# Stereocontrol in Radical Polymerization of $N,N$-Dimethylacrylamide and $N,N$-Diphenylacrylamide and Thermal Properties of Syndiotactic Poly(methyl acrylate)s Derived from the Obtained Polymers

Weihong Liu, Tamaki Nakano,* and Yoshio Okamoto**, †

Joint Research Center for Precision Polymerization (JRCPP)-Japan Chemical Innovation Institute (JCII),
Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464–8603, Japan
*Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST),
Ikoma 8916–5, Nara 630–0101, Japan
**Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464–8603, Japan

ABSTRACT: Free-radical polymerizations of $N,N$-dimethylacrylamide (DMAA) and $N,N$-diphenylacrylamide (DPAA) were carried out under various conditions. DMAA gave an isotactic-rich polymer in most cases, whereas DPAA gave a syndiotactic polymer. The polymerization stereochemistry was also affected by reaction solvents including toluene, tetrahydrofuran, and fluoroalcohols. It is notable that the stereochemistry of the polymerization depended on monomer concentration: a lower monomer concentration led to a higher isotacticity for DMAA polymerization and a higher syndiotacticity for DPAA polymerization. This effect was explained by assuming that there exist two types of growing radicals having different stereoselectivities. By optimizing the aforementioned reaction conditions, poly(DMAA) with diad isotacticity ($m$) of 77% (polymerization in toluene at $-78^\circ C$ at $[M]_o=0.1$ M) and poly(DPAA) with diad syndiotacticity ($r$) of 93% (polymerization in THF at $-98^\circ C$ at $[M]_o=0.22$ M) were obtained. Stereoregular poly(methyl acrylate)s were derived from the poly(DPAA)s. Thermal property of the poly(methyl acrylate)s with different tacticities was studied by DSC.
KEY WORDS Radical Polymerization / Tacticity / Stereochemistry / Concentration Effect / Solvent Effect / Acrylamides / Poly(methyl acrylate) /

Stereostructure of a vinyl polymer often significantly affects its physical and chemical properties. Therefore, stereocontrol of vinyl polymerizations is an important topic in macromolecular science. Control of the stereochemistry (tacticity) in free-radical polymerization is especially intriguing since there are only limited successful examples in spite of the convenience and industrial importance of radical polymerization.[1] Several methods have been devised to control the stereochemistry of radical polymerization of methacrylates,[1–3] acrylates,[4] acrylamides,[5,6] and vinyl esters.[7] It has been recognized that stereocontrol of acrylic monomers, in contrast to that of methacrylic counterparts, is generally difficult due to the lack of $\alpha$-CH$_3$ group: for example, methyl acrylate (MA) gives an atactic polymer regardless of reaction conditions of radical polymerization[8] while methyl methacrylate (MMA) affords a highly syndiotactic polymer by radical mechanism under selected conditions.[3] Hence, effective stereoregulation of the radical polymerization of acrylic monomers remains a challenging goal.

In the present work, we systematically investigated the stereochemistry of the radical polymerization of $N,N$-dimethylacrylamide (DMAA) and $N,N$-diphenylacrylamide (DPAA) under various conditions. DMAA has been reported to give a highly syndiotactic polymer[9] although we found that the polymerization of DMAA was isotactic-specific in this work. The former report seems to be based on wrong NMR peak assignments. We previously reported the preliminary results of the radical polymerization of DPAA affording a syndiotactic

polymer.[5] This paper describes the details of the polymerization of the two monomers.

The poly(DPAA) obtained in this work was converted to poly(MA) by polymer reaction,[5] and a syndiotactic poly(MA) with diad syndiotacticity ($r$) of up to 93% was successfully obtained. Such a highly syndiotactic poly-(MA) has never been prepared either by direct polymerization of MA or by chemical modification of other polymers excepting this work. The highest syndiotacticity so far reported may be $r=71\%$ for the poly(MA) derived from the radically prepared poly(trimethylsilyl acrylate).[10] We also studied the thermal properties of the stereoregular poly(MA)s along with other poly(MA)s with different tacticities.

## EXPERIMENTAL

### Materials

DMAA (Wako) was commercially available and distilled immediately before use. DPAA was prepared from acryloyl chloride and diphenylamine, and was purified according to our previous report.[5a] CF$_3$CH$_2$OH (Aldrich; purity > 99%), (CF$_3$)$_2$CHOH (Wako; purity > 99%), (CF$_3$)$_3$C(CH$_3$)OH (P.C.R.; purity > 97%) and (CF$_3$)$_3$COH (Aldrich; purity > 99%) were used as received. The other solvents were purified by distillation immediately before use. 2, 2'-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization from methanol. Benzoin (TCI), K$_2$S$_2$O$_8$ and Na$_2$SO$_3$ were used as received. Tri-$n$-butylborane ($n$Bu$_3$B) was obtained as a tetrahydrofuran (THF) solution (1.0M) (Aldrich) and

used after removal of the solvent.

