Iodine Transfer Radical Polymerization of Vinyl Acetate in Fluoroalcohols for Simultaneous Control of Molecular Weight, Stereospecificity, and Regiospecificity

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ABSTRACT: The simultaneous control of the tacticity and molecular weight of poly(vinyl acetate) during the radical polymerization of vinyl acetate (VAc) is reported for the first time. A series of fluoroalcohols [$(CF_3)_3COH$, $(CF_3)_2CHOH$, $PhC(CF_3)_2OH$, m-$C_6H_4\{C(CF_3)_2OH\}_2$] were employed as solvents for the iodine transfer radical polymerization of VAc, in which the molecular weight of the resultant polymer was determined by the monomer-to-transfer agent ratio and its tacticity was controlled by the solvent. Among the fluoroalcohols, the use of fluorodiol, m-$C_6H_4\{C(CF_3)_2OH\}_2$, not only led to a higher syndiotacticity ($r \sim 60\%$) but also improved the molecular weight control, resulting in narrow molecular weight distributions (MWD) ($M_w/M_n \sim 1.20$) in the presence of $CH_2I(CO_2Et)$ and an azo-initiator [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)] at 20 °C. High molecular weight polymers ($M_n > 7 \times 10^4$) with a relatively narrow MWD ($M_w/M_n < 1.6$) were obtained with the same system. The content of the head-to-head linkages was obviously lower in the fluoroalcohols (∼0.8%) than in the bulk (∼1.2%). Thus, the fluoroalcohols not only led to a higher syndiotacticity but also improved the molecular weight control and the regiospecificity by suppressing the head-to-head propagation.

Introduction

Vinyl acetate (VAc) is a very important monomer since its polymers are used in various industrial applications. Especially, the saponification or hydrolysis of the polymer leads to poly(vinyl alcohol) (PVA), which has been attracting much attention in the chemical, material, and medical fields because of a unique combination of its solubility in water, film orientation characteristics for the polarizer of a liquid crystal display, adhesive ability to a number of substrates, low toxicity, biodegradability, and biocompatibility.[1−7] These properties depend on its primary structure, such as molecular weight and tacticity, the control of which should thus improve the properties and further contribute to the development of the PVA-based materials.

However, VAc can be polymerized only via a neutral radical intermediate, which renders the primary structure of poly(vinyl acetate) (PVAc) difficult to control. Specifically, control of the molecular weight has been considered more difficult than for conjugated monomers, such as (meth)acrylates and styrenes, due to the highly reactive radical species of PVAc, which undergoes radical−radical termination and chain transfer to the methyl group of the acetoxy substituents on the polymer and the monomer. In addition, the stereochemistry during radical polymerization is also very hard to control due to the lack of efficient methods that can induce the directed insertion or addition of the monomer to the free radical growing end. Another structural defect inherent to PVAc is the head-to-head linkage caused by the misdirected insertion of the monomer, in which the two carbons of the vinyl group are not distinguished well in terms of the electric polarization.[8−10] Thus, the control of the chemospecificity, stereosepcificity, and regiospecificity during the radical polymerization of VAc would lead to an innovative PVA.

Controlled or living polymerization is one of the most promising methods for the production of polymers with controlled molecular weights and their distributions. As represented by the nitroxide-mediated polymerization,[11,12] the metal-catalyzed living radical polymerization or atom transfer radical polymerization,[13−17] and the reversible addition−fragmentation chain transfer (RAFT) or macromolecular design via interchange of xanthates (MADIX)[18,19] processes, there have been a tremendous number of reports on the living or controlled radical polymerization systems in the past decade. In recent years, there appeared effective systems even for the polymerization of VAc to afford the polymers with precisely controlled molecular weights and a narrow molecular weight distribution (MWD). They include the MADIX/RAFT,[20−28] iron-catalyzed,[29] degenerative iodine transfer,[30−32] cobalt-mediated,[33,34] and organotellium- and organostibine-mediated processes.[35] Most of them are based on the degenerative chain transfer process, which accomplishes the molecular weight control via a fast interconversion between the growing radical and the covalent dormant species in the presence of a radical initiator.

As for the tacticity control during the radical polymerizations, protic solvents like fluoroalcohols or Lewis acids like the lanthanide trifluoromethanesulfonates proved effective in the stereospecific radical polymerizations[36] of commercially available vinyl monomers, such as vinyl esters,[37] methacrylates,[38] and (meth)acrylamides.[39,40] During these polymerizations, the stereospecific chain growth was caused by the hydrogen-bonding or coordinative interaction of the solvents or the additives with the polar groups in the monomer and/or the growing species. For example, the syndiospecific radical polymerization of VAc proceeds in a bulky fluoroalcohol like $(CF_3)_3COH$, which most probably interacts with the carbonyl group of the monomer and/or the growing chain end via hydrogen bonding to induce steric

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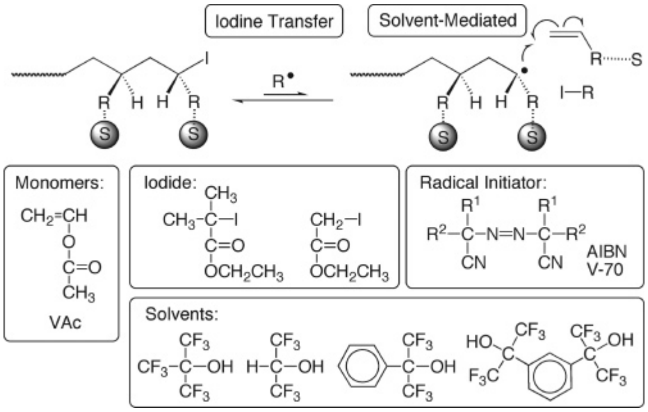
Scheme 1. Iodine Transfer Radical Polymerization of Vinyl Acetate in Fluoroalcohols



repulsion around the growing terminal.[37] The following saponification of the syndiotactic PVAc yielded the syndiotactic PVA with a higher melting temperature than that of the atactic PVA prepared by the conventional radical polymerization of VAc in the bulk and in methanol.

