Stereospecific Radical Polymerization of *N*-Methyl Methacrylamide

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ABSTRACT : *N*-Methyl methacrylamide (*N*-MMAm) was polymerized using radical initiators under various conditions. The triad tacticity of the obtained polymers was determined by 100 MHz ^{13}C NMR. The polymers were rich in syndiotactic configuration. At a given temperature, the syndiotacticity increased with an increase in solvent polarity. This solvent effect may have connection with the hydrogen bonding interaction among solvent, monomer, and growing species. The fraction of *rr* triad increased with decreasing polymerization temperature in all solvents. Monomer concentration also affected the stereochemistry of the polymerization. By optimizing conditions, a high *rr* specificity (*rr* = 95%) was achieved. Thermal property of the poly(*N*-MMAm)s with different tacticities was studied by DSC.
KEY WORDS   Radical Polymerization / Tacticity / Stereochemistry / Solvent Effect / Syndiotacticity / Methacrylamides /

Synthesis of the polymers having desired tacticity is important because properties of polymeric materials are often significantly affected by the stereoregularity of a main chain. This is especially the case for radical polymerization since a wide variety of polymers are produced by a radical process in industry. In this context, stereoregulation methods have been devised for the radical polymerization of several types of monomers including methacrylates and vinyl esters,[1] and efficient stereoregulation has been attained for methacrylates[2] and vinyl esters[3] by utilizing solvent effects. Effect of monomer concentration was applied to alter the stereochemistry of methacrylate[4] and acrylate[5] polymerizations. In addition, adequate design of monomers led to effective stereoregulation.[4-8]

In this work, the stereochemistry of radical polymerization of *N*-methyl methacrylamide (*N*-MMAm) was studied. This type of monomer is often used to prepare water-soluble polymers for biomedical purposes; however, the examples of stereochemical study on the polymerization of methacrylamide and its derivatives are limited and only moderate tacticity (syndiotactic triad (*rr*) of 65—68%) has been achieved.[9,10] Here, we report the first example of highly stereospecific radical polymerization of *N*-MMAm where the highest *rr* value of 95% was realized.

EXPERIMENTAL

Materials

N-MMAm (TCI) was purified by distillation under reduced pressure. α,α-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization from methanol. Diisopropyl peroxydicarbonate ((*i*-PrOCOO)$_2$) was kindly provided by NOF Co. (Aichi, Japan). Tri-*n*-butylborane ((*n*-Bu)$_3$B) was obtained as a tetrahydrofuran (THF) solution (1.0 M) (Aldrich) and

used after removal of the solvent. *N*, *N*-Dimethylaniline (DMA) was purified by distillation. The other reagents were purified by the usual methods.

Polymerization

Polymerization was carried out under a nitrogen atmosphere in a glass ampoule. The reactions in organic solvents at 60℃ and 40℃ were performed using AIBN or BPO and (*i*-PrOCOO)$_2$, respectively, those at 0℃ and 20℃ using benzoin under UV light irradiation (400-W high-pressure mercury lamp) or using a BPO/DMA initiator system, and that at −78℃ using (*n*-Bu)$_3$B in the presence of a small amount of air. The detailed procedure of the polymerization is the same as that reported for vinyl esters.[3] A water-soluble initiator system (K$_2$S$_2$O$_8$/Na$_2$SO$_3$) was applied for the polymerization in water. The obtained polymer was precipitated into a large excess of acetone and collected with a centrifuge, was purified by reprecipitation from water to acetone twice to remove unreacted monomer, and was dried under vacuum at 60℃ for 12 h.

Measurements

^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Gemini 2000 spectrometer (400 and 100 MHz for ^{1}H and ^{13}C measurement, respectively) in deuterium oxide (D$_2$O) (Euriso-Top, 99.9 D%) at 60℃. Water and dioxane were used as an internal standard for the ^{1}H and ^{13}C measurements (4.79 ppm and 66.5 ppm with reference to TMS for ^{1}H and ^{13}C NMR, respectively). The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by size exclusion chromatography (SEC) with standard polystyrenes using a Shodex System-21 SEC system equipped with a Shodex RI-71 S detector and Shodex KF-803 and KF-806 F columns connected in series (eluent, *N*, *N*-dimethylformamide (DMF); flow rate, 1.0 mL min^{-1}; 40℃).

