Syndiotactic- and Heterotactic-Specific Radical Polymerizations of *N-n*-Propyl-α-fluoroacrylamide and Phase-Transition Behaviors of Aqueous Solutions of Poly(*N-n*-propyl-α-fluoroacrylamide)

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ABSTRACT: Radical polymerization of *N-n*-propyl-α-fluoroacrylamide (NNPFAAm) was investigated in several solvents at low temperatures in the presence or absence of Lewis bases, Lewis acids, alkyl alcohols, silyl alcohols, or fluorinated alcohols. Different effects of solvents and additives on stereospecificity were observed in the radical polymerizations of NNPFAAm and its hydrocarbon analogs such as *N*-isopropylacrylamide (NIPAAm) and *N-n*-propylacrylamide (NNPAAm); for instance, syndiotactic (and heterotactic) specificities were induced in radical polymerization of NNPFAAm in polar solvents (and in toluene in the presence of alkyl and silyl alcohols), whereas isotactic (and syndiotactic) specificities were induced in radical polymerizations of the hydrocarbon analogs under the corresponding conditions. In

contrast, heterotactic specificity induced by fluorinated alcohols was further enhanced in radical polymerization of NNPFAAm. The effects of stereoregularity on the phase-transition behaviors of aqueous solutions of poly(NNPFAAm) were also investigated. Different tendencies in stereoregularity were observed in aqueous solutions of poly(NNPFAAm)s from those in solutions of the hydrocarbon analogs such as poly(NIPAAm) and poly(NNPAAm). The polymerization behavior of NNPFAAm and the phase-transition behavior of aqueous poly(NNPFAAm) are discussed based on possible fluorine–fluorine repulsion between the monomer and propagating chain-end, and neighboring monomeric units.

KEYWORDS: stereospecific polymers; radical polymerization; stimuli-sensitive polymers; hydrogen bonding; syndiotactic; heterotactic

INTRODUCTION Fluorine-containing compounds play an important role in the stereospecificity of radical polymerization. For example, fluorinated alcohols such as nonafluoro-*tert*-butanol (NFTB) induced or enhanced the stereospecificities when used as the solvent for the radical polymerizations of vinyl esters[1,2] and methacrylates.[3,4] The induced or enhanced stereospecificity depended on the structures of the monomers; syndiotactic specificity was induced in the radical polymerization of vinyl acetate and enhanced in those of methacrylates, whereas heterotactic specificity was induced in the radical polymerization of vinyl pivalate.

Introducing fluorine atoms in the side groups of monomers also affected the stereospecificity. For example, the radical polymerizations of vinyl 2,2-bis(trifluoromethyl)propionate[2,5] and vinyl pentafluorobenzoate[6] gave polymers with higher syndiotacticities than those of their hydrocarbon analogs. The radical polymerization of nonafluoro-*tert*-butyl acrylate also gave a polymer with higher syndiotacticity than that of poly(*tert*-butyl acrylate).[7,8] These results suggest that fluorinated side groups generally enhance syndiotactic specificity, except in the radical polymerization of 2,2,2-trifluoroethyl methacrylate, in which polymers with lower syndiotacticities than that of poly(ethyl methacrylate) were obtained.[9]

The introduction of a fluorine atom at the α-position of the vinyl group of an acrylic monomer also influenced stereospecificity. For example, the radical polymerizations of methyl α-fluoroacrylate (MFA),[10] ethyl α-fluoroacrylate (EFA),[11] α-fluoroacrylonitrile (FAN),[11] and *N*-methyl-α-fluoroacrylamide (NMFAAm)[12] gave syndiotactic-rich polymers, whereas their hydrocarbon analogs gave almost atactic polymers.

We reported that isotactic specificity was induced using polar solvents in the radical polymerizations of *N*-monosubstituted acrylamides such as *N*-isopropylacrylamide (NIPAAm).[13] Furthermore, isotactic and syndiotactic specificities were induced by adding Lewis bases[14,15] or alkyl alcohols[16,17] to the radical polymerizations of NIPAAm and *N*-*n*-propylacrylamide (NNPAAm). Adding fluorinated alcohols induced heterotactic specificity,[18,19] indicating that fluorine-containing compounds as additives also played a determining role in the stereospecificity of the radical polymerizations of

N-monosubstituted acrylamides. It is therefore assumed that introducing fluorine atoms at the α-positions of *N*-monosubstituted acrylamides further influences the stereospecificity induced by polar solvents, Lewis bases, alkyl alcohols, silyl alcohols, or fluorinated alcohols.

In the present paper, radical polymerization of *N-n*-propyl-α-fluoroacrylamide (NNPFAAm) was carried out under various conditions, under which isotactic, syndiotactic, or heterotactic specificities were induced in the radical polymerizations of *N*-monosubstituted acrylamides. A fluorine atom at the α-position had a significant effect on the stereospecificity, as summarized in Scheme 1.

<Scheme 1>

Aqueous solutions of poly(NIPAAm) and poly(NNPAAm) are known to show soluble-to-insoluble transitions.[20–25] The stereoregularity of a polymer significantly influences its phase-transition behavior;[16–18,26–28] therefore, the phase-transition behaviors of aqueous solutions of the poly(NNPFAAm)s obtained were also examined with respect to tacticity effects.

EXPERIMENTAL

Materials

Dimethyl 2,2´-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd.,

Osaka, Japan) was recrystallized from methanol (MeOH). Toluene (Kanto Chemical Co., Inc., Tokyo, Japan) was purified by washing with sulfuric acid, water, and 5% aqueous NaOH, followed by fractional distillation. MeOH (Kanto Chemical Co., Inc.) was fractionally distilled. EFA was prepared according to the literature.[11] Anhydrous ethanol (EtOH), *tert*-butanol (*t*BuOH) (Wako Pure Chemical Industries, Ltd., Osaka, Japan), tetrahydrofuran (THF), pyridine, acetone, acetonitrile, *N*,*N*-dimethylformamide (DMF), chloroform (CHCl$_3$) (Kanto Chemical Co., Inc.), 3-methyl-3-pentanol (3Me3PenOH), hexamethylphosphoramide (HMPA), 3,5-dimethylpyridine *N*-oxide (35DMPNO), triisopropylsilanol (TIPSiOH), 2,2,2-trifluoroethanol (TFE), samarium trifluoromethanesulfonate [Sm(OTf)$_3$] (Sigma-Aldrich Japan, Tokyo, Japan), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), MFA (supplied by Daikin Industries, Osaka, Japan), *n*-propylamine, 2-propanol (*i*PrOH), propylene carbonate (PC), *N*-ethylacetamide (NEtAcAm), triethylsilanol (TESiOH), diethyl(isopropyl)silanol (DEIPSiOH), NFTB, scandium trifluoromethanesulfonate [Sc(OTf)$_3$], yttrium trifluoromethanesulfonate [Y(OTf)$_3$], ytterbium trifluoromethanesulfonate [Yb(OTf)$_3$], (Tokyo Chemical Industry, Tokyo, Japan), and lithium trifluoromethanesulfonate (LiOTf) (Kishida Chemical Co., Ltd., Osaka, Japan) were used as received.

Synthesis of NNPFAAm

MFA (29.60 g, 0.249 mol) in MeOH (200 mL) was added dropwise at room temperature to a stirred solution of *n*-propylamine (29.32 g, 0.496 mol) in MeOH (400 mL). After

stirring the mixture for 24 h at room temperature, the solvent was evaporated. The residue was distilled under reduced pressure (6 mmHg, b.p. 113 °C) to give 31.34 g of NNPFAAm (96.14%). Using EFA instead of MFA gave NNPFAAm in 87.62% yield. NNPFAam: colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$ at 35 °C), δ 6.30 (br, 1H), 5.67 (dd, 1H, ^2J = 3.2 Hz, $^3J_{H,F\ trans}$ = 48.5 Hz), 5.09 (dd, 1H, ^2J = 3.2 Hz, $^3J_{H,F\ cis}$ = 15.5 Hz), 3.32 (q, 2H, ^3J = 7.0 Hz), 1.59 (sext, 2H, ^3J = 7.0 Hz, ^3J = 7.6 Hz), 0.96 (t, 3H, ^3J = 7.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$ at 35 °C), δ 159.69 (d, $^2J_{C,F}$ = 30.66 Hz), 156.70 (d, $^1J_{C,F}$ = 271.61 Hz), 98.67 (d, $^2J_{C,F}$ = 15.09 Hz), 41.24, 22.79, 11.40.