Considering these developments in the control of the molecular weight and tacticity by the radical polymerizations, we have been investigating the simultaneous control of both of these variables in the radical polymerization of various monomers.[41] Quite recently, the stereospecific and living/controlled polymerizations of acrylamides,[42−44] methacrylates,[45,46] and vinyl amides[47] have been achieved with the appropriate combination of stereospecific and living radical polymerizations. In the present study, we report the simultaneous control of the molecular weight and tacticity of PVAc for the first time by conducting the iodine transfer radical polymerization of VAc in fluoroalcohols. We thus employed several fluoroalcohols including $(CF_3)_3COH$ and other new ones that have not been studied for their stereospecific radical polymerization, in conjunction with an alkyl iodide such as $(CH_3)_2CI(CO_2Et)$ and $CH_2I(CO_2Et)$ for the best dual control (Scheme 1). Specifically, we found that a combination of m-$C_6H_4\{C(CF_3)_2OH\}_2$ and $CH_2I(CO_2Et)$ in the presence of an azo-initiator with a relatively low half-life decomposition temperature [V-70; 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)] gave PVAc with a narrow MWD ($M_w/M_n \sim 1.2$) and a high syndiotacticity ($r \sim 60\%$) at 20 °C. Lower head-to-head linkage contents were observed in the fluoroalcohols for the main-chain units and the growing terminal. Interaction of fluoroalcohols with monomer and the model growing terminal was further investigated using ^1H and ^{13}C NMR spectroscopy.

Experimental Section

Materials. Vinyl acetate (Wako, >98%) was distilled under reduced pressure to remove the inhibitors. α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, >95%) was used as received. 1,1,1,3,3,3-Hexafluoro-2-propanol (Wako, >99%), $PhC(CF_3)_2OH$ (Wako, >99%), and m-$C_6H_4\{C(CF_3)_2OH\}_2$ (Wako, >97%) as solvents and n-octane as an internal standard for gas chromatography were distilled from calcium hydride and bubbled with dry nitrogen for 15 min immediately before use. $(CF_3)_3COH$ (Aldrich, >99%) was bubbled with dry nitrogen and used without further purification. Ethyl 2-iodoisobutyrate (**1**) was prepared according to the literature.[48] Ethyl iodoacetate (**2**) (Aldrich, >98%) was distilled under reduced pressure before use. The 1,3-diacetoxybutane (**3**) was prepared by reaction of 1,3-butanediol (0.20 mol; Wako, >98%) and acetic anhydride (1.00 mol;Kanto, >97%) in pyridine at 100 °C for 1 h and purified by distillation (15 mmHg, 102 °C).

Polymerization. Typically, a mixture of VAc (4.19 g, 48.7 mmol), n-octane (0.53 mL), **1** (0.086 mL, 0.49 mmol), and AIBN (160 mg, 0.97 mmol) was degassed by three cycles of freeze−vacuum−thaw; then the solution was evenly charged in eight glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with n-octane as an internal standard. The polymer was isolated by precipitation into cold n-hexane (−78 °C) after dilution with THF (ca. 15 mL). The filtrated precipitate was evaporated to dryness under reduced pressure and dried under vacuum at room temperature for 12 h to give the product polymer quantitatively. Polymerization procedure in the presence of fluoroalcohols was carried out similarly. PVAc was saponified as follows. A 10% methanol solution of NaOH (1 mL) was added to a solution of PVAc (0.2 g) in methanol (9 mL), and then the mixture was stirred for 2 h at 40 °C to give PVA as the methanol-insoluble part. The polymer was collected by filtration, washed with methanol containing a small amount of acetic acid and with acetone, and then dried under vacuum for 12 h at 60 °C.

Measurements. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography [Shimadzu GC-8A equipped with a thermal conductivity detector and a 3.0 mm i.d. × 2 m stainless steel column packed with SBS-200 (Shinwa Chemical Industries Ltd.) supported on Shimalite W; injection and detector temperature = 200 °C, column temperature = 120 °C] with n-octane as an internal standard under He gas flow. ^1H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at 25 °C on a Varian Gemini 2000 spectrometer, operating at 400 MHz, and ^{13}C NMR spectra were recorded at 95 °C and 100 MHz. The triad tacticity of the polymer was determined on the area of the methine carbon of the backbone (^{13}C NMR) or the hydroxyl proton of the side group (^1H NMR).[8−10,49,50] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of PVAc were determined by size-exclusion chromatography (SEC) in THF 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 a Jasco PU-980 precision pump and a Jasco 930-RI detector. The columns were calibrated against eight standard polystyrene samples (Shodex; $M_p = 520-900000$; $M_w/M_n = 1.01-1.14$).

Results and Discussion

1. Search of the Best Systems for the Simultaneous Control of Molecular Weight and Tacticity. **(a) Polymerization in Various Fluoroalcohols.** For the purpose of the simultaneous control of the molecular weight and tacticity during the radical polymerization of VAc, various fluoroalcohols were tested in the iodine transfer radical polymerization because their structures not only are crucial for the tacticity control but also may affect the molecular weight control. During the radical polymerization of VAc without iodine compounds, the syndiotacticity of the produced polymers increased as the bulkiness and/or acidity of the fluoroalcohol increased.[37] Thus, we first employed a series of bulky fluoroalcohols [$(CF_3)_3COH$, $(CF_3)_2CHOH$, $PhC(CF_3)_2OH$, m-$C_6H_4\{C(CF_3)_2OH\}_2$] as solvents for the iodine transfer radical polymerization of VAc. Among them, the cummyl-type fluoroalcohols, $PhC(CF_3)_2OH$ and m-$C_6H_4\{C(CF_3)_2OH\}_2$, have not been employed for the radical polymerization of VAc without iodine compounds while $(CF_3)_3COH$ and $(CF_3)_2CHOH$ have already been proved effective for the syndiospecific radical polymerization.[37] VAc was polymerized in the bulk or in the fluoroalcohols (VAc/fluoroalcohol = 1/1 v/v) with AIBN in the presence of ethyl 2-iodoisobutyrate (**1**) as the degenerative transfer agent ($[VAc]_0/[\mathbf{1}]_0/[AIBN]_0 = 100/1/2$) at 60 °C. As shown in Figure 1, a quantitative and efficient