## Polymerization

Polymerization was carried out in a glass ampule under a nitrogen atmosphere. The polymerization using $n\text{Bu}_3\text{B}$ was conducted as follows. $n\text{Bu}_3\text{B}$ was added with a hypodermic syringe to a monomer solution kept at a reaction temperature. The polymerization reaction was initiated by introducing a small amount of air with a syringe. The reaction was terminated by adding a small amount of methanol solution of 2,6-di-t-butyl-p-cresol. The polymerization with other initiators was carried out by usual methods. The obtained poly(DMAA) was precipitated into hexane or acetone, purified by precipitation from a water solution to an acetone-hexane mixture (4/1, v/v), and dried under vacuum at 80°C for 24 h. The obtained poly(DPAA) was precipitated into methanol, separated by centrifugation, and dried under vacuum at 60°C for 24 h.

## Conversion of Poly(DMAA) and Poly(DPAA) to Poly(MA)

*Conversion of Poly(DMAA) to Poly(MA).* A typical procedure is as follows.[6] Poly(DMAA) (20 mg) was placed in a glass ampule with a magnetic stirring bar. Dioxane (5 mL) and 12N hydrochloric acid (5 mL) was added in order, and the mixture was heated with stirring at 90°C for 5 days. After cooling, the reaction mixture was poured into water (30 mL). The precipitates were collected with a centrifuge, washed with water, dried *in vacuo* at 40°C for 3 h, and methylated in benzene with an ethereal solution of diazomethane. The obtained poly-(MA) was precipitated into hexane, separated with a centrifuge, and dried *in vacuo* at 60°C for 8 h.

*Conversion of Poly(DPAA) to Poly(MA).* The reaction was performed under a modified condition with some modifications according to our previous work.[5a] A typical procedure is as follows. Poly(DPAA) (20 mg) was placed with a magnetic stirring bar in a glass ampule equipped with a three-way stopcock which was then evacuated and flushed with nitrogen. Methanol (0.8 mL) and sulfuric acid (1.2 mL) was added in order using syringe through the three-way stopcock, and the mixture was heated with stirring at 90°C for 24 h. After cooling, the mixture was poured into aqueous hydrochloric acid (1 N, 10 mL). The precipitates were collected with a centrifuge, washed with water, and dried *in vacuo* at 40°C for 3 h. The methylation procedure was described above. The yield of poly(MA) was 97%.

## Measurements

^{1}H and ^{13}C NMR spectra were measured with a Varian Gemini 2000 spectrometer at 400 and 100 MHz, respectively. The center peak of chloroform-d was used as an internal standard (77.0 ppm) in ^{13}C measurement. The size exclusion chromatographic (SEC) analysis was accomplished on a Shodex System-21 SEC system equipped with an ultraviolet detector (254 nm) and a refractive index detector using a Shodex KF-803 and a KF-806L columns connected in series (eluent, THF). The molecular weight of the polymers was calibrated with standard polystyrenes. The degree of polymerization (DP) of poly(DPAA) was measured as poly(MA) derived from the original polymers. Differential scanning calo-

rimetry (DSC) measurement was performed on a Seiko SSC-5200 calorimeter at a heating rate of 10°C min$^{-1}$ under a nitrogen atmosphere. The midpoint of the heat capacity transition was taken as $T_g$.

# RESULTS AND DISCUSSION

## Tacticity Determination for Poly(DMAA) and Poly (DPAA)

The results of the polymerization are summarized in Tables I—III. The tacticity of the polymers was estimated by ^{1}H NMR method as follows. The diad tacticity of polyacrylates can often be determined by ^{1}H NMR in $CDCl_3$ using methylene proton signals.[8,10] However, the methylene protons of poly(DMAA) have been reported to give complicated, overlapped splitting pattern in $CDCl_3$.[9,11] In the present study, we found that the methylene protons of poly(DMAA) show a peak splitting pattern similar to those of polyacrylates by ^{1}H NMR measurement in DMSO-$d_6$ at a high temperature (100°C). Figure 1 shows the methylene region of the ^{1}H NMR spectra of the two poly(DMAA) samples with different tacticities obtained in this work (run 1 in Table I and run 3 in Table II). The methylene proton peaks are split into three parts due to the main-chain stereochemistry, that is, downfield meso, racemo, and upfield meso signals, and the upfield meso signal was clearly separated from the other peaks. Therefore, diad meso content can be calculated according to an equation:

$$m\% = 2(A_1/(A_1+A_2)) \times 100 \qquad (1)$$

where $A_1$ is the area of upfield meso signal and $A_2$ is the combined area of the racemo and downfield meso signals as indicated in the figure.

An alternative, indirect method for the tacticity determination of poly(DMAA) is the analysis of poly(MA) derived from it by hydrolysis and methylation. A syndiotactic-rich poly(DMAA) (run 1 in Table I, $m/r = 42/58$ as determined as poly(DMAA)) was hydrolyzed in a 12 N HCl/dioxane (1/1, v/v) mixture at 90°C for 5 days according to Porter's method.[6] The NMR measurement showed that this sample's tacticity was $m/r = 42/58$, which is coincident with that measured by the direct ^{1}H NMR analysis. In this work, the former method was adopted for all poly(DMAA) samples.