Polymerization

The typical polymerization procedure was as follows. NNPFAAm (0.6557 g, 5.0 mmol), NFTB (2.3604 g, 10 mmol), and MAIB (0.0115 g, 5.0×10^{-2} mmol) were dissolved in toluene to prepare 5 mL of solution. A total of 4 mL of this solution was transferred to a glass ampoule and cooled to −40 °C. The glass ampoule was degassed and filled with nitrogen three times. The mixture was irradiated at a distance of ca. 5 cm from a UV-LED lamp (λ = 375 nm, Optocode Co., Tokyo, Japan) to initiate polymerization. After 12 h, the polymerization mixture was poured into diethyl ether (400 mL). The precipitated polymer was collected by centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

^{1}H, ^{13}C, and ^{19}F NMR spectra were measured using an ECX-400 spectrometer (JEOL

Ltd., Tokyo, Japan) operated at 400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F. The molecular weights and molecular-weight distributions of the polymers were determined by size-exclusion chromatography (SEC); the chromatograph was calibrated using standard polystyrene samples. SEC was performed with an HLC 8220 chromatograph (Tosoh Corp., Tokyo, Japan) equipped with TSK gel columns (SuperHM-M and SuperHM-H, both 6.5 mm ID × 150 mm long; Tosoh Corp.). DMF containing LiBr (10 mmol L^{-1}) was used as the eluent at 40 °C and a flow rate of 0.35 mL min^{-1}. The polymer concentration was 1.0 mg mL^{-1}. The transmittance of an aqueous solution of poly(NNPFAAm) (0.1 w/v%) was monitored as a function of temperature at a wavelength of 500 nm using a UV/VIS spectrophotometer (V-550, JASCO Corp., Tokyo, Japan) equipped with a Peltier thermostated single-cell holder (ETC-505, JASCO Corp.). The temperature was changed at a rate of 0.5 °C min^{-1} from 2 °C to 70 °C, held at 70 °C for ca. 15 min, then changed at a rate of 0.5 °C min^{-1} from 70 °C to 2 °C. The cloud point (T_c) in the heating and cooling processes was taken as the temperature at which the transmittance was 50%. When some transparency remained even above the phase-transition temperature, the T_c was defined as the temperature at which the average transmittance before and after the phase transition was observed.

NMR Evaluation of Stereoregularity of Poly(NNPFAAm)

The stereoregularity of poly(NMFAAm) was examined by ^{1}H, ^{13}C, and ^{19}F NMR

spectroscopy in CDCl$_3$ at 55 °C or in deuterated dimethyl sulfoxide (DMSO-d_6) at 100 °C.[29] Proton chemical shifts were referenced to internal TMS (δ = 0.00 ppm). Carbon chemical shifts were referenced to the solvents (CDCl$_3$: δ = 77.0 ppm DMSO-d_6: δ = 39.6 ppm). Fluorine chemical shifts were referenced to hexafluorobenzene (δ = −162.5 ppm) as an internal standard. The ^{1}H NMR signals of the methylene groups in the main chain measured in CDCl$_3$ at 55 °C showed poor splitting as a result of stereoregularity (Figure 1a). Those measured in DMSO-d_6 at 100 °C showed splitting as a result of dyad tacticity similar to that of poly(MFA)[10] (Figure 1b). However, it was difficult to evaluate the dyad tacticity because of overlapping of the signal caused by the solvent.

<Figure 1>

The ^{13}C NMR signals of the quaternary carbon measured in CDCl$_3$ at 55 °C also showed poor splitting as a result of stereoregularity, but those measured in DMSO-d_6 at 100 °C showed splitting as a result of triad tacticity, similar to those of poly(MFA)[10], poly(EFA),[11] and poly(NMFAAm).[12] The resolution, however, was low compared with those in the NMR spectra of other polymers.

The ^{19}F NMR signals of the fluorine atom at the α-position showed splitting as a result of stereoregularity longer than triad stereosequences, regardless of the type of solvent used. The spectral pattern observed in DMSO-d_6 at 100 °C was similar to those for

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poly(MFA),[10] poly(EFA),[11] and poly(FAN).[11] The signals were therefore assigned in terms of triad stereosequences, as shown in Figure 1b, according to the assignments in the literature.[10,11] The triad tacticity determined from the ^{19}F NMR signals was in good agreement with that determined from the ^{13}C NMR signals. However, in the ^{19}F NMR spectrum in CDCl$_3$ at 55 °C, the signal intensity distribution did not explain the triad tacticity determined from the ^{13}C NMR signals. This suggests that the spectral pattern observed in CDCl$_3$ at 55 °C was more complicated than that in DMSO-d_6 at 100 °C. ^{19}F NMR analysis of poly(NNPFAAm) in DMSO-d_6 at 100 °C was therefore chosen to determine the tacticity at the triad level.

RESULTS AND DISCUSSION

Radical Polymerization of NNPFAAm in Various Solvents at −40 °C

Radical polymerization of NNPFAAm was carried out in toluene at −40 °C for 12 h (Table 1, runs 1 and 2). Polymers slightly rich in syndiotacticity (rr = 35.0%) were obtained, regardless of the monomer concentration. The rr content (35.0%) agreed well with those observed for α-fluorinated acrylic polymers prepared by radical polymerization, such as poly(MFA) (34%),[10] poly(EFA) (34%),[11] poly(FAN) (29%),[11] and poly(NMFAAm) (34%).[12] The first-order Markovian probabilities of m-addition by r-ended radicals ($P_{r/m}$) and of r-addition by m-ended radicals ($P_{m/r}$) were calculated using the following equations: $P_{r/m} = mr/(2mm + mr)$ and $P_{m/r} = mr/(2rr + mr)$. The sums of $P_{r/m}$ and $P_{m/r}$ were quite close to unity, indicating that the stereoregularities of

the obtained polymers almost obeyed Bernoullian statistics. The probabilities of r-addition by m-ended and r-ended radicals were calculated to be ca. 0.60 and 0.59, respectively. Taking into account that a polymer with r = 53% was obtained by NNPAAm polymerization under the corresponding conditions,[17] it seems that introducing a fluorine atom at the α-position of NNPAAm slightly enhanced the syndiotactic specificity.

<Table 1>

As reported previously,[13,30] using polar solvents increases the m-dyad contents of the polymers obtained by radical polymerization of NIPAAm at low temperatures. Radical polymerization of NNPFAAm was carried out in several solvents more polar than toluene (Table 1, runs 3−12). Unlike the NIPAAm polymerizations, the syndiotacticities increased when polar solvents such as pyridine, CH_3CN, and DMF, but not $CHCl_3$, were used. In particular, a polymer with rr = 51.1% was obtained by NNPFAAm polymerization in CH_3CN. Using a mixed solvent (CH_3CN/pyridine = 1:1, v/v) slightly increased the rr-triad content compared with those obtained using CH_3CN and pyridine individually (Table 1, runs 6, 8, and 13). Lowering the temperature enhanced the syndiotactic specificity slightly (Table 1, runs 9 and 14). Polymerization was therefore carried out in a mixed solvent (CH_3CN/DMF = 1:1, v/v) at −80 °C. A polymer with an rr-triad content of 55.9% was obtained, although the polymer yield was reduced (Table

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1, run 15 and Figure 2b). It is assumed that polar solvents enhance the syndiotactic specificity of radical polymerization of NNPFAAm, although the reason is not at present clear.

