} (Run 1—3), 2.2 mol L^{-1} (Run 4—13), $[AIBN]_o$ = 0.15 mol L^{-1} (Run 1—3, 8, 9, 12), $[n\text{Bu}_3B]_o$ = 0.2 mol L^{-1} (Run 4—7, 10, 11, 13), UV radiation (Run 2, 9). [b] Et_2O-insoluble part. [c] Determined by SEC (PSt standard, THF). [d] Determined by 400 MHz ^1H NMR of PVA (Run 1—3, 8, 9, 12), by 125 MHz ^{13}C NMR (Run 4—7, 10, 11, 13) in DMSO-d_6. [e] Data were cited from ref 9b. [f] 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%.

EXPERIMENTAL

Materials

VAc (Wako) was purified by distillation. $(CF_3)_3COH$ (Aldrich; purity >99%), CF_3CH_2OH (Aldrich; purity >99%), $(CF_3)_2CHOH$ (Wako; purity >99%), $(CH_3)_3CCOOH$ (Wako; purity >98%), $(CH_3)_3COH$ (TCI; purity >99%) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Tri-*n*-butylborane ($n\text{Bu}_3B$) was obtained as a tetrahydrofuran (THF) solution (1.0 M) (Aldrich) and used after removal of the solvent.

Polymerization

Polymerization was carried out under a dry nitrogen atmosphere in a dried glass tube equipped with a three-way stopcock. The reactions at 60°C were performed using AIBN and those at 20°C and 0°C under UV light irradiation (400-W high-pressure mercury lamp). The polymerizations at −20°C, −50°C, and −78°C were conducted using $n\text{Bu}_3B$ as follow.[4, 13] A solvent and VAc were mixed in glass ampule under nitrogen and the solution was cooled to reaction temperature. $n\text{Bu}_3B$ was added and the reaction was initiated by introducing a small amount of air with a syringe. After a prescribed polymerization time, the reaction mixture was diluted with acetone and poured into a larger amount of diethyl ether. The precipi-

tated poly(VAc) was filtered and dried under vacuum at 60°C. The obtained poly(VAc) was saponified as follows. To a solution of poly(VAc) in methanol, a 10% methanol solution of NaOH was added, and the mixture was stirred for one day at room temperature to give methanol-insoluble products (PVA). The obtained PVA was collected by filtration, washed 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) 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 G3000 H_{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 GEMINI 2000 spectrometer (400 MHz for ^1H) or UNITY-INOVA (500 MHz for ^1H) in dimethylsulfoxide-d_6 (DMSO-d_6) at room temperature (^1H) or at 80°C (^{13}C). The melting points of a solvent mixture were measured using a SEIKO SSC5200 differential scanning calorimeter at cooling and heating rate of 3°C min^{-1}.

Table II. Effects of monomer concentration and temperature on the polymerization of VAc in $(CF_3)_2CHOH^a$

Run	$[VAc]_o$ mol L^{-1}	Temp. °C	Time h	Yield[b] %	M_n^c ×10^{-3}	M_w/M_n^c	Tacticity[d]			
							mm	*mr*	*rr*	*r*
1	5.4	60	24	85	41	3.3	17.7	52.5	29.8	56.1
2	4.4	60	24	80	53	2.4	17.0	52.7	30.3	56.6
3	3.3	60	24	75	51	2.1	15.6	52.7	31.7	58.0
4[e]	2.2	60	24	44	47	1.7	15.2	53.4	31.4	58.1
5	2.2	0	24	20	116	1.6	14.3	50.2	35.5	60.6
6	5.4	−20	96	32	63	2.3	15.6	48.5	35.9	60.1
7	4.4	−20	96	43	72	1.9	14.2	47.9	37.9	61.9
8	3.3	−20	96	20	65	1.8	13.5	47.6	38.9	62.7
9	2.2	−20	96	1	69	1.6	12.7	48.7	38.6	63.0
10	2.2	−50	144	27	79	2.6	10.1	49.2	40.7	65.3
11	5.4	−78	144	95	88	3.3	11.7	44.4	43.9	66.1
12	4.4	−78	144	90	75	2.5	10.6	44.7	44.7	67.1
13	3.3	−78	144	89	60	3.9	10.0	42.2	46.8	68.4
14	2.2	−78	144	73	71	2.0	7.9	43.6	48.5	70.3