It should be noted that the triad isotacticity $(mm)$ of poly(DMAA) can be determined on the basis of N-methyl proton signals in ^{1}H NMR.[12] In addition, the tacticity analysis of poly(DMAA) by means of ^{13}C NMR is difficult due to the severe overlap of the signals of the main-chain carbons and N–CH$_3$ groups: accurate assignments for the carbonyl signals have not yet been performed.[11,12]

Direct ^{1}H NMR measurement of poly(DPAA) results in broad signals with insufficient resolution for tacticity determination. Hence, to determine the diad tacticity of poly(DPAA), the original polymer needs to be converted to poly(MA) for NMR analysis. The conversion by hydrolysis in a mixture of concentrated sulfuric acid and methanol (6/4, v/v) at 90°C under nitrogen and methylation with diazomethane has been proven to undergo no racemization of the main chain.[5a]

**Table I.** Free-radical polymerization of DMAA[a]

| Entry | Initiator | Solvent | Temp. °C | Yield[b] % | $M_n$[c] ×10⁻⁴ | $M_w/M_n$[c] | Tacticity[d] m/r |
|-------|-----------|---------|------|-------|------|--------|---------|
| 1 | $K_2S_2O_8$-$Na_2SO_3$ | $H_2O$ | 60 | >99 | 0.56 | 1.42 | 42/58 |
| 2 | AIBN | None | 60 | 83 | 0.80 | 2.94 | 49/51 |
| 3 | $n$Bu₃B-air | None | 0 | 95 | 0.62 | 2.40 | 50/50 |
| 4 | $n$Bu₃B-air | None | −20 | 94 | 0.75 | 2.40 | 50/50 |
| 5 | $n$Bu₃B-air | None | −78 | 95 | 1.39 | 3.25 | 51/49 |
| 6 | AIBN | 2-Propanol | 82 | 19 | 0.23 | 1.79 | 45/55 |
| 7 | AIBN | 2-Propanol | 60 | 87 | 0.25 | 1.88 | 45/55 |
| 8 | Benzoin-UV | 2-Propanol | 0 | 93 | 0.78 | 1.68 | 50/50 |
| 9 | $n$Bu₃B-air | 2-Propanol | −78 | >99 | 0.52 | 2.61 | 57/43 |
| 10 | AIBN | THF | 67 | 70 | 0.32 | 2.18 | 47/53 |
| 11 | AIBN | THF | 60 | >99 | 0.32 | 2.39 | 47/53 |
| 12 | Benzoin-UV | THF | 0 | >99 | 0.58 | 3.10 | 51/49 |
| 13 | $n$Bu₃B-air | THF | −78 | >99 | 0.42 | 1.37 | 62/38 |
| 14 | BPO | Toluene | 110 | 53 | 0.48 | 3.06 | 51/49 |
| 15 | AIBN | Toluene | 60 | 96 | 1.15 | 2.04 | 53/47 |
| 16 | $n$Bu₃B-air | Toluene | 0 | >99 | 1.83 | 3.21 | 61/39 |
| 17 | $n$Bu₃B-air | Toluene | −78 | >99 | 2.44 | 3.71 | 72/28 |
| 18 | $n$Bu₃B-air | $CF_3CH_2OH$ | 0 | >99 | 1.35 | 2.43 | 48/52 |
| 19 | $n$Bu₃B-air | $(CF_3)_2CHOH$ | 0 | 75 | 1.08 | 1.97 | 51/49 |
| 20 | $n$Bu₃B-air | $(CF_3)_2CH_3COH$ | 0 | >99 | 0.47 | 1.82 | 52/48 |
| 21 | $n$Bu₃B-air | $(CF_3)_3COH$ | 0 | 65 | 0.93 | 2.28 | 63/37 |

[a] Conditions: $[DMAA]_0 = 1.0$ M(runs 1 and 6—21) or 9.8 M(runs 2—5), $[n Bu_3 B]_0 = 0.10$ M(runs 9, 13, 16—21) or 0.05 M(runs 3—5), [AIBN, Benzoin or $K_2S_2O_8]_0 = 0.02$ M; time = 24 h. [b] Acetone-insoluble part(run 1), hexane-insoluble part(runs 2—21). [c] Determined by SEC. [d] Determined by ¹H NMR(400 MHz, DMSO-$d_6$, 100°C).

**Table II.** Effect of monomer concentration on the stereochemistry of polymerization of DMAA[a]

| Entry | Initiator | Solvent | $[M]_0$ M | Temp. °C | Yield[b] % | $M_n$[c] ×10⁻⁴ | $M_w/M_n$ | Tacticity[d] m/r |
|-------|-----------|---------|------|------|-------|------|--------|---------|
| 1 | $n$Bu₃B-air | Toluene | 4.0 | −78 | >99 | 6.52 | 5.47 | 66/34 |
| 2 | $n$Bu₃B-air | Toluene | 0.5 | −78 | 92 | 1.71 | 4.57 | 75/25 |
| 3 | $n$Bu₃B-air | Toluene | 0.1 | −78 | 89 | 2.17 | 1.75 | 77/23 |
| 4 | $n$Bu₃B-air | Toluene | 4.0 | −20 | 99 | 5.00 | 5.90 | 58/42 |
| 5 | $n$Bu₃B-air | Toluene | 0.1 | −20 | 99 | 0.31 | 2.50 | 67/33 |
| 6 | $n$Bu₃B-air | Toluene | 4.0 | 0 | 99 | 3.26 | 5.82 | 56/44 |
| 7 | $n$Bu₃B-air | Toluene | 0.1 | 0 | 97 | 0.32 | 2.27 | 66/34 |
| 8 | $n$Bu₃B-air | $(CF_3)_3COH$ | 5.0 | 0 | 36 | 1.54 | 1.73 | 50/50 |
| 9 | $n$Bu₃B-air | $(CF_3)_3COH$ | 2.0 | 0 | 48 | 3.77 | 1.77 | 59/41 |
| 10 | AIBN | Toluene | 4.0 | 60 | 99 | 5.88 | 3.13 | 51/49 |
| 11 | AIBN | Toluene | 0.1 | 60 | 99 | 0.22 | 2.65 | 55/45 |