<Figure 2>

Radical Polymerization of NNPFAAm in the Presence of Lewis Bases or Lewis Acids

We reported that adding phosphoric acid derivatives such as HMPA to the NIPAAm and NNPAAm polymerizations induced syndiotactic specificity through formation of a hydrogen-bonding-assisted 1:1 complex of the monomer and the Lewis base.[14,17] The effect of HMPA on the stereospecificity of radical polymerization of NNPFAAm was therefore examined in toluene at low temperatures (Table 2, runs 1–3). Adding HMPA increased the syndiotacticities of the polymers and decreased the polymer yields significantly (Table 1, run 1 and Table 2, run 1). This tendency corresponds with those observed in both NIPAAm and NNPAAm polymerizations. The syndiotacticity gradually increased with decreasing polymerization temperature, and a polymer with rr = 50.7% was obtained at −80 °C. This result differed from the tendencies in NIPAAm and NNPAAm polymerizations, in which HMPA most effectively induced syndiotactic specificity at −60 °C under the corresponding conditions.[14,17]

<Table 2>

Radical polymerization of NNPFAAm was also examined in the simultaneous presence of HMPA and MeOH (Table 2, run 4), because isotactic specificity was induced in NIPAAm polymerization by a combined effect of HMPA and the less bulky alcohol.[31] The *rr*-triad content decreased slightly, but isotactic specificity was not induced. The effect of 35DMPNO was then examined (Table 2, run 5) because 35DMPNO induced isotactic specificity in NIPAAm and NNPAAm polymerizations.[15,30] However, induction of isotactic specificity was not observed. Radical polymerizations of NNPFAAm in MeOH in the presence of catalytic amounts of metal triflates were carried out (Table 2, runs 6–10) because metal triflates such as $Y(OTf)_3$ were reported to catalyze isotactic-specific radical polymerization of NIPAAm to give polymers with over 90% *m*-dyads.[32,33] The *mm*-triad content of the obtained polymers increased slightly compared with that in MeOH in the absence of metal triflates (see Table 1, run 11), but were much lower than those of poly(NIPAAm)s prepared under the corresponding conditions. These results suggest that NNPFAAm does not readily give isotactic polymers, probably because of repulsion between fluorine atoms at the α-positions of the propagating chain-end, penultimate, and antepenultimate monomeric units, and/or the incoming monomers in the propagation reaction.

Radical Polymerization of NNPFAAm in the Presence of Alkyl, Silyl, or

Fluorinated Alcohols

We reported that adding alkyl alcohols such as 3Me3PenOH to NIPAAm and NNPAAm polymerizations induced syndiotactic specificity.[16,17] The effects of alkyl alcohols on the stereospecificity of radical polymerization of NNPFAAm were therefore examined in toluene at low temperatures (Table 3). Unlike the cases of NIPAAm and NNPAAm polymerizations, adding alkyl alcohols induced heterotactic specificity in the radical polymerization of NNPFAAm. The induced heterotactic specificity increased with increasing bulkiness of the added alcohols (Table 3, runs 3–6 and 9), but was scarcely affected by polymerization temperature (Table 3, runs 7–10). A polymer with $mr =$ 65.9% was obtained by NNPFAAm polymerization at −20 °C in the presence of 3Me3PenOH.

Silyl alcohols also induced syndiotactic specificity in NIPAAm polymerization.[34] The effects of silyl alcohols were examined. Silyl alcohols, as well as alkyl alcohols, induced heterotactic specificity in NNPFAAm polymerization. The induced heterotactic specificity was further enhanced. A polymer with $mr =$ 69.0% was obtained by NNPFAAm polymerization at −40 °C in the presence of TIPSiOH. This value (69.0%) is close to 70%, which is the highest heterotacticity obtained for poly(NIPAAm)s prepared by radical polymerization in the presence of fluorinated alcohols.[18]

<Table 3>

Radical polymerization of NNPFAAm was then investigated in the presence of fluorinated alcohols (Table 4). A further improvement in the heterotactic specificity was observed for NNPFAAm polymerization compared with NIPAAm polymerization under the corresponding conditions. In particular, a polymer with $mr = 82.6\%$ was obtained in the presence of NFTB at −40 °C (Table 4, run 7 and Figure 2c). To the best of our knowledge, this is the highest level of heterotacticity so far reported for homopolymers prepared by radical polymerization.[18,35]

<Table 4>

NMR Analysis of Hydrogen-Bonding Interactions between NNPFAAm and Alkyl Alcohols

Both alkyl and fluorinated alcohols induced heterotactic specificity in NNPFAAm polymerization, although the former induced syndiotactic specificity in NIPAAm polymerization. To investigate the reason for this difference in the induced stereospecificities, we conducted an NMR analysis of a mixture of NNPFAAm and 3Me3PenOH in toluene-d_8 at 0 °C.

The ^{13}C NMR signal of the carbonyl carbon showed a down-field shift on addition of 3Me3PenOH (Figures 3a and b). This suggested that the carbonyl oxygen formed hydrogen bonds with 3Me3PenOH. The ^{1}H NMR signal of the amide proton showed a down-field shift on addition of 3Me3PenOH. This suggested that the amide proton also

formed hydrogen bonds with the oxygen in 3Me3PenOH. The ^{19}F NMR signal of the

α-fluorine also showed a down-field shift. It has been reported, however, that covalently

bonded fluorine atoms hardly act as hydrogen-bonding acceptors.[36] Consequently,

NNPFAAm and 3Me3PenOH formed a 1:2 complex through cooperative hydrogen

bonding, O–H⋯O=C–N–H⋯O(H) (Scheme 2), as in the case of NIPAAm and

tBuOH.[16] This means that not the complex structure, but rather the fluorine atom at the

α-position should be responsible for inducing heterotactic specificity.

<Figure 3>

<Scheme 2>

Table 5 summarizes the $P_{r/m}$ and $P_{m/r}$ data for the radical polymerizations of

NNPFAAm, NNPAAm, and NIPAAm in toluene in the presence of 3Me3PenOH. The

$P_{m/r}$ for the NNPFAAm polymerization indicates that 3Me3PenOH significantly

increases r-selectivity by m-ended radicals in the NNPFAAm polymerization, even

more than in the NNPAAm and NIPAAm polymerizations. Propagation by m-ended

radicals was considered to occur in a mechanism similar to that proposed for

syndiotactic-specific NIPAAm polymerization in previous papers.[14,16] The $P_{r/m}$ value for

NNPFAAm polymerization was higher than those for the NNPAAm and NIPAAm

polymerizations. This indicates that the m-selectivity by the r-ended radicals in the

NNPFAAm polymerization is higher than those in the NNPAAm and NIPAAm

polymerizations. It is therefore believed that the conformation near the propagating chain-end of the *r*-ended radicals was particularly affected by repulsion between the fluorine atoms at the α-positions of the chain-end, penultimate, and antepenultimate monomeric units, resulting in enhanced *m*-selectivity by the *r*-ended radicals in a mechanism similar to that proposed for heterotactic-specific NIPAAm polymerization in a previous paper.[18]

<Table 5>

NMR Analysis of Hydrogen-Bonding Interactions between NNPFAAm and Fluorinated Alcohols

NMR analysis of a mixture of NNPFAAm and NFTB was also carried out (Figures 3a and c). Adding NFTB caused a down-field shift of the ^{13}C NMR signal of the carbonyl group, indicating that the carbonyl oxygen formed hydrogen bonds with NFTB. In contrast, the ^{1}H NMR signal of the amide proton showed an up-field shift on addition of NFTB. These results suggested that the amide proton was free from hydrogen bonding, as was seen for the combination of NIPAAm and NFTB.[18] This was also supported by a significant up-field shift of the ^{19}F NMR signal because formation of C=O···H–O hydrogen bonds would increase the electron density at the α-position in the α,β-unsaturated carbonyl moiety.