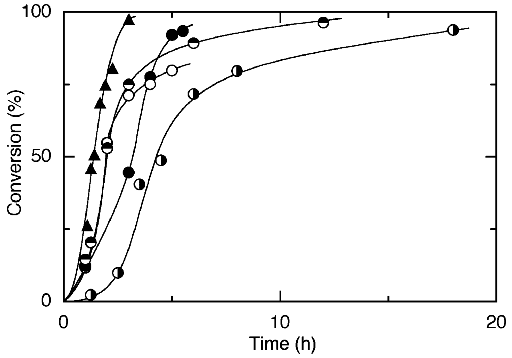


Figure 1. Time−conversion curves for the polymerization of vinyl acetate (VAc) with **1**/α,α-azobis(isobutyronitrile) (AIBN) in bulk or fluoroalcohols at 60 °C; $[VAc]_0 = 10$ (bulk) or 5.0 (fluoroalcohols) M; $[VAc]_0/[\mathbf{1}]_0 = 100$; $[AIBN]_0/[\mathbf{1}]_0 = 2$; in bulk (▲), $(CF_3)_3COH$ (●), $(CF_3)_2CHOH$ (○), $PhC(CF_3)_2OH$ (◑), and $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ (◓).

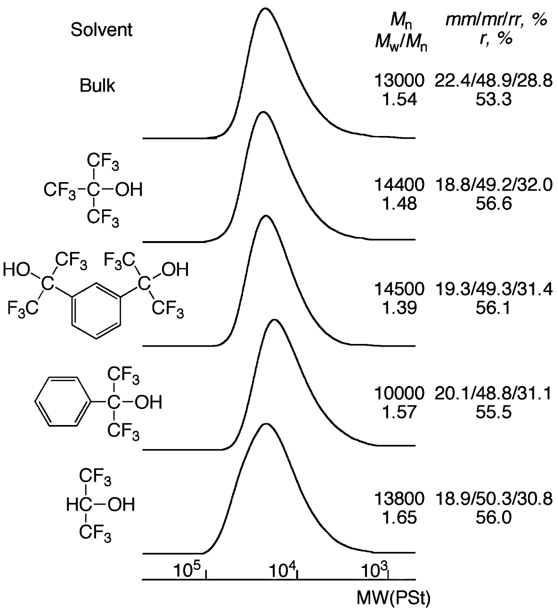


Figure 2. Size-exclusion chromatograms of poly(vinyl acetate) obtained in the same experiments as for Figure 1.

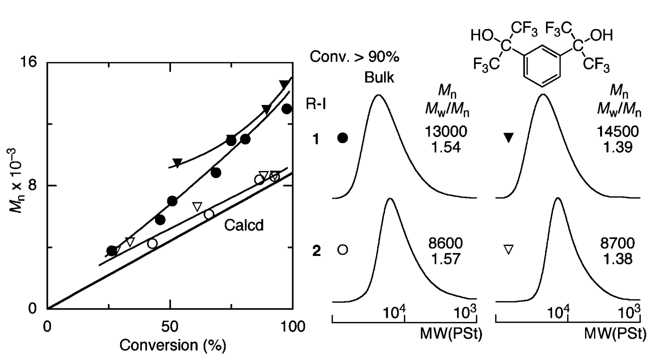


Figure 3. M_n and M_w/M_n curves of poly(vinyl acetate) obtained with **1**/ or **2**/α,α-azobis(isobutyronitrile) (AIBN) in bulk or $m\text{-}C_6H_4\{C(CF_3)_2\text{-}OH\}_2$ at 60 °C; $[\text{vinyl acetate}]_0 = 10$ (bulk) or 5.0 (fluoroalcohols) M; $[\text{vinyl acetate}]_0/[\mathbf{1}]_0 = 100$; $[AIBN]_0/[\mathbf{1}]_0 = 2$; in bulk with **1** (●) or **2** (○); in $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ with **1** (▼) or **2** (▽), respectively. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per one iodide molecule.

polymerization with a short induction period occurred even in the fluoroalcohols, similar to the bulk polymerization with the iodine compound (filled triangles in Figure 1). The polymerization rate and the induction period were slightly dependent on the fluoroalcohols.

Figure 2 compares the SEC curves of the polymers obtained by the iodine transfer radical polymerization in the fluoroalcohols and in the bulk. The iodine transfer radical polymerization proved effective in controlling the molecular weights even in the fluoroalcohols, where the number-average of molecular weights (M_n) increased in direct proportion to the monomer conversion. In all the cases, the M_ns were slightly higher than the calculated values assuming that one alkyl iodide (**1**) molecule generates one polymer chain. As discussed later, this is attributed to the structure of the degenerative transfer agent, and a finer tuning of the iodine compound is needed. The MWDs were relatively narrow during the polymerization and depended on the structure of the solvents. The fluorodiol, $m\text{-}C_6H_4\{C(CF_3)_2\text{-}OH\}_2$, gave the narrowest MWD ($M_w/M_n \sim 1.3$) under the stated conditions.

The tacticity of the polymers was examined by ^1H NMR spectroscopy after the saponification of the PVAc to PVA (see also Figure 2). The tacticity of the polymers obtained in the fluoroalcohols exhibited a higher racemo dyad content than in the bulk ($r = 53.3\%$) and was dependent on the solvent structure. The contents were almost the same as those obtained in the free radical polymerization in the absence of the alkyl iodides. This means that the alkyl iodide does not affect the tacticity. $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ had the excellent ability to induce a high syndiotacticity ($r = 56.1\%$) comparable to the highest racemo content ($r = 56.6\%$) with $(CF_3)_3COH$ as already reported.[37] The fluorodiol is also less expensive than $(CF_3)_3COH$. These results suggest the use $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ as one of the promising candidates for the further fine control of not only the stereospecificity but also the molecular weight.