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The sample solution was made by dissolving polymers (5 mg) in 0.5 M aq. LiBr (0.05 mL) and then diluted with DMF (0.25 mL). Differential scanning calorimetry (DSC) measurement was performed on a Seiko SSC-5200 calorimeter at a heating rate of $10°C$ min^{-1} under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Triad Tacticity Determination

Tacticity of poly(N-MMAm) has not been reported so far though the main-chain stereochemistry of polymethacrylamide,[9] poly(2-hydroxy-4-N-methacrylamidobenzoic acid), poly(2-hydroxy-5-N-methacrylamidobenzoic acid), poly(N-(4-(4-methoxyphenylacetyloxy)phenyl)methacrylamide), poly(N-methacryloyl-(L)-leucine methyl ester), and poly(6-deoxy-6-methacryloylamido-D-glucopyranose)[10] has been analyzed by means of ^{1}H and ^{13}C NMR spectroscopies. The NMR peak assignments for the last three polymers are based on that for polymethacrylamide reported by Hatada et al.[9] Figures 1 and 2 depict the 400 MHz ^{1}H and 100 MHz ^{13}C spectra of the three selected polymers obtained in this work in D$_2$O solution, respectively. As shown in Figures 1 and 2, the peaks corresponding to the α-methyl proton, and α-methyl, and the quaternary carbons are sensitive to the triad configuration and the resolution was sufficient to allow the determination of triad tacticity. It should be noted that peak shape and peak position slightly varied depending on tacticity in the NMR spectra. This may be due to some difference in conformation or intra- and intermolecular hydrogen-bonding behaviors of the polymers induced by the configurational difference. In contrast to the α-methyl and the quaternary carbons, the methylene carbon showed insufficient information to determine diad tacticity. In the present work, the NMR peaks of the polymers were assigned as indicated in the figures based on those for polymethacrylamide,[9] since the peak splitting pattern of poly(N-MMAm) was very similar to that of polymethacrylamide. The triad tacticity obtained from the three spectra (α-methyl (^{1}H), α-methyl (^{13}C), and quaternary carbon (^{13}C)) well corresponded to each other. Since the α-methyl carbon spectrum gave a better resolution for the triad tacticity than the others, the triad tacticity shown in the tables was estimated using the methyl signals.

Solvent Effect on Stereochemistry

The polymerization of N-MMAm was carried out at 60 °C in various solvents (Table I). The polymerizations proceeded homogeneously except in THF and toluene to give products in relatively high yields. Although the obtained polymers were insoluble in less polar solvents such as CHCl$_3$, toluene, THF, and benzene, they were soluble in polar solvents such as water, methanol, and DMF, indicating that no crosslinking involving the NH hydrogen transfer took place. Such a reaction occurs in the anionic polymerization of N-MMAm.[11]

The stereochemistry of the polymerization was obviously dependent on the solvent. This is interesting because solvent effect in radical polymerization is considered to be generally small except in some polymerization systems. We have recently reported that hydrogen-
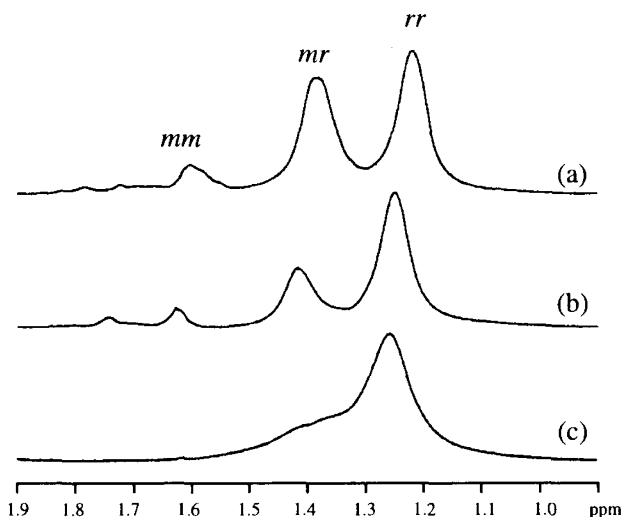
Figure 1. ^{1}H NMR spectra of poly(N-MMAm)s (α-CH$_3$ region): run 9 in Table I (a); run 2 in Table I (b); run 5 in Table II (c) [400 MHz, D$_2$O, 60°C].