To investigate the stoichiometry of the NNPFAAm–NFTB complex, ^{1}H NMR analysis

was carried out on solutions of $[\text{NNPFAAm}]_0 + [\text{NFTB}]_0 = 0.25$ mol L^{-1} in toluene-d_8 at 0 °C. Figure 4a shows the changes in the chemical shift of the vinylidene proton *trans* to the fluorine atom (HC=CF; *trans*) of NNPFAAm resulting from variations in the initial proportion of NNPFAAm. The plots roughly obeyed a quadratic equation. The stoichiometry of the complex was evaluated by the Job's method via eq (1):[37]

$$[\text{NNPFAAm - NFTB}] = \frac{\delta\,(H\text{C=CF; } trans) - \delta\,(H\text{C=CF; } trans)_f}{\delta\,(H\text{C=CF; } trans)_c - \delta\,(H\text{C=CF; } trans)_f} \text{ x } [\text{NNPFAAm}]_0 \quad (1)$$

where $\delta(H\text{C=CF; } trans)$ and $\delta(H\text{C=CF; } trans)_f$ are the chemical shifts of the sample mixture and NNPFAAm alone, respectively. We reported that the chemical shift of NIPAAm varied with $[\text{NIPAAm}]_0$ as a result of self-association. The chemical shift of NNPFAAm alone at the corresponding concentration was equated to $\delta(H\text{C=CF; } trans)_f$ (Figure 4a). The chemical shift for the saturated mixture, $\delta(H\text{C=CF; } trans)_c$, was calculated from the intercept of the quadratic fit to the data in Figure 4a since the saturation value should be independent of NNPFAAm concentration. A maximum was observed at an initial proportion of NNPFAAm = 0.5 (Figure 4b). This result indicates that NNPFAAm and NFTB formed a 1:1 complex through hydrogen bonding, C=O···H–O (Scheme 3), as in the case of a combination of NIPAAm and NFTB, and the polymerization proceeded by a mechanism similar to that proposed in a previous paper for heterotactic-specific NIPAAm polymerization, in which the monomer formed a 1:1 complex with fluorinated alcohols.[18]

<Figure 4>

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<Scheme 3>

The equilibrium constant (K) of the NNPFAAm–NFTB complex was determined from

the changes in the ^{1}H NMR chemical shift of the vinylidene proton *trans* to the fluorine

atom (HC=CF; *trans*) of NNPFAAm. Figure 5 shows the relationship between the

change in the chemical shift and the $[NFTB]_0/[NNPFAAm]_0$ ratio at constant

$[NNPFAAm]_0$ (5.0×10^{-2} mol L^{-1}) in toluene-d_8 at several temperatures. K was

determined from the data in Figure 5 by nonlinear least-squares fitting of the data to eq

(2):[38]

$$\Delta\delta = \frac{\Delta\delta'}{2} \left(b - \sqrt{b^2 - 4X} \right) \quad (2)$$

$$b = 1 + X + \frac{1}{(K[NNPFAAm]_0)}$$

$$X = [NFTB]_0 / [NNPFAAm]_0$$

where $\Delta\delta$ and $\Delta\delta'$ are the changes in the chemical shift of the vinylidene proton *trans* to

the fluorine of NNPFAAm for the given solution and a saturated solution, respectively

(Table 6).

<Figure 5>

<Table 6>

A van't Hoff plot of the K values obtained is shown in Figure 6. The enthalpy (ΔH) and

entropy (ΔS) of complex formation were evaluated as -14.0 ± 0.3 kJ mol^{-1} and $-8.5 \pm$

0.9 J mol^{-1} K^{-1}, respectively, from eq (3):

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

where R is the gas constant and T is the absolute temperature. The K values at temperatures below 0 °C were calculated on the assumption that ΔH was constant.

<Figure 6>

Application of the K values for the polymerization conditions gives the values shown in Table 6 for the degree of association (α) of NNPFAAm. The K values for the NNPFAAm–NFTB complex were smaller than those for the NIPAAm–NFTB complex, regardless of the temperature.[18] This is probably because the basicity of the C=O group of NNPFAAm, which has an electron-withdrawing fluorine atom, is weaker than that of NIPAAm. However, NNPFAAm formed the complex quantitatively in the presence of NFTB (2.0 mol L^{-1}) at −40 °C, regardless of the NNPFAAm concentration.

NFTB significantly increased $P_{r/m}$ and $P_{m/r}$ for NNPFAAm polymerization compared with those for NIPAAm polymerization (Table 5). This suggested that m-selectivity by the r-ended radicals and r-selectivity by the m-ended radicals were enhanced simultaneously by repulsion between the fluorine atoms at the α-positions of the monomeric units near the propagating chain-end and at the incoming monomer, in addition to repulsion between fluorine atoms in the hydrogen-bonded alcohols.

^{1}H NMR Analysis of Stereosequences Near the Initiating Chain-End

End-group analysis of polymers by NMR spectroscopy often provides important information for understanding the polymerization mechanism.[39,40] The ^{1}H NMR signals of the methoxy groups in the MAIB fragments exhibited splitting, probably as a result of stereosequences near the initiating chain-end (Figure 7). Although the present polymerization did not proceed in a living manner, this splitting should provide stereoselectivities of the initiating species, such as dimer and trimer radicals.

<Figure 7>

The signals of the methoxy groups split roughly into four peaks, probably as a result of triad stereosequence near the initiating chain-end. The intensities of the peaks at the lowest and highest magnetic fields increased and decreased, respectively, in the spectrum of poly(NNPFAAm) with $r = 73.1\%$ (Table 1, run 13), compared with that with $r = 59.5\%$ (Table 1, run 2). This suggests that the peaks at the lowest and highest magnetic fields are at least assignable to rr- and mm-triads at the initiating chain-end. The fraction of the peaks of the rr-triad of poly(NNPFAAm) with $r = 73.1\%$ was evaluated to be ca. 50%. If the stereoselectivities obey Bernoullian statistics from the beginning of the polymerization reaction, the r-selectivity of dimer and trimer radicals is calculated to be 0.71. This value agreed well with those of the m-ended (0.755) and r-ended (0.722) propagating radicals. This suggests that the dimer radicals already prefer r-addition rather than m-addition under the given conditions (Scheme 4).

<Scheme 4>

Heterotactic poly(NNPFAAm) with mr = 82.6% (Table 4, run 7) also showed major peaks assignable to rr-triads. This means that dimer radicals and r-trimer radicals favor r-addition, even in the heterotactic-specific polymerization system. The peaks assignable to the rr-triad further split into more than three peaks. This indicates that the splitting reflects stereostructures longer than pentad sequences near the initiating chain-end. In fact, the highest peak in the spectrum of the heterotactic polymer differs from that of the syndiotactic polymer (Figures 7b and c). These results suggest that the addition of fluorinated alcohols should in principle enhance syndiotactic specificity. However, the stereoselectivity of the r-ended radicals is inverted after the chain length of the propagating radicals is longer than at least a tetramer. In a previous paper,[18] we proposed that repulsion of fluorine atoms in fluorinated alcohols bound to the amide groups at the antepenultimate and chain-end monomeric units was responsible for conformational change near the propagating chain-end, resulting in the m-addition of r-ended radicals. The reason for the r-selectivity of r-trimer radicals was probably that the MAIB fragment on the r-trimer radicals was not bulky enough to significantly induce repulsion between the fluorine atoms, as compared with the polymer chain.

Phase-Transition Behaviors of Aqueous Solutions of Poly(NNPFAAm)

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The phase-transition behaviors of aqueous solutions of poly(NNPFAAm)s were examined. Figure 8 shows the temperature dependences of the transmittances of aqueous solutions of poly(NNPFAAm) with an r-dyad content of 59.5% (Table 1, run 2) and of poly(NNPAAm) with an r-dyad content of 60.4%.[41] In the heating process, the T_c of poly(NNPFAAm) was observed at a higher temperature than that of poly(NNPAAm), indicating that introducing fluorine atoms at the α-position of the monomeric units slightly increased the phase-transition temperature, as does the introduction of methyl groups.[42] In contrast, in the cooling process, the T_c of poly(NNPFAAm) was observed at a slightly lower temperature than that of poly(NNPAAm). The hysteresis, which is a retardation in the cooling process versus the heating process, was larger than that for poly(NNPAAm), because the differences in T_c between the heating and cooling processes (ΔT_c) were calculated to be 5.6 °C for the poly(NNPFAAm) and 1.5 °C for the poly(NNPAAm).