(b) Structure of the Alkyl Iodide. To study the effects of the structure of the alkyl iodide on the molecular weight control, ethyl iodoacetate (**2**) was employed as another degenerative transfer agent for the VAc polymerization with AIBN in the bulk or in $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ at 60 °C. The VAc polymerizations with **2**/AIBN also smoothly proceeded and almost quantitatively irrespective of the solvents.

Figure 3 shows the molecular weight dependence on the monomer conversions for the polymers obtained using the **1** or **2**/AIBN systems in the bulk or in the fluorodiol. The M_ns of the polymer with **2** were much closer to the calculated values than with **1**. This is probably due to the higher reactivity of the primary radical derived from **2**. More specifically, the tertiary and conjugated radical derived from **1** is less reactive than the secondary and unconjugated radical at the growing PVAc terminal, which results in the slower addition of the former radical species and then a higher recombination or disproportionation probability during the early stage of the polymerization. Thus, **2** proved to be a better degenerative transfer agent in controlling the molecular weight during the radical polymerization of VAc. These results prompted us to further investigate the systems with **2** in $m\text{-}C_6H_4\{C(CF_3)_2OH\}_2$ for the better dual control of the molecular weight and tacticity.

(c) Temperature and Monomer Concentration. In the free radical polymerization of VAc in fluoroalcohols in the absence of alkyl iodides, lowering the monomer concentration by increasing the solvent amount and lowering the reaction temperature enhanced the syndiospecificity.[37] Thus, we investigated the VAc polymerizations with **2** in $m\text{-}C_6H_4\{C(CF_3)_2\text{-}OH\}_2$ at a lower temperature (20 °C) by varying the monomer concentration ($[M]_0 = 2.0-10$ M). As an azo-initiator effective at a low temperature, V-70 was employed in lieu of AIBN. The VAc polymerization proceeded even at 20 °C, as shown in Figure 4. The initial rate of the polymerization increased with the decreasing monomer concentration although, at the lowest

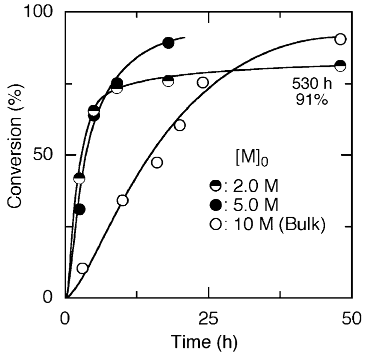


Figure 4. Time−conversion curves for the polymerization of vinyl acetate at 20 °C with **2**/2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in bulk or *m*-$C_6H_4\{C(CF_3)_2OH\}_2$: [vinyl acetate]$_0$ = 10 (bulk) (○), 5.0 (●), or 2.0 (◓) M; [vinyl acetate]$_0$/[**2**]$_0$ = 100; [V-70]$_0$/[**2**]$_0$ = 2.

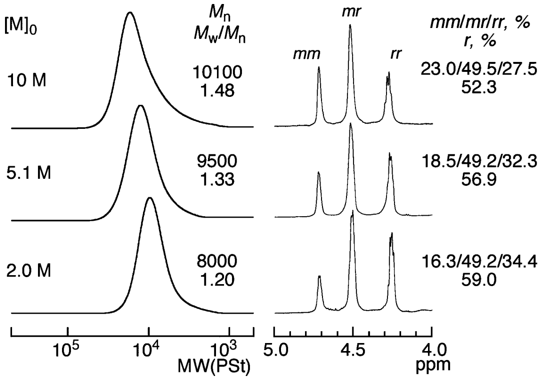


Figure 5. Size-exclusion chromatograms of poly(vinyl acetate) and ^{1}H NMR spectra (hydroxyl proton region, DMSO-d_6) of the corresponding poly(vinyl alcohol) obtained with **2**/2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in bulk or *m*-$C_6H_4\{C(CF_3)_2OH\}_2$: [vinyl acetate]$_0$ = 10 (bulk), 5.0, or 2.0 M; [vinyl acetate]$_0$/[**2**]$_0$ = 100; [V-70]$_0$/[**2**]$_0$ = 2.

concentration, it plateaued around an 80% monomer conversion. This indicates that the fluoroalcohol interacts with VAc to enhance the monomer reactivity and/or with the azo-initiator to accelerate its decomposition rate, which results in a faster polymerization.

Figure 5 shows the SEC curves of the PVAc obtained with **2**/V-70 at 20 °C by varying the monomer concentration. The molecular weights obtained at 20 °C were also well controlled, and the MWDs were narrower than that at 60 °C even in the bulk (M_w/M_n < 1.5). In addition, the narrower MWDs were obtained at a lower monomer concentration. At the lowest monomer concentration ([M]$_0$ = 2.0 M), the PVAc with very narrow MWDs (M_w/M_n = 1.20) was obtained.

The stereochemistry of the polymers was also evaluated by ^{1}H NMR spectroscopy after saponification to PVA (see also Figure 5). As in the radical polymerization without iodine compounds,[36] the tacticity of the polymer obtained at a lower temperature and a lower [M]$_0$ showed a higher syndiotacticity. More specifically, the racemo triad fraction (*rr*) increased to 34% at [M]$_0$ = 2.0 M.

Another series of polymerizations were examined using a series of fluoroalcohols at 20 °C with a low monomer concentration ([M]$_0$ = 2.0 M). Figure 6 shows the M_n, M_w/M_n, and SEC traces of the polymers obtained in the fluoroalcohols. The M_n of the polymers increased with the monomer conversion and agreed with the calculated values assuming that one molecule of **2** generates one polymer chain. Their MWDs were relatively narrow except for hexafluoro-2-propanol and became broader in the following order: *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ (M_w/M_n = 1.20) < $PhC(CF_3)_2OH$ (1.46) ~ $(CF_3)_3COH$ (1.46) < bulk (1.48) < $(CF_3)_2CHOH$ (2.67). The polymerization in $(CF_3)_2CHOH$ apparently suffers from some side reactions, most probably due to the hydrogen abstraction from the more or less activated C−H bond in the hexafluoroisopropyl group by the active growing radical species of PVAc.