bonding interaction of fluoroalcohol with a monomer and a growing polymer significantly affects the stereochemistry of methacrylate and vinyl ester polymerizations.[2,3] In the present systems, rr specificity of the polymerization appeared to increase with an increase in the solvent polarity. This may have a connection with the hydrogen-bonding interaction among solvent, monomer, and growing polymer. However, unlike in the polymerization of methacrylates and vinyl esters, in the present systems, the NH group of the side chain in addition to the carbonyl group may also contribute to hydrogen-bonding interaction. Although the solvent effect cannot be completely rationalized, it may be assumed that hydrogen-bonding interaction between the monomer and the growing chain decrease syndiotactic specificity.

Temperature Dependence of Stereochemistry

Temperature effect on the polymerization stereochemistry was investigated in several solvents (Table II). By lowering polymerization temperature, rr specificity increased in all the solvents tested here. However, polymer yield decreased with a decrease in temperature and at $-78°C$ the polymer was obtained only in (CH$_3$)$_2$CHOH. The polymer with a high rr triad content of 95% was obtained by the polymerization in (CH$_3$)$_2$CHOH at $-78°C$. This is the highest syndiotacticity for the radical polymerization of methacrylamides to the best of our knowledge. A high syndiotactic specificity (rr=95%) has been reported for the radical polymerization of methacrylic acid at low temperature.[12] The rr content observed here is comparable to this specificity. Using the tacticity data obtained at different temperatures shown in Table II, the thermodynamic parameters of the polymerization were calculated. The difference in activation parameters between isotactic-specific and syndiotactic-specific propagations was estimated by the plots according to the following equation:[13]

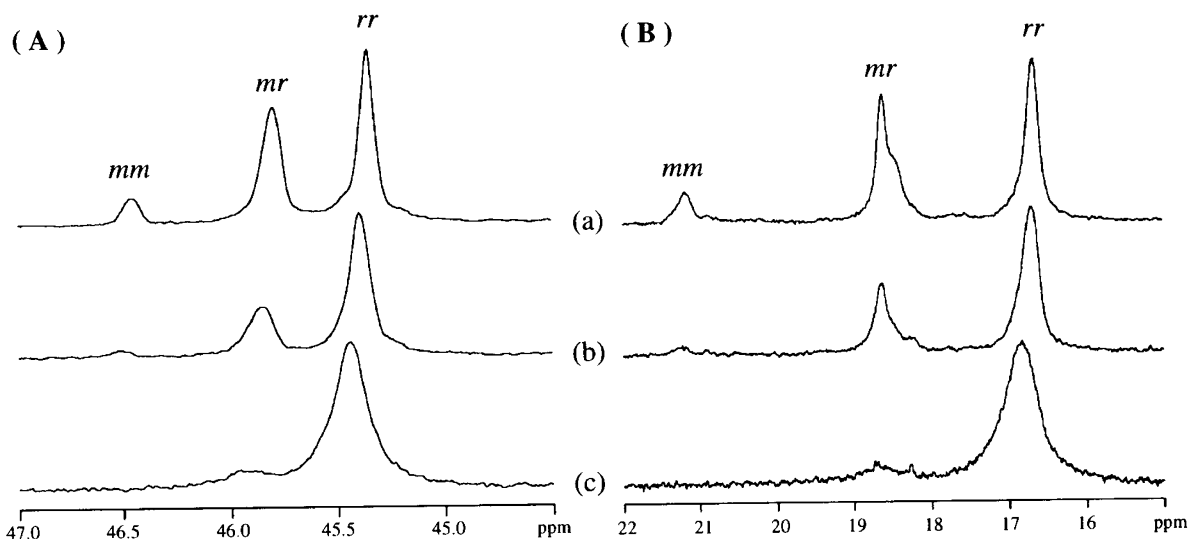$$\ln(P_i/P_s) = (\Delta S_i - \Delta S_s)/R - (\Delta H_i - \Delta H_s)/RT \qquad (1)$$

Figure 2. ^{13}C NMR spectra of poly(*N*-MMAm)s (quaternary carbon region (A) and α-CH$_3$ region (B)): run 9 in Table I (a); run 2 in Table I (b); run 5 in Table II (c) [100 MHz, D$_2$O, 60℃].