<Figure 8>

The temperature and sharpness of the phase transition of aqueous poly(NNPAAm)s increased with increasing r-dyad content, and syndiotactic poly(NNPAAm)s with an r-dyad content greater than 67.3% exhibited large hysteresis (ca. 15 °C) under the same conditions.[43] The effects of the r-dyad content of poly(NNPFAAm) on the phase-transition behaviors were examined. Figure 9 shows the temperature dependences

of the transmittances of aqueous solutions of poly(NNPFAAm)s with r-dyad contents of

59.5% (Table 1, run 2) and 74.5% (Table 1, run 15). Unlike the case of aqueous

poly(NNPAAm), as the r-dyad content increased, the temperature and sharpness of the

phase transition in the heating process decreased, and some transparency remained even

above the T_c. Furthermore, poly(NNPFAAm) with an r-dyad content of 74.5% exhibited

smaller hysteresis (13.7 °C) than those of poly(NNPAAm)s with lower r-dyad contents.

<Figure 9>

Figure 10 shows the relationship between ΔT_c and the average r-dyad length $(\bar{n}_r)$,

calculated from $\bar{n}_r = (rr + mr/2)/(mr/2)$,[44] in syndiotactic-rich poly(NNPFAAm)s. The

relationship for syndiotactic-rich poly(NNPAAm)s is also plotted. The hysteresis

increased gradually with increasing $\bar{n}_r$, and increased moderately above $\bar{n}_r = 3.57$. This

result is in contrast with that observed for poly(NNPAAm)s, in which the hysteresis

increased greatly at $\bar{n}_r = 3.06$. In a previous paper,[43] we proposed that formation of

intramolecular hydrogen bonds by monomeric units in syndiotactic stereosequences

made dehydrated polymers more hydrophobic when the $\bar{n}_r$ was longer than ca. 3

(Scheme 5). This caused large hysteresis by strong aggregation of syndiotactic polymers

in dehydrated states. In the dehydrated state, the polymer was believed to adopt a helical

conformation. This was supported by quantum-chemical calculations for a syndiotactic

octamer.[45] In the case of dehydrated poly(NNPFAAm)s, however, repulsion between

fluorine atoms at the α-positions in neighboring monomeric units may arise. This repulsion is assumed to influence the stability of the ordered structure in the dehydrated state, which is formed by cooperative hydrogen-bonding, as shown in Scheme 5. As a result, the dependences of the $\bar{n}_r$ values on hysteresis in the phase transitions of aqueous poly(NNPFAAm)s would differ from those of poly(NNPAAm)s.

<Figure 10>

<Scheme 5>

We previously reported that the sharpness of the phase transition increased and also hysteresis was significantly reduced when the content of heterotactic stereosequences in poly(NIPAAm)s increased.[18] The effects of heterotacticity in poly(NNPFAAm)s on the phase-transition behaviors were therefore examined. Figure 11 shows the temperature dependences of the transmittances of aqueous solutions of poly(NNPFAAm)s with *mr*-triad contents of 73.9% (Table 4, run 5) and 82.1% (Table 4, run 8). In the case of poly(NNPFAAm) with *mr* = 73.9%, the sharpness of the phase transition in both the heating and cooling processes increased, and the hysteresis was significantly reduced (see Figure 9). These results correspond to the tendencies observed for heterotactic poly(NIPAAm)s. In contrast, in the case of poly(NNPFAAm) with *mr* = 82.1%, the sharpness of the phase transition increased in the heating process, but decreased in the cooling process. Furthermore, the hysteresis was larger than that for *mr* = 73.9%. The

reason is not at present clear. However, these results suggest that highly heterotactic polymers exhibit large hysteresis, or a fluorine atom at the α-position in highly heterotactic poly(NNPFAAm)s influences the aggregation states of the dehydrated polymers.

<Figure 11>

CONCLUSIONS

Radical polymerization of NNPFAAm was investigated in several solvents at low temperatures in the presence or absence of Lewis bases, Lewis acids, alkyl alcohols, silyl alcohols, or fluorinated alcohols; these were reported to induce syndiotactic, isotactic, or heterotactic specificity in NIPAAm polymerization. Syndiotactic-rich poly(NNPFAAm)s were obtained in polar solvents such as CH_3CN, whereas isotactic-rich polymers were obtained by NIPAAm polymerization under the corresponding conditions. Isotactic specificity was not induced in NNPFAAm polymerization, even when Lewis acids or Lewis bases, which induced isotactic specificity in NIPAAm polymerization, were added. Alkyl alcohols induced heterotactic specificity, although they induced syndiotactic specificity in NIPAAm polymerization. Furthermore, heterotactic specificity was enhanced by fluorinated alcohols in NNPFAAm polymerization compared with that in NIPAAm polymerization. These results indicate that the fluorine atom at the α-position significantly influences the

stereospecificity of radical polymerization of *N*-monosubstituted acrylamides.

The phase-transition behaviors of aqueous solutions of poly(NNPFAAm)s with different tacticities were also examined. It appeared that the tacticity effect was quite different from those observed for poly(NIPAAm)s and poly(NNPAAm)s. This result suggests that the fluorine atoms at the α-position of the monomeric units also influence the phase-transition behaviors of aqueous solutions of poly(*N*-monosubstituted acrylamide)s.

Acknowledgment

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TABLE 1 Radical Polymerization of NNPFAAm in Various Solvents at −40 °C for 12 h[a]

Run	Solvent	Yield /%	Triad tacticity/%[b]			r Dyad[c] /%	M_n[d] $\times 10^{-4}$	M_w[d] / M_n	$P_{m/r}$	$P_{r/m}$	$P_{m/r}+$ $P_{r/m}$
			mm	mr	rr						
1	Toluene	87	16.1	48.9	35.0	59.5	11.7	2.8	0.602	0.411	1.013
2[e]	Toluene	85	16.0	49.0	35.0	59.5	7.1	2.8	0.605	0.412	1.017
3	CHCl$_3$	27	9.4	61.3	29.3	60.0	3.4	1.5	0.765	0.511	1.277
4	CH$_2$Cl$_2$	34	10.5	50.8	38.7	64.1	2.9	1.5	0.708	0.396	1.104
5	THF	40	8.9	49.6	41.5	66.3	3.0	1.7	0.737	0.374	1.111
6	Pyridine	75	6.4	45.3	48.3	71.0	7.0	1.8	0.779	0.319	1.098
7	Acetone	28	9.8	45.1	45.1	67.7	3.0	1.5	0.697	0.333	1.030
8	CH$_3$CN	24	9.1	39.8	51.1	71.0	2.1	1.6	0.686	0.280	0.966
9	DMF	30	8.8	42.6	48.6	69.9	2.9	1.5	0.708	0.305	1.013
10	PC	81	11.8	42.9	45.3	66.8	20.4	1.8	0.645	0.321	0.966
11	MeOH	28	9.1	50.4	40.5	65.7	4.5	1.6	0.734	0.384	1.118
12	NEtAcAm	71	13.1	41.1	45.7	66.3	36.4	1.6	0.610	0.310	0.920
13[f]	CH$_3$CN+pyridine	57	6.6	40.6	52.8	73.1	4.6	1.7	0.755	0.278	1.033
14[g]	DMF	11	7.6	41.8	50.6	71.5	3.5	2.1	0.733	0.293	1.025
15[h]	CH$_3$CN+DMF	3	7.0	37.1	55.9	74.5	2.6	1.4	0.726	0.249	0.975

a. [NNPFAAm]$_0$=1.0 mol L^{-1}, [MAIB]$_0$=1.0×10^{-2} mol L^{-1}.

b. Determined from ^{19}F NMR signals.

c. Calculated from the triad tacticities with the equation: $r=mr/2+rr$.

d. Determined by SEC (polystyrene standards).

e. [NNPFAAm]$_0$=0.5 mol L^{-1}, [MAIB]$_0$=1.0×10^{-2} mol L^{-1}.

f. CH$_3$CN + pyridine = 1:1 vol/vol.

g. at –60°C.

h.   CH$_3$CN + DMF = 1:1 vol/vol, at –80°C, for 48 h.