[a] $[AIBN]_o$ = 0.03 mol L^{-1} (Run 1—4), $[AIBN]_o$ = 0.15 mol L^{-1} (Run 5), UV radiation (Run 5), $[nBu_3B]_o$ = 0.2 mol L^{-1} (Run 6—14). [b] Et_2O-insoluble part. [c] Determined by SEC (PSt standard, THF). [d] Determined by 400 MHz ^{1}H NMR (Run 1—9), by 125 MHz ^{13}C NMR (Run 10—14) of PVA in DMSO-d_6. [e] The tacticity of *mm/mr/rr* = 18.7/49.7/31.6 (r = 56.4) has been reported for the polymerization at $[AIBN]_o$ = 0.15 mol L^{-1} in ref 9 b.
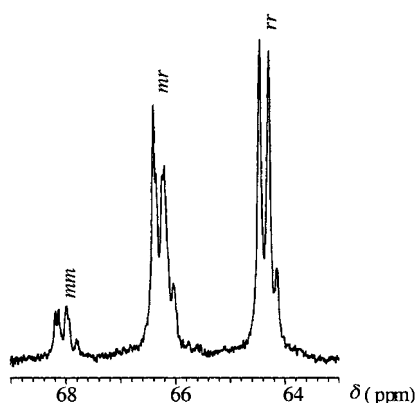
Figure 1. 125 MHz ^{13}C NMR spectra (methine region) of PVA obtained in run 11 in Table I (DMSO-d_6).

RESULTS AND DISCUSSION

Solvent Effects

The polymerization of VAc was carried out in various solvents using AIBN as the initiator at 60°C and 20°C or using nBu_3B at −20°C, −50°C, and −78°C (Table I). The data of runs 1—3, 8, 9, 12, and 13 are cited from our recent report for comparison.[9b] The reactions for runs 4—7, 10, and 11 at −78°C were performed in this study. We did not examine these reactions in our previous study because the polymerization systems seemed to be solid and we assumed that the reaction would not take place in the solid state. However, as shown in the table, the polymerizations at −78°C in the solid state except for that in C_6H_5OH and CH_3COOH afforded polymers. Although the stereochemistry of the polymerizations in t-C_4H_9OH and $(CH_3)_3CCOOH$ at −78°C was similar to that of the bulk polymerization, the fluoroalcohols, CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_3COH$, resulted in a higher syndiotacticity of the products compared to the bulk polymerization. This indicates that the stereoeffect is due not simply to low temperature commonly to the all solvents but specific to the fluoroalcohols. The syndiotaciticity (r = 70.3%) of the polymer obtained in $(CF_3)_2CHOH$ at −78°C was comparable to that in $(CF_3)_3COH$ at −78°C, although at 20°C, $(CF_3)_3COH$ afforded the polymer with about a 7% higher r content than $(CF_3)_2CHOH$. Figure 1 shows the ^{13}C NMR (methine carbon) spectra of the PVA obtained through the polymerization in $(CF_3)_2CHOH$ at −78°C (runs 11 in Table I). The spectra showed that the r-enhancing effect of $(CF_3)_2CHOH$ is only slightly lower than that of $(CF_3)_3COH$.

In search of a more efficient control of the stereochemistry, the polymerization in a mixture of $(CF_3)_2CHOH$ and $(CF_3)_3COH$ was investigated for various ratios of the two solvents. However, the diad r content was between 72.2% (the value for the polymerization in pure $(CF_3)_3COH$) and 70.3% (the value for the polymerization in pure $(CF_3)_2CHOH$); no special effect on the stereochemistry using the mixed solvent systems was observed.