Table I. Solvent effect on radical polymerization of *N*-MMAm at 60℃ [a]

Run	Solvent	Initiator	Yield [b] %	M_n [c] ($\times 10^4$)	M_w/M_n [c]	Tacticity/% [d] mm/mr/rr
1	H$_2$O	K$_2$S$_2$O$_8$/Na$_2$SO$_3$	98	—	—	1/25/73
2	DMF	AIBN	82	0.6	2.6	3/28/69
3	CH$_3$OH	AIBN	>99	0.6	2.8	3/28/69
4	CH$_3$CH$_2$OH	AIBN	>99	0.9	2.3	3/29/68
5	(CH$_3$)$_2$CHOH	BPO	74	1.1	2.3	3/31/66
6	CF$_3$CH$_2$OH	AIBN	97	1.0	2.1	4/37/59
7	(CF$_3$)$_2$CHOH	AIBN	>99	1.0	2.2	5/38/57
8	THF [e]	BPO	86	0.6	2.6	6/34/60
9	Toluene [e]	AIBN	93	0.6	3.7	8/41/51

[a] [Monomer]$_0$=1 mol L^{-1}. [Initiator]$_0$=0.02 mol L^{-1}. Time=24 h. [b] Acetone-insoluble part. [c] Determined by SEC (polystyrene standard) in DMF at 40℃. [d] Determined by ^{13}C NMR (100 MHz) in D$_2$O at 60℃. [e] Polymer separated out from the medium during the polymerization.

Table II. Temperature effect on radical polymerization of *N*-MMAm [a]

Run	Solvent	Initiator	Temp ℃	Time h	Yield [b] %	M_n [c] ($\times 10^4$)	M_w/M_n [c]	Tacticity/% [d] mm/mr/rr
1	(CF$_3$)$_2$CHOH	BPO	60	24	74	1.1	2.3	3/31/66
2	(CF$_3$)$_2$CHOH	(*i*-PrOCO$_2$)$_2$	40	24	96	0.8	2.2	2/29/69
3	(CF$_3$)$_2$CHOH	Benzoin/UV	20	24	87	1.9	2.2	2/23/75
4	(CF$_3$)$_2$CHOH	Benzoin/UV	0	48	68	1.8	2.6	~0/19/81
5	(CF$_3$)$_2$CHOH	(*n*-Bu)$_3$B/Air	−78	24	7	0.8	2.4	~0/ 5 /95
6	H$_2$O	K$_2$S$_2$O$_8$/Na$_2$SO$_3$	90	12	100	—	—	3/29/68
7	H$_2$O	K$_2$S$_2$O$_8$/Na$_2$SO$_3$	60	24	98	—	—	~0/26/74
8	H$_2$O	K$_2$S$_2$O$_8$/Na$_2$SO$_3$	40	24	100	—	—	~0/24/76
9	H$_2$O	K$_2$S$_2$O$_8$/UV	20	24	86	—	—	~0/18/82
10	H$_2$O	K$_2$S$_2$O$_8$/Na$_2$SO$_3$/UV	0	48	73	—	—	~0/16/84
11	THF [e]	BPO	60	24	86	0.6	2.6	6/34/60
12	THF [e]	(*i*-PrOCO$_2$)$_2$	40	24	96	0.6	2.8	4/32/64
13	THF [e]	Benzoin/UV	20	24	40	0.4	3.1	3/26/68
14	THF [e]	Benzoin/UV	0	48	45	0.4	2.3	2/26/72
15	DMF	AIBN	60	24	82	0.6	2.6	3/28/69
16	DMF	AIBN	40	24	70	0.5	3.5	2/26/72
17	DMF	BPO/DMA	20	24	25	0.4	3.9	1/20/79
18	DMF	BPO/DMA	0	48	19	0.4	3.6	~0/19/81

[a] [Monomer]$_0$=1 mol L^{-1}. [Initiator]$_0$=0.02 mol L^{-1}. [b] Acetone-insoluble part. [c] Determined by SEC (polystyrene standard) in DMF at 40 ℃. [d] Determined by 100 MHz ^{13}C NMR in D$_2$O at 60℃. [e] Polymer separated out from the medium during the polymerization.