[a] Conditions: $[n Bu_3 B]_0 = 0.05$ M (runs 1, 2, 4, 6, and 9), 0.02 M (runs 3, 5, and 7), $[AIBN]_0 = 0.02$ M; time, 24 h. [b] Hexane-insoluble part. [c] Determined by SEC. [d] Determined by ¹H NMR(400 MHz, DMSO-$d_6$, 100°C).

## Polymerization of DMAA

Table I shows the result of free-radical polymerization of DMAA under various conditions. In most cases, the reaction systems were homogeneous; those in toluene at −78°C and in bulk gelled. The polymerization in water gave a syndiotactic-rich polymer as shown in Figure 1 (A) (run 1 in Table I), but the syndiotacticity ($r = 58\%$) observed here is much lower than the reported value ($r = 90\%$) of the sample obtained under the similar conditions,[9c] suggesting the previous tacticity determination may not be accurate.

The bulk polymerization gave almost atactic polymers regardless of reaction temperature. The polymerizations in 2-propanol and THF at 60°C resulted in similar reaction stereochemistry to that in water at the same temperature. In these solvents, lowering reaction temperature gave higher $m$ specificity and the polymers rich in $m$ diad were obtained at −78°C while the polymers rich in $r$ diad were produced at 60°C or higher temperature. The polymerization in toluene afforded the polymers rich in isotacticity at all temperatures tested here in con-

trast to those in water, 2-propanol, and THF. The effect of temperature in toluene was similar to that in 2-propanol and THF; $m$ specificity reached 72% in the polymerization in toluene at −78°C. Radical polymerization usually affords polymers rich in syndiotacticity rather than isotacticity.[1,3,7] The formation of the isotactic-rich polymer is known for the polymerization of bulky monomers.[2,6]

The isotacticity of the polymers seems to increase with a decrease of solvent polarity; for instance at 60°C, $H_2O$ (42%)< 2-propanol (45%)<THF (47%)<toluene (53%). In the radical polymerization of triphenylmethyl methacrylate, two types of growing radicals with different meso selectivity have been assumed to explain the remarkable influence of monomer concentration and solvent on tacticity.[2] More details about the proposed growing speices are given in the text section with relation to monomer concentration effect. The solvent effect found here may also be explained by assuming two types of growing radicals with different stereoselectivity whose structure or interchange rate may be affected by solvent.

The polymerization in $(CF_3)_3COH$ led to an increased

**Table III.** Radical polymerization of DPAA [a]

| Entry | Initiator | Solvent | Temp. °C | Yield [b] % | DP [c] | $M_w/M_n$ [c] | Tacticity [d] m/r |
|-------|-----------|---------|----------|-------------|--------|---------------|-------------------|
| 1[e] | AIBN | DMF/H$_2$O (2/1, v/v) | 60 | 91 | 67 | 1.89 | 24/76 |
| 2[e] | nBu$_3$B-air | 2-Propanol | 0 | 63 | 59 | 2.44 | 23/77 |
| 3[e] | nBu$_3$B-air | CF$_3$CH$_2$OH | 0 | 42 | 43 | 2.48 | 26/74 |
| 4 | nBu$_3$B-air | (CF$_3$)$_2$CHOH | 0 | 23 | 33 | 1.41 | 26/74 |
| 5[e] | nBu$_3$B-air | (CF$_3$)$_2$CH$_3$COH | 0 | 59 | 37 | 1.50 | 32/68 |
| 6[f] | nBu$_3$B-air | (CF$_3$)$_3$COH | 0 | 84 | 75 | 5.66 | 27/73 |
| 7[e] | nBu$_3$B-air | Et$_2$O | 0 | 83 | 64 | 2.35 | 20/80 |
| 8 | nBu$_3$B-air | Anisole | 0 | 87 | 92 | 2.91 | 20/80 |
| 9 | AIBN | DMF | 60 | 70 | 45 | 1.46 | 20/80 |
| 10 | nBu$_3$B-air | DMF | 0 | 99 | 130 | 3.12 | 18/82 |
| 11 | nBu$_3$B-air | DMF | −20 | 99 | 397 | 4.06 | 16/84 |
| 12 | nBu$_3$B-air | DMF | −50 | 85 | 605 | 2.98 | 13/87 |
| 13 | AIBN | THF | 60 | 71 | 23 | 1.74 | 20/80 |
| 14 | nBu$_3$B-air | THF | 0 | 36 | 28 | 1.83 | 18/82 |
| 15 | nBu$_3$B-air | THF | −78 | 56 | 56 | 1.62 | 9/91 |
| 16 | nBu$_3$B-air | THF | −98 | 82 | 51 | 2.08 | 7/93 |
| 17 | AIBN | Toluene | 60 | 83 | 67 | 6.66 | 20/80 |
| 18 | nBu$_3$B-air | Toluene | 0 | 97 | 148 | 3.70 | 18/82 |
| 19 | nBu$_3$B-air | Toluene | −20 | 97 | 437 | 2.93 | 18/82 |
| 20 | nBu$_3$B-air | Toluene | −78 | 75 | 383 | 2.28 | 13/87 |
| 21[f] | nBu$_3$B-air | THF | −78 | 95 | 130 | 3.12 | 14/86 |