TABLE 2 Radical Polymerization of NNPFAAm in the Presence of Lewis Base or Lewis Acid[a]

Run	Additive	Solvent	Temp.	Yield	Triad tacticity/%[b]			r Dyad[c]	M_n[d]	M_w[d]	$P_{m/r}$	$P_{r/m}$	$P_{m/r}+$
			°C	/%	mm	mr	rr	/%	$\times 10^{-4}$	$/M_n$			$P_{r/m}$
1[e]	HMPA	Toluene	–40	23	9.8	46.5	43.7	67.0	3.9	2.3	0.702	0.347	1.049
2[e]	HMPA	Toluene	–60	8	8.8	45.6	45.6	68.4	2.9	2.4	0.721	0.333	1.054
3[e]	HMPA	Toluene	–80	3	8.0	41.3	50.7	71.4	2.3	1.5	0.722	0.290	1.012
4[f]	HMPA+MeOH	Toluene	–80	7	9.8	49.7	40.5	65.4	3.5	1.5	0.717	0.380	1.097
5[g]	35DMPNO	CHCl$_3$	–60	21	10.0	51.5	38.5	64.3	3.5	1.5	0.720	0.401	1.121
6[h]	Sc(OTf)$_3$	MeOH	–20	20	12.2	51.9	35.9	61.9	6.6	1.8	0.679	0.420	1.099
7[h]	Y(OTf)$_3$	MeOH	–20	54	13.1	52.7	34.2	60.6	6.7	1.6	0.668	0.436	1.104
8[h]	Yb(OTf)$_3$	MeOH	–20	62	11.8	52.2	36.0	62.1	6.8	1.7	0.689	0.421	1.110
9[h]	Li(OTf)	MeOH	–20	45	10.1	51.6	38.3	64.1	5.8	1.7	0.719	0.402	1.122
10[h]	Sm(OTf)$_3$	MeOH	–20	63	9.0	58.5	32.5	61.8	4.0	2.3	0.764	0.474	1.237

a. $[\text{NNPFAAm}]_0$=1.0 mol L^{-1}, $[\text{MAIB}]_0$=1.0$\times 10^{-2}$ mol L^{-1}.

b. Determined from ^{19}F NMR signals.

c. Calculated from the triad tacticities with the equation: $r=mr/2+rr$.

d. Determined by SEC (polystyrene standards).

e. $[\text{HMPA}]_0$=2.0 mol L^{-1}.

f. $[\text{HMPA}]_0$=$[\text{MeOH}]_0$=2.0 mol L^{-1}.

g. $[\text{35DMPNO}]_0$=2.0 mol L^{-1}.

h. $[\text{NNPFAAm}]_0$=0.5 mol L^{-1}, $[\text{MAIB}]_0$=0.5$\times 10^{-2}$ mol L^{-1}, $[\text{M(OTf)}_x]_0$=0.5$\times 10^{-1}$ mol L^{-1}.

TABLE 3 Radical Polymerization of NNPFAAm in Toluene in the Presence of Alkyl Alcohol or Silyl Alcohol[a]

Run	Additive	Temp. °C	Yield /%	Triad tacticity/%[b]			r Dyad[c] /%	M_n[d] $\times 10^{-4}$	M_w[d] / M_n	$P_{m/r}$	$P_{r/m}$	$P_{m/r}+$ $P_{r/m}$
				mm	mr	rr						
1	None	0	90	17.8	50.1	32.1	57.2	11.8	3.7	0.585	0.438	1.023
2	None	–40	86	16.1	49.0	34.9	59.4	8.2	2.4	0.604	0.413	1.017
3	MeOH	–40	44	9.1	58.4	32.5	61.7	4.9	1.7	0.762	0.473	1.235
4	EtOH	–40	68	8.4	60.6	31.0	61.3	5.3	1.8	0.783	0.494	1.276
5	iPrOH	–40	69	7.8	63.8	28.4	60.3	4.9	1.8	0.804	0.529	1.332
6	tBuOH	–40	85	7.2	65.5	27.3	60.1	6.2	1.7	0.819	0.546	1.365
7	3Me3PenOH	0	>99	7.7	65.2	27.1	59.7	5.1	2.2	0.810	0.546	1.356
8	3Me3PenOH	–20	91	6.4	65.9	27.7	60.7	5.4	2.0	0.837	0.543	1.380
9	3Me3PenOH	–40	91	5.8	65.3	28.9	61.6	6.9	1.9	0.848	0.531	1.379
10	3Me3PenOH	–60	48	6.3	65.6	28.1	60.9	5.1	1.9	0.838	0.539	1.377
11	TESiOH	–40	76	6.7	62.8	30.4	61.8	6.6	2.1	0.824	0.508	1.332
12	DEIPSiOH	–40	84	6.8	59.1	34.0	63.6	6.3	2.1	0.812	0.465	1.277
13	TIPSiOH	–40	91	4.0	69.0	27.0	61.5	5.4	2.1	0.896	0.561	1.457

a. $[NNPFAAm]_0=0.5$ mol L^{-1}, $[MAIB]_0=0.5\times10^{-2}$ mol L^{-1}, $[Alcohol]_0=2.0$ mol L^{-1}.

b. Determined from ^{19}F NMR signals.

c. Calculated from the triad tacticities with the equation: $r=mr/2+rr$.

d. Determined by SEC (polystyrene standards).

TABLE 4 Radical Polymerization of NNPFAAm in the Presence of Fluorinated Alcohol (RfOH)[a]

Run	Additive	$[NNPFAAm]_0$ mol L^{-1}	Temp. °C	Yield /%	Triad tacticity/%[b] mm	mr	rr	r Dyad[c] /%	M_n[d] $\times 10^{-4}$	M_w[d] / M_n	$P_{m/r}$	$P_{r/m}$	$P_{m/r}+$ $P_{r/m}$
1	TFE	1.0	–40	60	11.4	64.8	23.8	56.2	4.5	2.1	0.739	0.576	1.315
2	HFIP	0.5	0	77	14.1	70.9	15.0	50.5	3.0	1.4	0.716	0.702	1.418
3	HFIP	0.5	–20	47	13.2	72.7	14.1	50.5	2.3	1.5	0.733	0.720	1.453
4	HFIP	0.5	–40	23	12.3	74.4	13.3	50.5	2.4	1.3	0.752	0.737	1.488
5	HFIP	1.0	–40	60	13.7	73.9	12.4	49.4	4.8	2.2	0.730	0.749	1.479
6	HFIP	0.5	–60	17	11.9	71.8	16.3	52.2	1.8	1.3	0.751	0.688	1.440
7	NFTB	0.5	–40	29	3.0	82.6	14.4	55.7	2.7	2.3	0.932	0.741	1.674
8	NFTB	1.0	–40	73	3.7	82.1	14.2	55.3	8.0	3.5	0.917	0.743	1.660

a. $[NNPFAAm]_0/[MAIB]_0=100$. $[RfOH]_0=2.0$ mol L^{-1}.

b. Determined from ^{19}F NMR signals.

c. Calculated from the triad tacticities with the equation: $r=mr/2+rr$.

d. Determined by SEC (polystyrene standards).

TABLE 5 $P_{m/r}$ and $P_{r/m}$ for Polymerizations of NIPAAm, NNPAAm, and NNPFAAm in Toluene in the Presence of 3Me3PenOH or NFTB

Monomer	Added alcohol	Temp. °C	$P_{m/r}$	$P_{r/m}$
NIPAAm[a]	3Me3PenOH	−60	0.733	0.314
NNPAAm[b]	3Me3PenOH	−40	0.694	0.259
NNPFAAm	3Me3PenOH	−20	0.837	0.543
NIPAAm[c]	NFTB	−40	0.814	0.614
NNPFAAm	NFTB	−40	0.932	0.741

a. Calculated with *mm*=8%, *mr*=44% and *rr*=48%.[18]

b. Calculated with *mm*=8.3%, *mr*=37.7% and *rr*=54.0%.[45]

d. Calculated with *mm*=8%, *mr*=70% and *rr*=22%.[18]

TABLE 6 Equilibrium constants (K) for the interaction between NNPFAAm and NFTB, and degree of association (α) in the polymerization system[a]

Temperature	K		α[b]	
°C	L mol^{-1}	[NNPFAAm]$_0$:	0.5 mol L^{-1}	1.0 mol L^{-1}
60	56.4		0.99	0.98
45	72.1		0.99	0.99
25	105		0.99	0.99
0	171		1.00	0.99
−20	(281)[c]		1.00	1.00
−40	(498)[c]		1.00	1.00

a. NMR conditions: [NIPFAAm]$_0$=5.0□10^{-2} mol L^{-1}, in toluene-d_8.

b. Calculated with [NFTB]$_0$=2.0 mol L^{-1}.

c. Calculated from van't Hoff relationship.