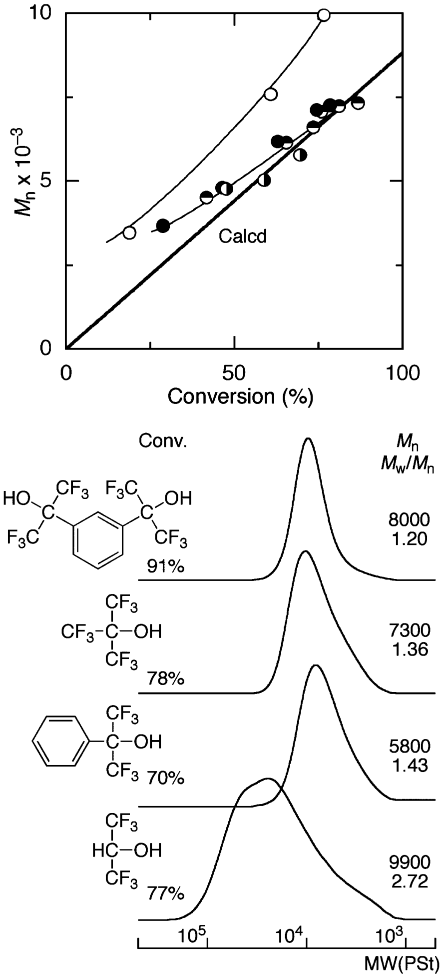


Figure 6. Polymerization of vinyl acetate with **2**/2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in various fluoroalcohols at 20 °C: [vinyl acetate]$_0$ = 2.0 M; [**2**]$_0$ = 20 mM; [V-70]$_0$ = 40 mM; in $(CF_3)_3COH$ (●), $(CF_3)_2CHOH$ (○), $PhC(CF_3)_2OH$ (◑), and *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ (◓). The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per one **2** molecule.

Table 1 summarizes the molecular weights and tacticities of the polymers obtained with **2**/V-70 in the fluoroalcohols at 20 °C. The tacticity of the obtained polymer was dependent on the fluoroalcohol but did not correlate with the MWDs. Among the fluoroalcohols that all gave a high syndiotacticity in comparison with that in the bulk, $(CF_3)_3COH$ was the most effective for the tacticity control (*r* = 60%). In terms of the simultaneous control, *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ proved to be the best which resulted in a relatively high syndiotacticity (*r* = 59%) and the narrowest MWD (M_w/M_n = 1.20) in combination with the iodine transfer polymerization with **2**.

(d) Synthesis of High Molecular Weight Polymer. When considering the good results for the molecular weight control with **2** in the fluorodiol, we aimed to synthesize high molecular weight polymers in *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ at 20 °C by varying the [VAc]$_0$/[**2**]$_0$ ratio from 100 to 1000 while the [**2**]$_0$/[V-70]$_0$ ratio remained constant ([**2**]$_0$/[V-70]$_0$ = 5). The polymerizations

Table 1. Dependence of Molecular Weight Distributions and Tacticity of Poly(vinyl acetate) on Solvent[a]

solvent	conv, %	M_n[b]	M_w/M_n[b]	*mm*/*mr*/*rr*, %[c]	*r*, %[d]
bulk	91	10100	1.47	23.0/49.5/27.5	52.3
m-$C_6H_4\{C(CF_3)_2OH\}_2$	91	8000	1.20	16.3/49.2/34.4	59.0
$PhC(CF_3)_2OH$	70	5000	1.36	16.7/49.2/34.1	58.7
$(CF_3)_3COH$	78	7100	1.31	14.4/50.5/35.1	60.4
$(CF_3)_2CHOH$	77	9900	2.72	16.8/49.5/33.7	58.5

[a] Polymerization conditions: $[\text{vinyl acetate}]_0/[\mathbf{2}]_0/[\text{V-70}]_0 = 100/1/2$, $[\text{vinyl acetate}]_0 = 10$ (bulk) or 2.0 M (in fluoroalcohols) at 20 °C. [b] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography. [c] The contents of isotactic (*mm*), heterotacic (*mr*), and syndiotactic (*rr*) triads determined by ^{1}H NMR spectroscopy of the corresponding poly(vinyl alcohol) in DMSO-d_6 at rt. [d] The content of racemo dyad (*r*) was calculated by the equation $r = rr + mr/2$.

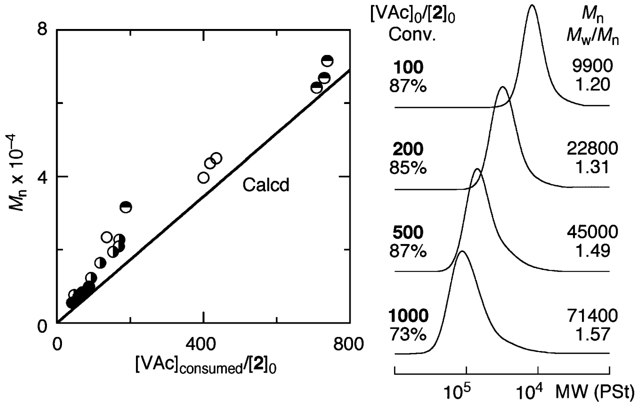


Figure 7. M_n curves of poly(vinyl acetate) obtained with varying the $[\text{vinyl acetate}]_0/[\mathbf{2}]_0$ ratio in m-$C_6H_4\{C(CF_3)_2OH\}_2$ at 20 °C; $[\text{vinyl acetate}]_0 = 2.0$ M; $[\text{vinyl acetate}]_0/[\mathbf{2}]_0 = 100$ (●), 200 (◑), 500 (○), or 1000 (◒); $[2,2'\text{-azobis(4-methoxy-2,4-dimethylvaleronitrile)}]_0/[\mathbf{2}]_0 = 0.2$. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per one **2** molecule.