Effects of Temperature and Monomer Concentration

Since we found that $(CF_3)_2CHOH$ is as effective as $(CF_3)_3COH$ in enhancing the syndiotactic specifity of the VAc polymerization, the polymerization in $(CF_3)_2CHOH$ was examined in detail. First, the effects

Table III. Activation parameters for the polymerization of VAc in fluoroalcohols

Solvent	$\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$/cal mol^{-1} [a]	$\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$/cal mol^{-1} K^{-1} [a]
None[b]	-10 ± 40	-0.3 ± 0.2
CF$_3$CH$_2$OH	150 ± 30	0.1 ± 0.1
(CF$_3$)$_2$CHOH	500 ± 40	1.0 ± 0.2
(CF$_3$)$_3$COH[b]	550 ± 50	0.9 ± 0.2

[a]The range of errors was estimated based on the errors in tacticity determination ($\pm 0.5\%$; see Table I). [b]The data were cited from ref 9b.
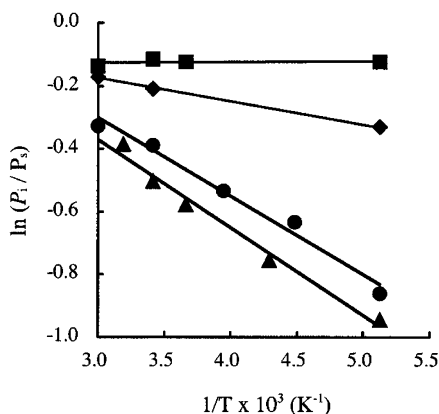
Table IV. Activation parameters for the polymerization of VAc at various concentrations in (CF$_3$)$_2$CHOH

Concentration/mol L^{-1}	$\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$/cal mol^{-1} [a]	$\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$/cal mol^{-1} K^{-1} [a]
5.4	400 ± 40	0.7 ± 0.2
4.4	420 ± 40	0.7 ± 0.2
3.3	420 ± 40	0.6 ± 0.2
2.2	500 ± 40	1.0 ± 0.2

[a]The range of errors was estimated based on the errors in tacticity determination ($\pm 0.5\%$; see Table I).

Figure 2. Temperature dependence of tacticity in the polymerization of VAc in bulk ( ) CF$_3$CH$_2$OH( ), (CF$_3$)$_2$CHOH( ), and (CF$_3$)$_3$COH( ). The plots for the bulk polymerization and those in (CF$_3$)$_3$COH were made using the data reported in ref 9b. In the plots for the polymerization in CF$_3$CH$_2$OH and (CF$_3$)$_2$CHOH, the data at $-78°$C were obtained in this work and the others were cited from ref 9b.
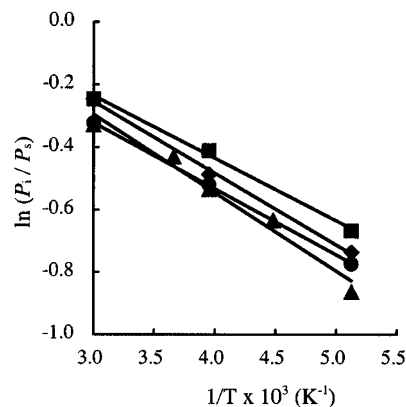
Figure 3. Monomer concentration dependence of tacticity in the polymerization of VAc in (CF$_3$)$_2$CHOH. Monomer concentration: 5.4 mol L^{-1} ( ), 4.4 mol L^{-1} ( ), 3.3 mol L^{-1} ( ), 2.2 mol L^{-1} ( ). In the plot for the polymerization at 2.2 mol L^{-1}, the data at $-78°$C were obtained in this work and the others were cited from ref 9b.

of the monomer concentration and temperature during the polymerization were investigated (Table II). At a constant monomer concentration of 2.2 M, a lower temperature resulted in a higher r content of the polymer. It was interesting that at the constant [M] of 2.2 M, the yield of polymer decreased with a decrease in temperature in the range of 60—$-20°$C, but it increased to 73% at $-78°$C. This drastic increase in the yield may have a connection to the fact that the system appeared to be solid at $-78°$C. At all the temperatures, a lower [M] (a higher solvent concentration) resulted in a higher r specficitiy of the polymerization.