FIGURE 1 ¹H, ¹³C, and ¹⁹F NMR spectra of poly(NNPFAAm) measured (a) in CDCl₃ at 55 °C and (b) in DMSO-*d₆* at 100 °C.

FIGURE 2 ^{19}F NMR spectra of poly(NNPFAAm)s prepared (a) in toluene at −40 °C (Table 1, run 1), (b) in CH$_3$CN + pyridine at −80 °C (1:1, v/v) (Table 1, run 15), and (c) in toluene at −40 °C in the presence of NFTB (Table 4, run 7).

FIGURE 3 ^{1}H, ^{13}C, and ^{19}F NMR spectra of NNPFAAm (0.125 mol L^{-1}) measured in toluene-d_8 at 0 °C in the absence or presence of alcohols: (a) none, (b) 3Me3PenOH (0.125 mol L^{-1}), and (c) NFTB (0.125 mol L^{-1}).

FIGURE 4 (a) Changes in the chemical shifts of the vinylidene proton *trans* to the fluorine atom (*H*C=CH; *trans*) of NNPFAAm in the presence of NFTB (●), ([NNPFAAm]$_0$ + [NFTB]$_0$ = 0.25 mol L^{-1}, in toluene-d_8 at 0 °C), and (b) Job's plots for the association of NNPFAAm with NFTB. The plot marked (□) denotes the chemical shift of NNPFAAm alone at the corresponding concentration.

FIGURE 5 Changes in the chemical shifts of the vinylidene proton *trans* to the fluorine atom (*H*C=CF; *trans*) of NNPFAAm in toluene-d_8 at various temperatures, resulting from variations in the $[NFTB]_0/[NNPFAAm]_0$ ratio.

FIGURE 6 van't Hoff plot for 1:1 complex formation between NNPFAAm and NFTB

in toluene-d_8.

FIGURE 7 ^{1}H NMR spectra of methoxy groups in the MAIB fragments of poly(NNPFAAm)s prepared at $-40\ ^\circ$C (a) in toluene (Table 1, run 2), (b) in CH$_3$CN + pyridine (Table 1, run 13), and (c) in toluene in the presence of NFTB (Table 4, run 7), measured in DMSO-d_6 at 100 $^\circ$C.

FIGURE 8 Temperature dependences of the light transmittance ($\lambda = 500$ nm) of aqueous solutions of (a) poly(NNPFAAm) with $r = 59.5\%$ and (b) poly(NNPAAm) with $r = 60.4\%$ (0.1 w/v%, heating and cooling rates $= 0.5$ °C min^{-1}).
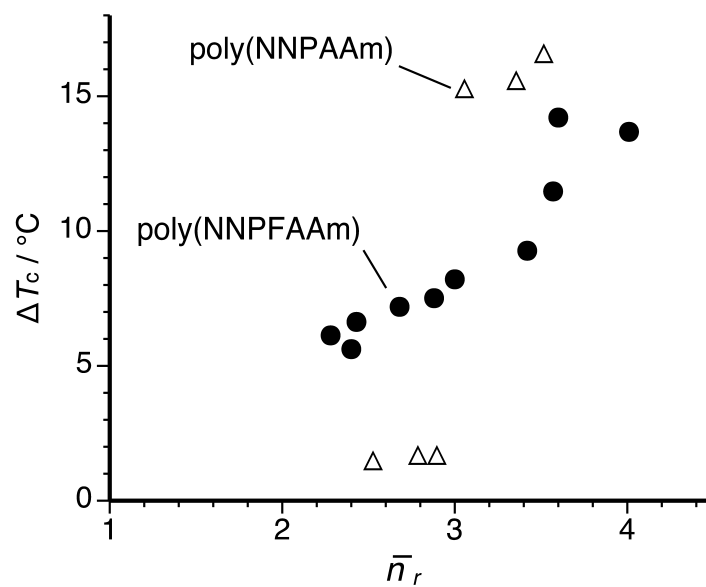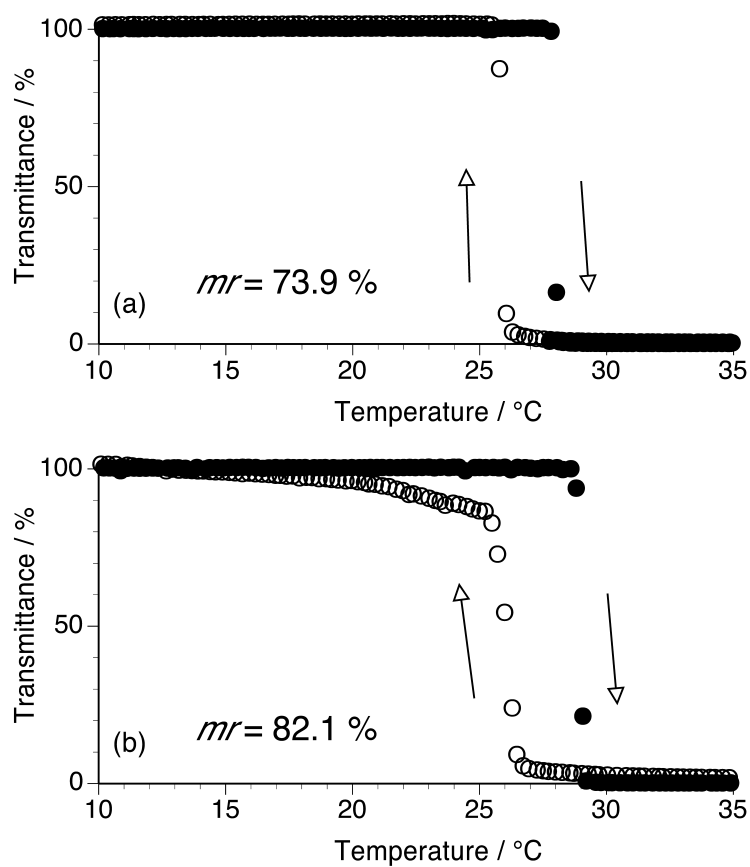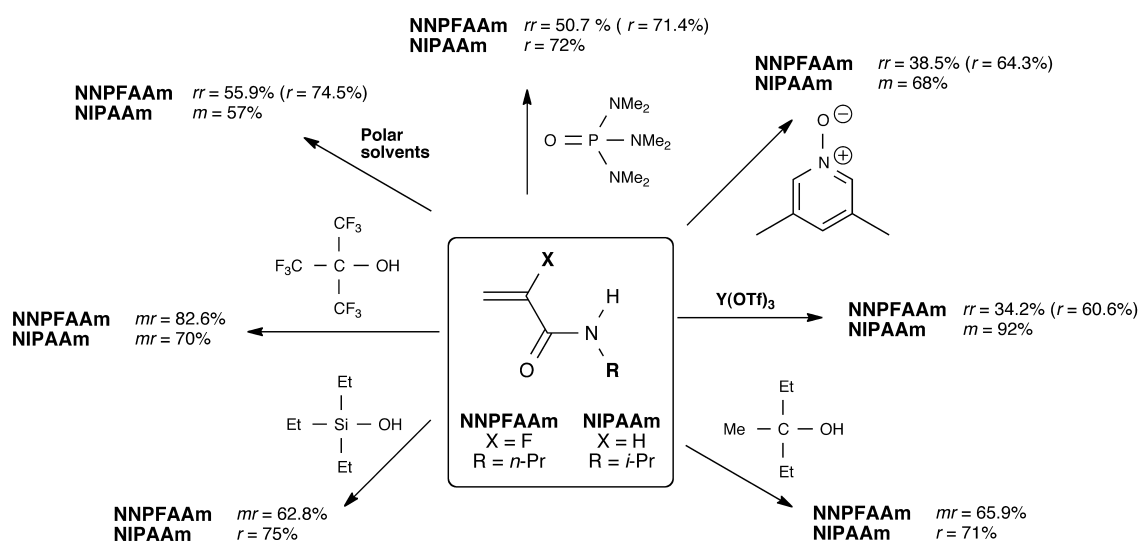
FIGURE 9 Temperature dependences of the light transmittance ($\lambda = 500$ nm) of aqueous solutions of (a) poly(NNPFAAm) with $r = 59.5\%$ and (b) with $r = 74.5\%$ (0.1 w/v%, heating and cooling rates = 0.5 °C min^{-1}).