[a] Conditions: $[DPAA]_0 = 0.22$ M, $[AIBN] = 0.02$ M, $[nBu_3B]_0 = 0.1$ M; time, 24 h. [b] MeOH-insoluble part. [c] Determined as poly(MA) by SEC. [d] Determined by $^1$H NMR of poly(MA) derived from the original polymer (400 MHz, CDCl$_3$, 60°C). [e] Polymer separated out from the medium during the polymerization. [f] $[DPAA]_0 = 1.1$ M.
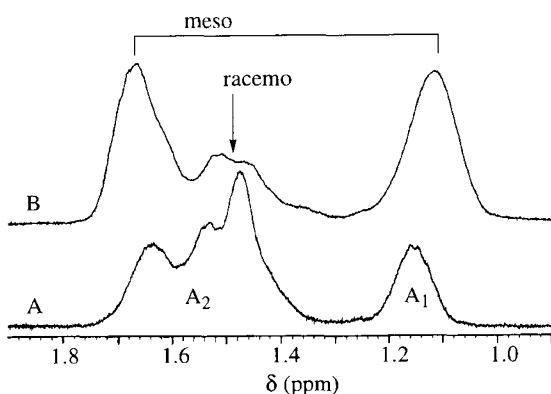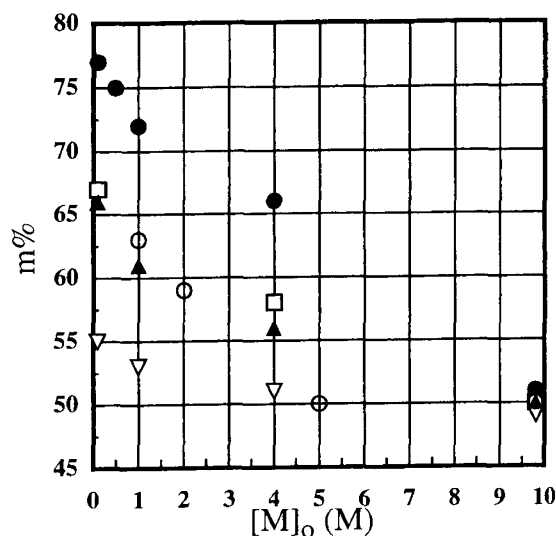


**Figure 1.** $^1$H NMR spectra of poly(DMAA)s ( A, run 1 in Table I; B, run 3 in Table II) [400 MHz, DMSO-$d_6$, 100°C].



**Figure 2.** Monomer concentration effect on the stereochemistry of the polymerization of DMAA (● toluene, −78°C; □ toluene, −20°C; ▲ toluene, 0°C; ▽ toluene, 60°C; ○ (CF$_3$)$_3$COH, 0°C).

$m$ specificity while the other fluoroalcohols had only negligible effects. We have recently reported that bulky fluoroalcohols including (CF$_3$)$_3$COH remarkably affect the stereochemistry of polymerization of vinyl esters and methacrylates and the effects depended on the structure of the monomer and alcohol.[3,7] The effects have been ascribed to the hydrogen-bonding interaction between the carbonyl group of monomer and/or growing species and the hydroxyl group of alcohol. A similar mechanism is assumed to be responsible for the effect of (CF$_3$)$_3$COH in this work.

*DMAA Monomer Concentration Effect*

Clear monomer concentration effects were found in the polymerization of DMAA [Table I ($[M]_0 = 1.0$ M and 9.8 M), Table II, and Figure 2]. Though monomer concentration effect on the stereochemistry has been found in the anionic and coordination polymerization,[13] there are only few examples for radical polymerization. Re-

cently, we found that the stereochemistry of radical polymerization of triphenylmethyl methacrylate was remarkably dependent on monomer concentration.[2] A clear concentration effect was also found in the radical polymerization of 1,1,1,3,3,3-hexafluoro-2-propyl acrylate at low temperature.[4] In the present work, monomer concentration effect on the stereochemistry in the polymerization of DMAA in toluene and (CF$_3$)$_3$COH was investigated. As shown in Table I ($[M]_0 = 1.0$ M and 9.8 M) and Table II, in both solvents, a higher $m$ specificity was observed at a lower monomer concentration. The effect was more obvious at lower temperature (Figure 2). At −78°C, by lowering $[M]_0$ from 9.8 to 0.1 M in toluene, $m$-specificity increased from 51% to 77%. The $m$ content

of 77% (run 3 in Table II) is considered to be the highest for the radical polymerization of DMAA.