were almost quantitative for all the concentrations, and the rate increased with the increasing $[\mathbf{2}]_0$ or $[\text{V-70}]_0$. Figure 7 shows the M_n values and SEC curves of the polymers obtained with **2**/V-70 in m-$C_6H_4\{C(CF_3)_2OH\}_2$ at different $[\text{VAc}]_0/[\mathbf{2}]_0$ ratios with various conversions, in which $[\text{VAc}]_{\text{consumed}}/[\mathbf{2}]_0 = ([\text{VAc}]_0/[\mathbf{2}]_0) \times$ conversion. The M_n was inversely proportional to $[\mathbf{2}]_0$ and in good agreement with the calculated values assuming that one polymer is formed per **2** molecule (diagonal solid lines in the plot). As the $[\text{VAc}]_0/[\mathbf{2}]_0$ ratio increased, the MWD value became somewhat broader. However, it was fairly narrow ($M_w/M_n \sim 1.60$) even at $[\text{VAc}]_0/[\mathbf{2}]_0 = 1000$ in comparison to those obtained in the bulk under similar conditions ($M_w/M_n = 3.19$ at 85% conversion). These results again indicated that the fluorodiol has some effect on enhancing the molecular weight control in addition to the stereospecificity control.

2. Effects of Fluoroalcohols on Head-to-Head Linkage for Possible Control of Regiospecificity. (a) End-Group Analysis. To clarify the chain-end structure from the degenerative iodine transfer polymerization in the fluorodiol, the PVAc obtained with **2**/V-70 in m-$C_6H_4\{C(CF_3)_2OH\}_2$ at 20 °C was analyzed by ^{1}H NMR spectroscopy (Figure 8). Besides the large absorptions (*a*−*c*) attributed to the repeat units of VAc at 1.5−2.2 and 4.8−5.2 ppm, there are several characteristic signals originating from **2**. The methylene and ethyl ester protons at the α-end, *f*, *g*, and *h*, were seen at 2.3, 4.1, and 1.2 ppm, respectively. In addition, the methine (*e*) and methylene protons (*d*) at the iodide *ω*-terminal VAc unit, which was formed via the head-to-tail addition, were observed at 6.8 and 2.7 ppm, respectively. The highly downfield-shifted peaks (*i* and *i′*) at 9.4−9.8 ppm are attributed to the aldehyde chain ends caused by the decomposition of the secondary C−I terminal by moisture during the polymerization or the recovery process.[29−31] The peak (*j*) at 6.1 ppm is also ascribed to the olefin group of the conjugated aldehyde formed via the following elimination of acetic acid from the adjacent VAc unit to the aldehyde terminal. Of special note is the $-CH_2-I$ terminal observed at 3.2 ppm, which formed via the head-to-head monomer addition (Scheme 2).[29−31] Similar spectra were observed for the polymers obtained in the other fluoroalcohols and in the bulk while the peak intensity ratios were slightly different.

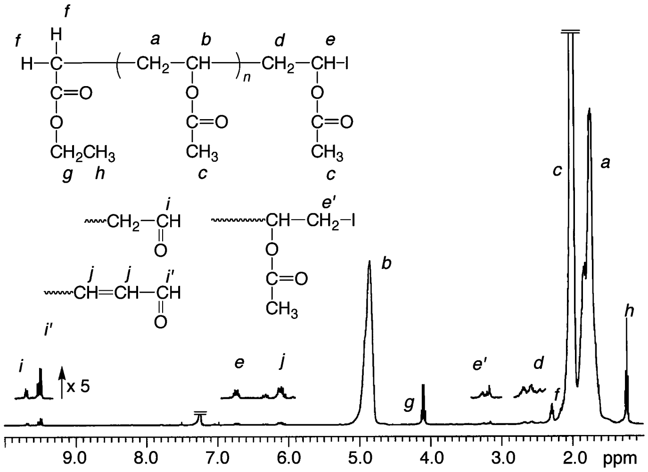


Figure 8. ^{1}H NMR spectrum of poly(vinyl acetate) ($M_n = 6100$, $M_w/M_n = 1.30$) obtained with **2**/2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in m-$C_6H_4\{C(CF_3)_2OH\}_2$ at 20 °C; $[\text{vinyl acetate}]_0 = 2.0$ M; $[\mathbf{2}]_0 = 20$ mM; $[\text{V-70}]_0 = 40$ mM.

Table 2 shows the number-average degree of polymerization [DP_n(NMR, α-end)] and M_n(NMR, α-end), which were determined from the peak intensity ratio (2*b*/*g*) of the ethyl ester-protons (*g*) at the α-terminal to the main-chain methine protons (*b*) adjacent to the oxygen atom of the VAc units. In most cases, the M_n(NMR, α-end) values were close to the calculated values [M_n(calcd)], assuming that one molecule of the iodine compound generates one polymer chain, and also nearly consistent with the molecular weights obtained by SEC [M_n(SEC)] though based on the polystyrene calibration. These results indicate that one polymer chain is generated from one molecule of the alkyl iodide even in those fluoroalcohols and results in a controlled chain length. However, in $(CF_3)_2CHOH$, the M_n(NMR, α-end) was higher than M_n(calcd) and M_n(SEC), which suggests undesirable chain transfer reactions.

The number-average content of the $-CH_2-I$ terminal in one polymer chain ($-CH_2-I$, %) can be calculated from the peak intensity ratio of the primary iodide *ω*-end (*e′*) to the α-end (*g*) (see also Table 2). The content in the fluoroalcohols was around 25−30%, which was clearly lower than in the bulk (∼70%). This means that the formation of the primary alkyl iodide is suppressed in the fluoroalcohols.