FIGURE 10 Relationship between ΔT_c and $\bar{n}_r$ in syndiotactic-rich poly(NNPFAAm)s and poly(NNPAAm)s.
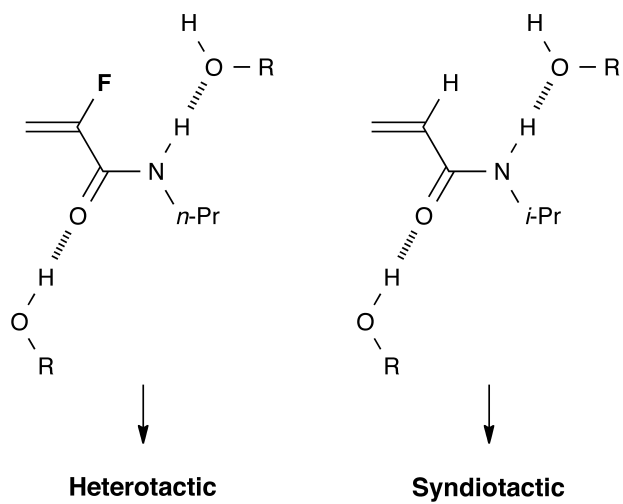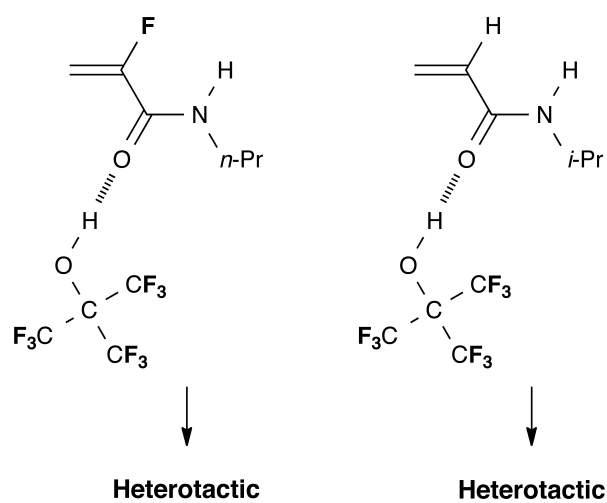
FIGURE 11 Temperature dependences of the light transmittances ($\lambda = 500$ nm) of aqueous solutions of (a) poly(NNPFAAm) with $mr = 73.9\%$ and (b) with $mr = 82.1\%$ (0.1 w/v%, heating and cooling rates = 0.5 °C min^{-1}).
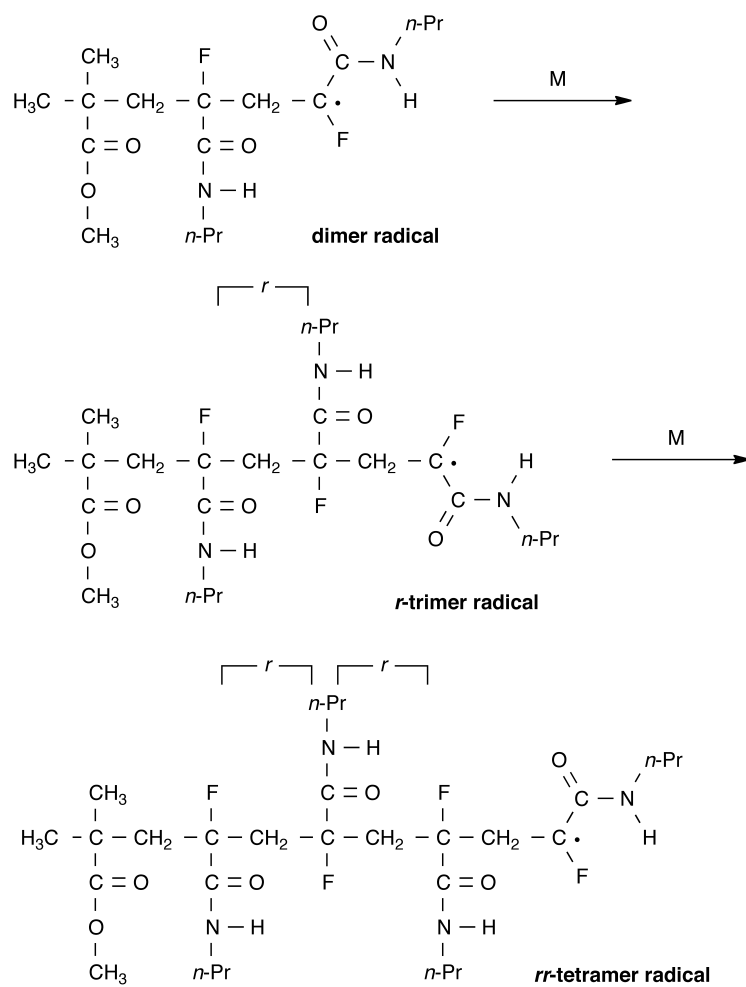
NNPFAAm rr = 50.7 % (r = 71.4%)
NIPAAm r = 72%

NNPFAAm rr = 55.9% (r = 74.5%)
NIPAAm m = 57%

NNPFAAm rr = 38.5% (r = 64.3%)
NIPAAm m = 68%

NNPFAAm mr = 82.6%
NIPAAm mr = 70%

NNPFAAm rr = 34.2% (r = 60.6%)
NIPAAm m = 92%

NNPFAAm mr = 62.8%
NIPAAm r = 75%

NNPFAAm mr = 65.9%
NIPAAm r = 71%

Polar solvents

Y(OTf)$_3$

NNPFAAm
X = F
R = n-Pr

NIPAAm
X = H
R = i-Pr

SCHEME 1 Effects of fluorine atom at the α-position on stereospecificity of radical polymerization of *N*-monosubstituted acrylamide derivatives.
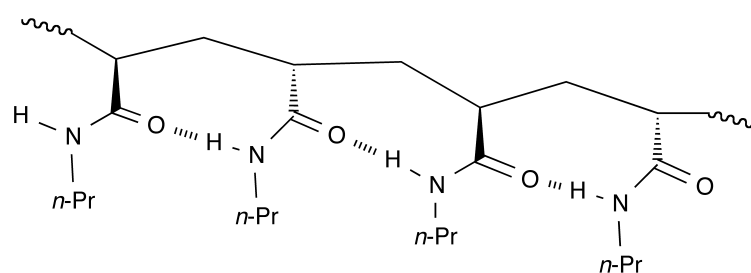
SCHEME 2 Proposed structures for 1:2 complexes of NNPFAAm and NIPAAm with alkyl alcohol (ROH).

SCHEME 3 Proposed structures for 1:1 complexes of NNPFAAm and NIPAAm with NFTB.

H$_3$C $-$ C $-$ CH$_2$ $-$ C $-$ CH$_2$ $-$ C •   CH$_3$ F O / n-Pr ... **dimer radical**

M →

r-trimer radical

M →

rr-tetramer radical

SCHEME 4 Formation of *rr*-tetramer radicals by *r*-addition of dimer radicals, followed by *r*-addition of *r*-trimer radicals.

SCHEME 5 Cooperative hydrogen-bonds formed between contiguous monomeric units

in syndiotactic stereosequences in dehydrated poly(NNPAAm).