where P_i and P_s are mole fractions of the isotactic and syndiotactic diads, respectively, and were calculated based on the triad tacticity according to $P_i = mm + mr/2$ and $P_s = rr + mr/2$. R is the gas constant (1.987 cal mol K^{-1}) and T is absolute temperature in eq 1. The Fordham plots are shown in Figure 3. All the solvent systems gave good linear plots, ensuring the precision of the parameter determination. The values of $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ and $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ determined based on the plots are summarized in Table III. In all the solvents, both $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ and $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ were positive, indicating that the syndiotactic propagation was favored by enthalpy, while the isotactic propagation was preferred by entropy. The stereospecificity of the polymerization is mainly governed by the enthalpic factor.

Monomer Concentration Effect

Stereochemistry of radical reaction is generally not sensitive to the concentration of substrates. However, we recently found that stereochemistry of radical polymerizations of triphenylmethyl methacrylate and some fluoroalkyl acrylates is significantly altered depending on the monomer concentration.[4,5] Therefore, effect of monomer concentration was also investigated for the present polymerization systems in THF and in water at 0°C (Table IV). There was a clear concentration effect in THF while no clear effect was found in water. In THF, a lower monomer concentration resulted in a higher rr specificity. Though the concentration effect in the polymerization of triphenylmethyl methacrylate has been explained based on the existence of conformers of growing species,[4] this may not necessarily be the case in the present systems. A simpler explanation for the concentration effect in THF may be that the presence of a larger amount of solvent at a lower monomer concentration make hydrogen-bonding interaction between the monomer and the growing chain weaker. The rr specificity was enhanced by destroying the interaction with a solvent as mentioned above. In addition, water seems to be polar enough to completely suppress the interaction even at a relatively high monomer concentration (2.0 M) resulting in the unchanged tacticity of the polymers at all the monomer concentrations.

Configurational Statistics and Analysis of Pentad Sequences of the Obtained Polymers

^{13}C NMR spectrum of the carbonyl region of poly(N-MMAm) gave more detailed stereochemical information compared with that of the quaternary carbon and (α-methyl carbon regions. Figure 4 shows the carbonyl carbon spectra of the two samples (runs 2 and 9 in Table I). The rather complicated spectra were decomposed into the peaks with a Gaussian-curve shape by peak simulation using a VNMR version 5.3 software package. In order to assign the long range tacticity sequences, we first tested if the two samples obey Bernoullian statistics by using triad tacticity information. The conditional probability $P_{r/m}$ that a monomer adds to a growing end having a racemo configuration in meso fashion and the reverse probability, $P_{m/r}$, are given by the following relations:[14]

$$P_{r/m} = mr/(2rr + mr) \qquad (2)$$

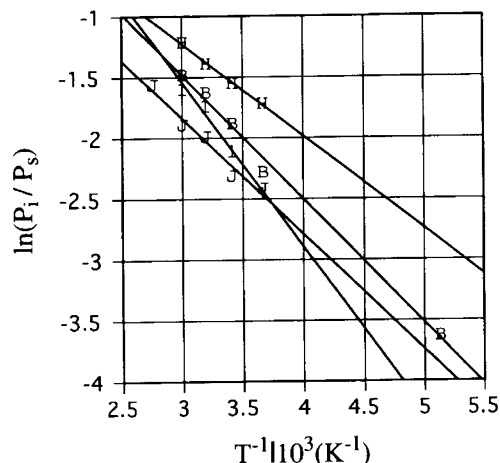$$P_{m/r} = mr/(2mm + mr) \qquad (3)$$

Figure 3. Temperature dependence of stereochemistry of N-MMAm polymerizations in H_2O (J), 2-propanol (B), DMF(1) and THF(H) ([M]$_o$ = 1.0 M).

Table III. Activation parameters for the radical polymerization of N-MMAm in various solvents [a]

Solvent	$\dfrac{\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}}{\text{cal deg}^{-1}}$	$\dfrac{\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}}{\text{cal deg}^{-1} \text{mol}^{-1}}$
2-PrOH	2021	3.11
H_2O	1889	2.01
THF	1504	2.08
DMF	2682	4.98

[a] [Monomer]$_o$ = 1 mol L^{-1}.