A more detailed analysis of the content was done at various monomer conversions for the polymerization with **2**/V-70 at 20 °C in the bulk and m-$C_6H_4\{C(CF_3)_2OH\}_2$ (Figure 9). The content of the primary alkyl iodide was consistently lower in the fluorodiol than in the bulk throughout the polymerizations. As the polymerization proceeded, the content of the primary alkyl iodide increased in both cases probably due to the accumulation of the less reactive C−I terminal.[30,31] Along with the increase in the content during the bulk polymerization, the MWDs became broader most probably due to the lower chain transfer constant of the primary alkyl iodide. In contrast, no

Scheme 2. Regiospecificity during Vinyl Acetate Radical Polymerization and the Following C−I Bond Formation

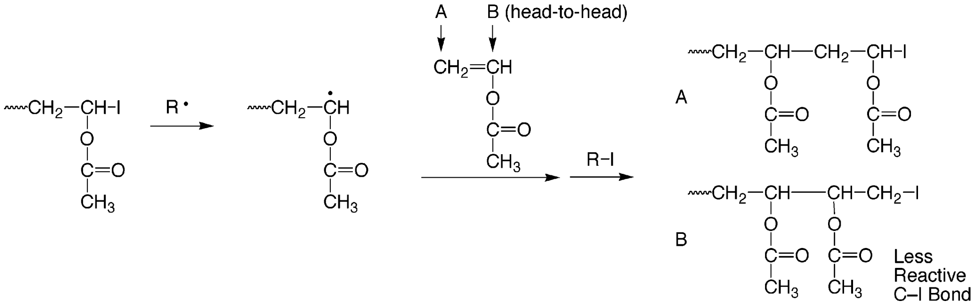


Table 2. ^{1}H NMR Analysis of Poly(vinyl acetate) Obtained via the Iodine Transfer Polymerization in Fluoroalcohols[a]

solvent	conv, %	DP_n(NMR, α-end)[b]	M_n(NMR, α-end)[b]	M_n(calcd)[b]	M_n(SEC)[d]	M_w/M_n[d]	$-CH_2-I$, %[b]
bulk	91	94	8300	8000	10100	1.48	69
m-$C_6H_4\{C(CF_3)_2OH\}_2$	76	73	6500	6800	7100	1.21	26
$PhC(CF_3)_2OH$	71	62	5600	6300	5600	1.46	27
$(CF_3)_3COH$	75	67	6000	6700	6900	1.46	31
$(CF_3)_2CHOH$	81	201	17 500	7200	9900	2.67	(48)

[a] Polymerization conditions: [vinyl acetate]$_0$/[**2**]$_0$/[V-70]$_0$ = 100/1/2, [VAc]$_0$ = 10 (bulk) or 2.0 M (in fluoroalcohols) at 20 °C. [b] The degree of polymerization [DP_n(NMR)], number-average molecular weight [M_n(NMR)], and the content of $-CH_2-I$ terminal were determined by ^{1}H NMR spectroscopy ($CDCl_3$, rt). [c] M_n(calcd) = MW(vinyl acetate) × [vinyl acetate]$_0$/[**2**]$_0$ × conv + MW(**2**). [d] The number-average molecular weight [M_n(SEC)] and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography in THF (polystyrene standard).

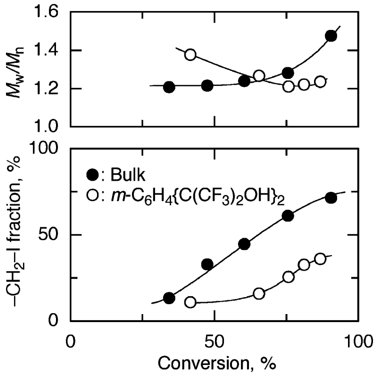


Figure 9. CH_2-I fraction at the ω-terminal and M_w/M_n curves of poly(vinyl acetate) obtained with **2**/2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in bulk or m-$C_6H_4\{C(CF_3)_2OH\}_2$ at 20 °C; [vinyl acetate]$_0$ = 10 (bulk) or 2.0 M (in m-$C_6H_4\{C(CF_3)_2OH\}_2$); [vinyl acetate]$_0$/[**2**]$_0$ = 100; [V-70]$_0$/[**2**]$_0$ = 2.

Table 3. Effect of Fluoroalcohols in the Free Radical Polymerization of Vinyl Acetate[a]

solvent	time, h	conv, %	M_n	M_w/M_n[b]	r, %[c]	1,2-glycol, %[c]
bulk	24	89	123000	1.95	52.7	1.21
CH_3OH	170	40	9900	1.81	53.6	1.20
m-$C_6H_4\{C(CF_3)_2$-$OH\}_2$	190	70	18000	5.70	61.2	0.80
$PhC(CF_3)_2OH$	120	57	8000	1.55	60.7	0.87
$(CF_3)_3COH$	120	48	11000	2.53	61.6	0.74
$(CF_3)_2CHOH$	120	67	11000	1.75	59.0	0.89

[a] Polymerization conditions: [vinyl acetate]$_0$ = 10 (bulk) or 2.0 M (in fluoroalcohols), [V-70]$_0$ = 200 mM, at 20 °C. [b] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography. [c] The contents of racemo dyad (r) and 1,2-glycol were determined by ^{1}H NMR spectroscopy of the corresponding poly(vinyl alcohol) in DMSO-d_6 at rt.

significant broadening was observed in the fluorodiol where the content of the $-CH_2-I$ content was lower. Thus, one reason for the better molecular weight control in the fluorodiol is a lower primary alkyl iodide fraction with a lower reactivity.