In order to explain the concentration effects in the radical polymerization of DMAA, we assume that two types of growing radicals having different stereoselectivity exist in the radical polymerization: one has higher $m$ specificity and the other has lower $m$ specificity. The two species are interchangeable in the reaction system. The structure difference between the two may be in conformation around growing end. The latter is initially formed on the monomer addition but it stereomutates with a rate comparable to monomer addition rate to the former as the former is thermodynamically more stable. Hence, at lower monomer concentration where the interchange rate may be higher than the monomer addition rate, higher $m$ specificity is attained. Because the effect was obvious in the work only at relatively low temperature, the energy barrier between the two species may be rather low. The same assumption was already proposed for the radical polymerization of triphenylmethyl methacrylate.[2]

### Polymerization of DPAA

Table III shows the result of free-radical polymerization of DPAA under various conditions. In 2-propanol, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-$t$-butanol, diethyl ether and a mixture of DMF and water, the resulting polymer separated out from the medium. In contrast to the DMAA polymerization, DPAA gave the polymers rich in $r$ diad under all conditions (Table III), indicating that monomer structure strongly affect the stereochemistry of the radical polymerization. In DMF, THF, and toluene, a higher $r$ specificity was attained at a lower temperature.

Solvent effect seems relatively small at higher temperatures. The polymerization in DMF, THF, and toluene resulted in the same $r$ specificity at 60°C. The reaction in a water-DMF mixture led to a slight decrease in syndiotacticity. However, it was found that solvent effect becomes more obvious at lower temperature, and THF led to a higher syndiotactic polymer than toluene at −78°C.

The alcoholic solvents including fluoroalcohols decreased $r$-specificity as observed in the polymerization at 0°C. This effect was larger with fluoroalcohols. Similar $r$-decreasing effects of fluoroalcohols have been reported for the polymerization of bulky methacrylates and vinyl esters.[3,7]

In THF at −98°C, an $r$ diad specificity of 93% was achieved (run 16 in Table III). This is the highest $r$ specificity reported for the polymerization of acrylic monomers. Chemical modification of this polymer led to a poly(MA) having the highest syndiotacticity (Figure 3).

Monomer concentration effect was studied also in DPAA polymerization. The polymerization in THF under similar condition to run 15 at $[M]_0 = 1.1$ M led to a polymer with $m/r = 14/86$ in 95% yield (run 21). This indicates that a lower monomer concentration led to a higher $r$ specificity contrary to the polymerization of DMAA. This result is similar to those in the polymerization of 1,1,1,3,3,3-hexafluoro-2-propyl acrylate in THF.[4]
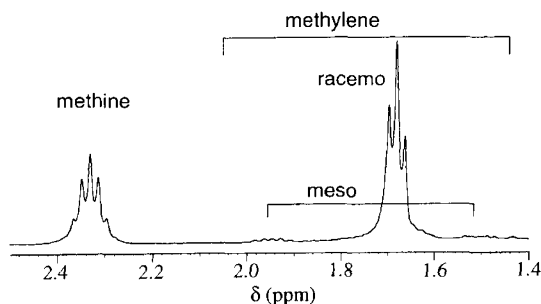


**Figure 3.** $^1$H NMR spectrum of poly(MA) derived from poly-(DPAA) (run 16 in Table III) [400 MHz, CDCl$_3$, 60°C].

### Activation Parameters for the Polymerization

The differences in activation enthalpy and activation entropy between isotactic and syndiotactic propagations was determined by the plots according to the following equation:[14]

$$\ln(P_i/P_s) = (\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})/R - (\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})/RT \qquad (2)$$

where $P_i$ and $P_s$ are mole fractions of isotactic and syndiotactic diads, respectively; $R$ is the gas constant (1.987 cal mol$^{-1}$ K$^{-1}$), and $T$ is the absolute temperature. This analysis was applied to the DMAA and DPAA polymerizations. Figure 4 shows the Fordham plots for DMAA polymerization at $[M]_0 = 1.0$ M. The activation parameters for the DMAA and DPAA polymerizations under various conditions are summarized in Table IV. The negative $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and the negative $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ values for the DMAA polymerization systems indicate that the $m$-specific propagation of DMAA polymerization is favored by enthalpy and disfavored by entropy. The positive $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and the negative $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ values for the DPAA systems mean the $r$-specific monomer addition is favored by both enthalpy and entropy.

In the polymerization of DMAA in toluene at different concentration, as shown in Table IV, both $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ decreased with a decrease in monomer concentration. This means that at a lower monomer concentration $m$-specific propagation is more favored by enthalpy and more disfavored by entropy. The increased $m$ specificity by lowering monomer concentration seems to be based on an enthalpic factor. This corresponds to the fact that the temperature effect was larger at a lower monomer concentration, which can be seen directly from Figure 2.