Figures 2 and 3 show the temperature dependence of tacticity during the polymerization of VAc in (CF$_3$)$_2$CHOH (Fordham plots[14]). The differences in activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) between the isotactic and syndiotactic-specific propa-

gations can be determined by the plot according to the following equation (1)[15]:

$$\ln\left(\frac{P_i}{P_s}\right) = \frac{\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}}{R} - \frac{\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}}{RT} \quad (1)$$

where P_i and P_s are the mole fractions of the isotactic and syndiotactic diads, respectively, R is the gas constant (1.987 cal deg^{-1} mol^{-1}), and T is 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 VAc polymerizations are summarized in Tables III and IV. The values for the polymerizations in bulk and in (CF$_3$)$_3$COH in Table III were cited from ref 9b. Although we have already reported the values for the reactions in (CF$_3$)$_2$CHOH and CF$_3$CH$_2$OH,[9b] they were recalculated in this study by incorporating the data points obtained at $-78°$C. The data points for the reactions at $-78°$C fit well with the other data points, and the newly obtained $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger}$

Table V. Large-scale synthesis of syndiotactic poly(VAC) in $(CF_3)_2CHOH^a$

VAc	$(CF_3)_2CHOH$	Yield[b]	M_n^c	M_w/M_n^c	Tacticity[d]			
mL (g)	mL	g (%)	$\times 10^{-3}$		*mm*	*mr*	*rr*	*r*
90 (84)	360	36 (43)	114	2.7	8.5	44.6	46.9	69.2

$^a[VAc]_o = 2.2$ mol L^{-1}, $[nBu_3B]_o = 0.2$ mol L^{-1}, Temp. $= -78°C$, Time $= 144$ h. ^{b}Et$_2$O-insoluble part. ^{c}Determined by SEC (PSt standard, THF). ^{d}Determined by 125 MHz ^{13}C NMR of PVA in DMSO-d_6.

$-\Delta S_s^{\ddagger}$ values for the two reaction systems are in fair agreement with the previous values ($\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} = 200 \pm 70$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger} = 0.3 \pm 0.3$ in CF_3CH_2OH; $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} = 520 \pm 70$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger} = 1.1 \pm 0.3$ in $(CF_3)_2CHOH$).[9b] This means that the polymerization at $-78°C$ in the seemingly solid state may proceed with a stereochemical mechanism similar to that at higher temperature in a solution. The results shown in the tables indicate that the syndiotactic-specific propagation in $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ is favored by enthalpy factors. The $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ values varied depending on the monomer concentration in $(CF_3)_2CHOH$.

Time vs. Polymer Yield and Time vs. Molecular Weight Relationships

The relationship between the polymerization time and polymer yield and that between the polymerization time and the molecular weight of polymer for the polymerization in $(CF_3)_2CHOH$ at $-78°C$ are shown in Figure 4. The reaction was rather sluggish under this condition probably because of the slow diffusion of the reactants in the reaction system, which seemed to be solid. However, the molecular weight of the products was the highest during the early stages of the polymerization and gradually decreased with the increasing polymerization time, which resembles the characteristic feature common to the radical polymerization systems in a solution, although the decrease in M_n according to the polymerization time was rather small. These results suggest that the reaction in $(CF_3)_2CHOH$ at $-78°C$ takes place in a manner similar to that during the solution polymerization. The reaction mixture may have a slightly softer structure than crystals in which molecules can diffuse, although the reaction mixture was almost solid. Another possibility was that the diffusion of the reactants might be much slower compared with the regular solution polymerization resulting in a slower bimolecular termination.