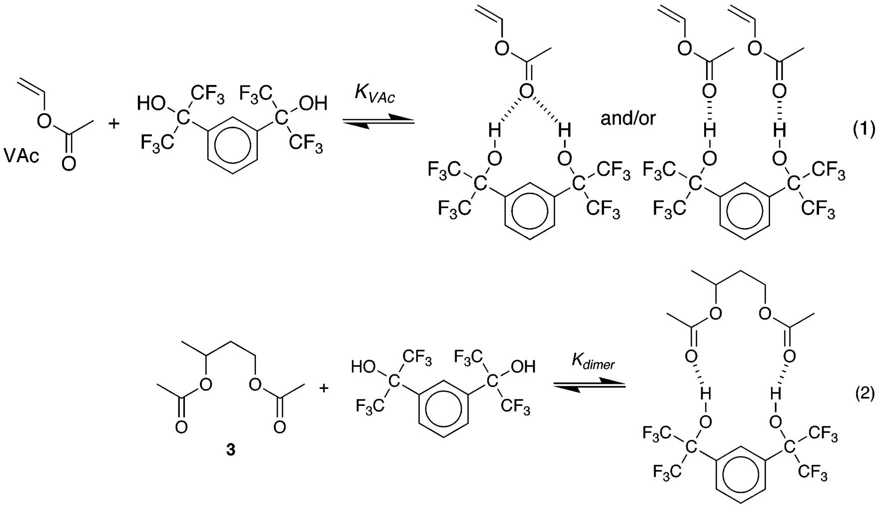
(b) Main-Chain Analysis. The formation of the primary alkyl iodide is the consequence of the head-to-head propagation. The decrease in the $-CH_2-I$ content at the polymer terminal thus suggests that the fluoroalcohols possibly suppress the head-to-head propagation or enhance the regiospecificity during the polymerization. The content of the head-to-head linkage in the main chain was thus evaluated for the free radical polymerization of VAc without the transfer agent in the bulk, methanol and various fluoroalcohols at 20 °C (Table 3). The content of the head-to-head 1,2-glycol linkages was measured by the ^{1}H NMR spectra of PVA derived from the PVAc.[8,9] The 1,2-glycol content in the bulk and MeOH was around 1.2%, which was almost the same as that reported. The content in the fluoroalcohols was around 0.8%, which was obviously lower than in the bulk and CH_3OH, and almost the same as those obtained in methanol at −78 °C, the lowest value ever reported.[9]

These results indicate that the fluoroalcohols as solvents can suppress the head-to-head monomer insertion, resulting in better control of the molecular weights in addition to the syndiospecific propagation. Thus, the fluoroalcohol enhances not only the stereospecificity but also the regiospecificity most probably via coordination to the monomer and/or the growing polymer terminal by inducing steric repulsion and differentiating the two vinyl carbons during propagation.

3. Interaction of Fluoroalcohol with Monomer and Chain End. The origin of the stereospecificity in the $(CF_3)_3COH$-induced syndiospecific radical polymerization has been considered to be due to the steric repulsion around the growing chain end, which is caused by the hydrogen-bonding interaction of the bulky fluoroalcohol with the monomer and/or the propagating radical species. Previous results based on the ^{1}H and ^{13}C NMR analyses of the mixture of VAc and the fluoroalcohol have revealed that the fluoroalcohol associates with the monomer at a 1:1 molar ratio.[36] To observe the effects of the fluorodiol on the radical polymerization of VAc, its mixture with VAc or a dimer of VAc (1,3-diacetoxybutane: **3**) as a model terminal was analyzed by ^{1}H and ^{13}C NMR (eqs 1 and 2 of Scheme 3).

In a similar way with $(CF_3)_3COH$, upon the addition of m-$C_6H_4\{C(CF_3)_2OH\}_2$ to the $CDCl_3$ solution of VAc or **3**, each carbonyl carbon of the monomer and the dimer shifted to a lower field, while the hydroxyl proton of the fluorodiol significantly shifted to a lower field, indicating that a hydrogen bond was formed between the two components. The stoichiometry of the

Scheme 3



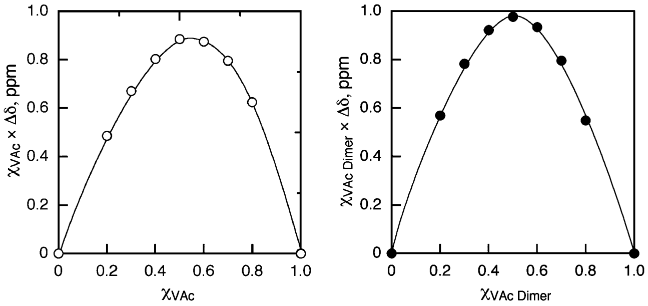


Figure 10. Job plots for the association of *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ with vinyl acetate or **3** evaluated from the changes in chemical shift (ppm) of the carbonyl carbon of vinyl acetate ($[VAc]_0$ or $[\mathbf{3}]_0 + [FOH]_0 =$ 1.0 M, 100 MHz, $CDCl_3$, 30 °C); χ_{VAc} and χ_{Dimer}: molar fraction of vinyl acetate and **3**, respectively.

interactions was evaluated by Job's method by varying the concentration of these components (Figure 10).[51−53] It was roughly suggested that a 1:1 complex was formed between the diol and the monoester, VAc (open circles), although the peak top shifted slightly to the right side, indicating that it may also contain the 1:2 complex. In contrast, the stoichiometry of the interaction between *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ and **3** was obviously 1:1 (filled circles), indicating the bidentate hydrogen bonding. These results suggest that the carbonyl oxygen of the ester and the hydroxyl group of the alcohol would not necessarily interact at a one-to-one molar ratio, and hence the fluorodiol could interact with the last two monomeric units at the growing terminal or with the growing terminal and the incoming monomer.

The equilibrium constants (*K*) of the complexes between the fluorodiol and the ester compounds were determined by a ^1H NMR titration experiment based on the assumption that these molecules interact at a 1:1 molar ratio.[53] The constants with VAc or with the dimeric compound was best fit to 2.12 or 4.20 L/mol, respectively. The fluorodiol thus prefers to associate with the dimeric ester rather than the monomeric. This also suggests that the fluorodiol that is associated with the incoming monomer at a 1:1 ratio favorably interacts with another ester such as that at the growing terminal unit. These specific interactions might contribute somewhat to the improvement in the selectivity.

Conclusion. The stereospecific controlled/living radical polymerization of VAc is possible using the alkyl iodide/azo-initiator system in fluoroalcohols, in which the alkyl iodide controls the molecular weight and the fluoroalcohols enhances the syndiotaticity. Especially, *m*-$C_6H_4\{C(CF_3)_2OH\}_2$ not only leads to a higher syndiotacticity but also improves the molecular weight control and the regiospecificity by suppressing the head-to-head propagation.

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