### Thermal Properties of Poly(MA) Derived from Poly-(DPAA)

As described so far, highly syndiotactic poly(DPAA) was synthesized and highly syndiotactic poly(MA) was obtained by chemical modification of the poly(DPAA). Highly syndiotactic poly(MA) has never been prepared before, and therefore, the tacticity-property relation for poly(MA)s with a wide range of tacticity is interesting. In order to shed light on this subject, the thermal properties of two syndiotactic poly(MA)s derived from the poly(DPAA)s of runs 16 and 20 in Table III ($r = 93\%$ and
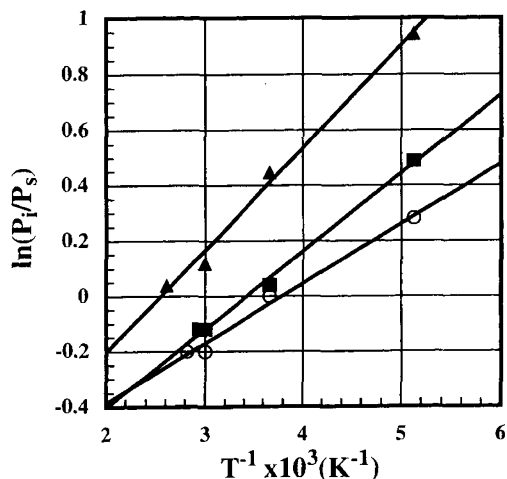
**Figure 4.** Temperature effect on the stereochemistry of DMAA polymerization in 2-propanol (○), THF (■), and toluene (▲) ($[M]_0$ = 1.0 M).



**Figure 5.** Methylene region of ^{13}C NMR spectra of poly(MA)s: (A) syndiotactic; (B) isotactic; (C) atactic [100 MHz, $CDCl_3$, 60℃].

**Table IV.** Activation parameters for the radical polymerization of $N,N$-disubstituted acrylamides under different conditions[a]
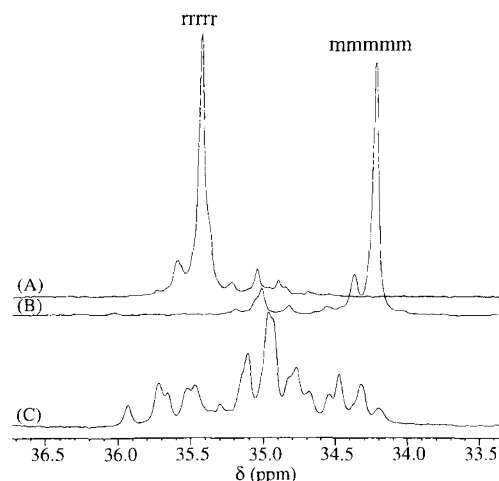
| Monomer | Solvent | $[M]_0$ | $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ <br> cal deg$^{-1}$ mol$^{-1}$ | $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ <br> cal mol$^{-1}$ |
|---------|---------|---------|------|------|
| DMAA | 2-Propanol | 1.0 | -1.6 | -430 |
| DMAA | THF | 1.0 | -1.9 | -561 |
| DMAA | None | 9.8 | -0.3 | -70 |
| DMAA | Toluene | 4.0 | -1.7 | -581 |
| DMAA | Toluene | 1.0 | -1.9 | -730 |
| DMAA | Toluene | 0.1 | -2.2 | -910 |
| DPAA | Toluene | 0.22 | -1.2 | 487 |
| DPAA | DMF | 0.22 | -0.6 | 692 |
| DPAA | THF | 0.22 | 0.2 | 948 |

[a] Calculated according to eq 2(see text).



**Figure 6.** DSC curves of poly(MA)s obtained by anionic polymerization ($m$ = 90%, $M_n$ = 2.73 × 10⁴, $M_w/M_n$ = 2.44, A₁, 1st heating; A₂, 2nd heating) and radical polymerization ($m$ = 46%, $M_n$ = 2.66 × 10⁴, $M_w/M_n$ = 1.94, B₁, 1st heating; B₂, 2nd heating) (heating rate: 10℃ min⁻¹, N₂ flow: 35 mL min⁻¹).
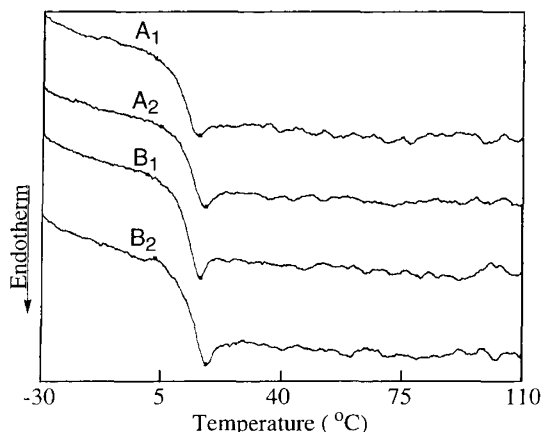
87%, respectively) were measured along with isotactic and atactic poly(MA) samples prepared independently. An isotactic polymer sample is available from our previous work (anionic polymerization of MA with $n$-BuLi in toluene at −42℃; $M_n$ = 2.73 × 10⁴, $M_w/M_n$ = 2.44, $m/r$ = 90/10)[13] and an atactic polymer was prepared by conventional radical polymerization of MA (polymerization using AIBN in toluene at 60℃; $M_n$ = 2.66 × 10⁴, $M_w/M_n$ = 1.94, $m/r$ = 46/54). The stereochemical difference among the three samples was confirmed on the basis of the methylene-region ^{13}C NMR spectra shown in Figure 5. The methylene peaks are sensitive to hexad sequence and the peaks have been assigned by Porter et al.[6] The spectra indicate that the syndiotactic and isotactic samples have predominant rrrr (60%) and mmmm (62%) hexad sequences, respectively.