The tacticity of the products varied depending on the reaction time during the polymerization which gave the data shown Figure 4. The polymer obtained 6 h after the initiation (15% polymer yield) and the one obtained 144 h after the initiation (73% polymer yield, run 15 in Table I) had *r* contents of 69.0% and 70.3% , re-
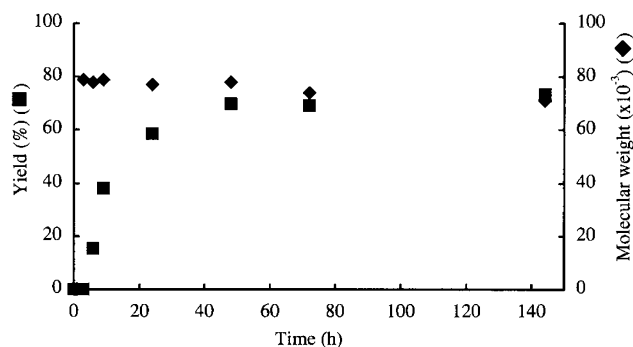

Figure 4. Yield and molecular weight in the polymerization of VAc in $(CF_3)_2CHOH$ at $-78°C$. Yield; ( ), Molecular weight; ( ). Reaction condition; $[VAc]_o = 2.0$ mol L^{-1}, $[nBu_3B]_o = 0.2$ mol L^{-1}.
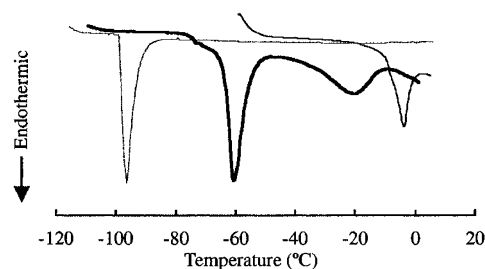

Figure 5. DSC thermograms of VAc, $(CF_3)_2CHOH$, and their mixture. VAc; (—), $(CF_3)_2CHOH$; (—), VAc/$(CF_3)_2CHOH$ = 1/4 (v/v); (—).

spectively. This is consistent with the monomer concentration effect in the preceding section because the monomer concentration decreased as the polymerization proceeded.

DSC Analysis of the Mixture of VAc and $(CF_3)_2CHOH$

In order to obtain information on the structure of the reaction system, a DSC analysis was performed on the mixture of VAc and $(CF_3)_2CHOH$ (Figure 5). For the analyses of the pure $(CF_3)_2CHOH$ and pure VAc of the heating runs, the alcohol and the monomer each indicated an endothermic peak at the position corresponding to the melting point. The mixture of $(CF_3)_2CHOH$ and VAc indicated two endothermic peaks at $-60°C$ and around $-20°C$, indicating that the solvent and the monomer do not independently crystallize but they form a complex when the reaction system is solidified at $-78°C$.

A Large-Scale Polymerization of VAc using (CF₃)₂-CHOH as Solvent

Taking advantage of the cost performance of $(CF_3)_2CHOH$, we performed the polymerization of VAc (90 mL (84 g)) in this solvent to obtain the syndiotactic PVA sample for the characterization of its physical properties (Table V). The reaction was carried out in a 1 L separable flask equipped with a mechanical stirrer. The reaction system was agitated for the initial 30 min of the polymerization and, after this period, the reaction mixture became too hard to stir. In this case, the polymerization system led to a polymer having an *r* content ($r = 69.2\%$) comparable to the smaller-scale polymerization, though the polymer yield was lower (36 g, 43%) than that in the smaller-scale reaction. If the reaction system was not initially stirred, the polymer having a low syndiotacticity ($r < 60\%$) was obtained, because most of the solvent with a higher melting point ($-4°C$) in the polymerization system was independently solidified. The results of the characterization of PVA derived from this polymerization will be published elsewhere.

In conclusion, during the radical polymerization of VAc at $-78°C$, $(CF_3)_2CHOH$ was found to be as effective as $(CF_3)_3COH$ in enhancing the syndiotactic-specific propagation. Although the reaction system was seemingly solid, the reaction smoothly proceeded. By utilizing the solvent effect of $(CF_3)_2CHOH$, which is much less expensive than $(CF_3)_3COH$, a syndiotactic poly(VAc) was prepared using 84 g of the monomer.

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