Figure 6 shows the DSC curves of the isotactic and atactic polymers. The two polymers showed single thermal transition peak at about 14℃ which seems to be based on glass transition temperature ($T_g$) both on the first and the second heating runs. In this range of tacticity of polymers ($m$ = 46—90%), $T_g$ appeared not to be affected by tacticity.

In contrast to these results, the syndiotactic polymers indicated three clear endothermic peaks in the range of 36—110℃ in addition to that based on glass transition

at about 10—12℃ on the first heating run (Figures 7 and 8). For the poly(MA) of $r$ = 87% (Figure 7), the three endothermic peaks disappeared on the second heating run which was performed immediately after the first heating (curve B). Although, on the third heating run after allowing the sample to stand at room temperature for 4 h, the three endothermic peaks was still not clearly observed (curve C), the peaks recovered on the fourth heating when the sample was allowed to stand at room temperature for 24 h after the third heating (curve D). Similar thermal properties were observed for the poly(MA) of $r$ = 93% (Figure 8). In this case, however, even immediately after the first run, the endothermic peak at about 110℃ recovered slightly on the second heating run while those at 47 and 76℃ did not appear (curve B). With the "waiting time" of 24 h after the second heating run, the endothermic peak at 110℃ was even stronger than the original intensity on the first heating run, and a new, broad exothermic peak appeared at about 70℃.

These observation may indicate that the syndiotactic poly(MA)s have crystalline domains (semi-crystalline)
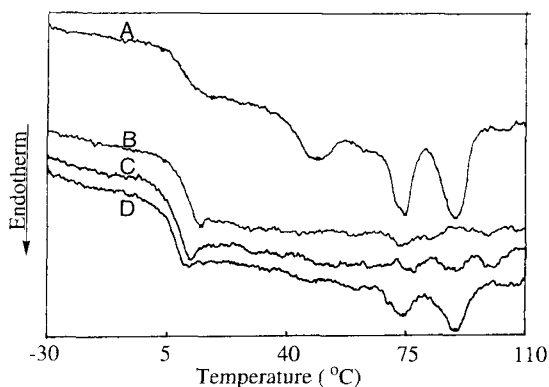
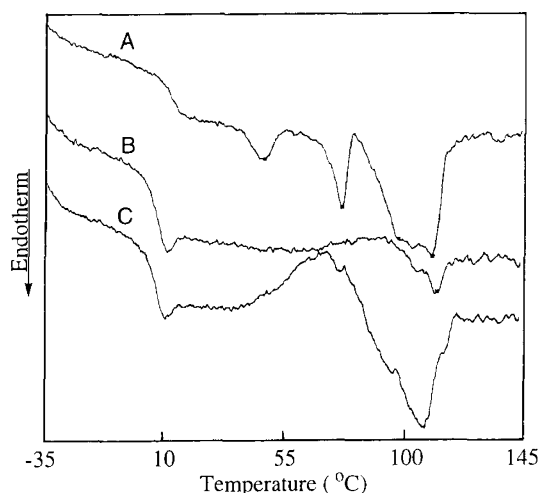**Figure 7.** DSC curves of poly(MA) derived from poly(DPAA) ($m$ = 13%, $M_n$ = 3.30 × 10⁴, $M_w/M_n$ = 2.28, A, 1st heating; B, 2nd heating; C, 3rd heating after the sample was allowed to stand for 8 h at r.t.; D, 4th heating after the sample was allowed to stand for 24 h at r.t., heating rate: 10℃ min⁻¹, N₂ flow: 35 mL min⁻¹).

while the isotactic and atactic polymers are completely amorphous. The observed recovery of the endothermic peaks, which can be assigned to the melting of crystalline domains, seems to correspond to crystallization process. The rate of crystallization appears lower for the polymer with lower syndiotacticity. For the polymer of $r$ = 93%, the structure of crystalline part may have changed during the heating and cooling processes. Similar thermal properties has been reported for syndiotactic poly($n$-butyl acrylate)s which showed melting endothermic peaks in addition to $T_g$ and the intensity of the endothermic peaks increased with an increase in $r$ content.[15]

## CONCLUSION

The diad tacticity of poly(DMAA) was accurately determined by direct ¹H NMR measurement in DMSO-$d_6$ at 100℃. The radical polymerization stereochemistry of the $N,N$-disubstituted acrylamides was significantly affected by the side chain structure as well as temperature and solvent; DMAA gave polymers rich in isotacticity in most cases while DPAA afforded syndiotactic polymers. Monomer concentration also affected the stereochemistry especially at lower polymerization temperature; a lower [M]₀ led to a polymer with a higher isotacticity in DMAA polymerization, whereas it led to a polymer with a higher syndiotacticity in DPAA polymerization. While an isotactic and an atactic poly(MA)s only exhibited a glass transition, the syndiotactic poly(MA)s derived from poly(DPAA)s exhibited melting transitions in addition to a glass transition, suggesting that the morphology of the polymers is semi-crystalline.

**Figure 8.** DSC curves of poly(MA) derived from poly(DPAA) ($m$ = 7%, $M_n$ = 4.39 × 10³, $M_w/M_n$ = 2.08, A, 1st heating; B, 2nd heating; C, 3rd heating after the sample was allowed to stand for 24 h at r.t., heating rate: 10℃ min⁻¹, N₂ flow: 35 mL min⁻¹).

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