Table IV. Monomer concentration effect on radical polymerization of N-MMAm at 0°C [a]

Run	Solvent	[M]$_o$ mol L^{-1}	Time h	Yield [b] %	Tacticity/% [c] mm/mr/rr
1	H_2O	2.0	70	100	~0/17/83
2	H_2O	1.0	48	73	~0/16/84
3	H_2O	0.5	70	100	~0/16/84
4	H_2O	0.2	70	100	~0/15/85
5	THF	2.0	70	86	3/27/70
6	THF	1.0	48	45	2/26/72
7	THF	0.5	70	93	2/21/77

[a] run 1—4: initiator = $K_2S_2O_8$/Na$_2$SO$_3$/UV; run 5—7: initiator = benzoin/UV; [initiator]$_o$ = 0.02M. [b] Acetone-insoluble part. [c] Determined by 100 MHz ^{13}C NMR in D$_2$O at 60°C.

If $P_{r/m} + P_{m/r} = 1$, then chain propagation obeys Bernoullian statistics. The sums of the $P_{r/m}$ and $P_{m/r}$ for the two samples ($P_{r/m} = 0.17$, $P_{m/r} = 0.82$ for run 2 in Table I; $P_{r/m} = 0.29$, $P_{m/r} = 0.72$ for run 9 in Table I) are 0.99 and 1.01, respectively, indicating the polymerizations can be described by a Bernoullian model. Thus, the pentad tacticity can be calculated by using Bernoullian statistics. The assignment of pentad sequences was achieved as indicated in the figure by comparison of the experimental peak area and the calculated tacticity values as listed in Table V. This assignment is similar to those of polymethacrylamide[9] and poly(methyl methacrylate).[15]

Thermal Properties of the Polymers

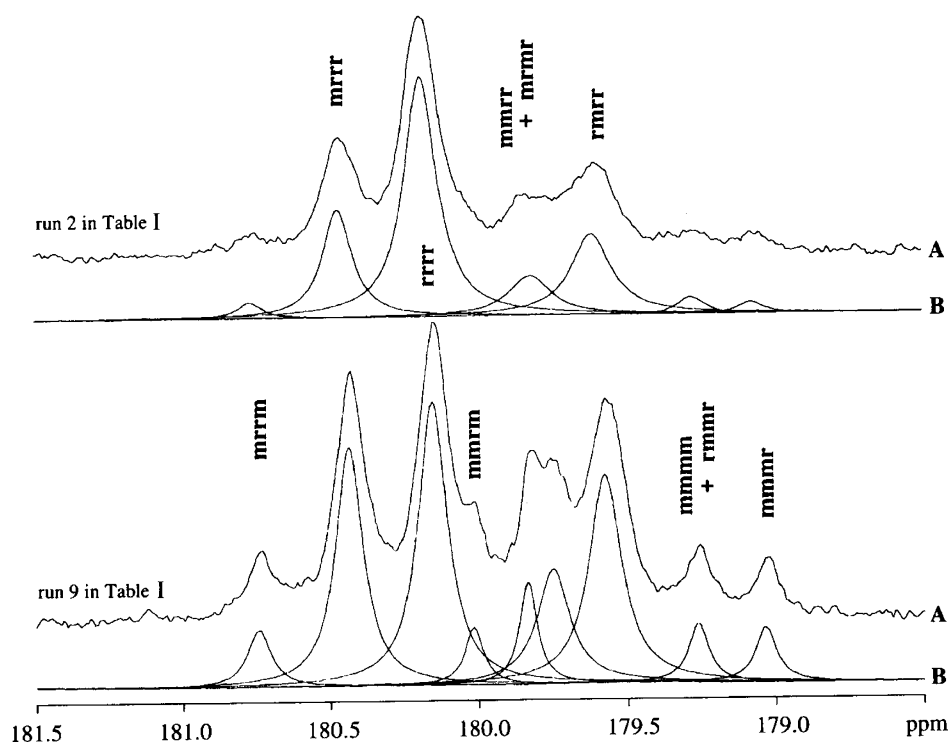Figure 5 shows the DSC curves of the two samples

Figure 4. Carbonyl carbon region of ^{13}C NMR spectra of poly(N-MMAm)s: original (A) and simulated (B) spectra [100 MHz, D_2O, 60℃].
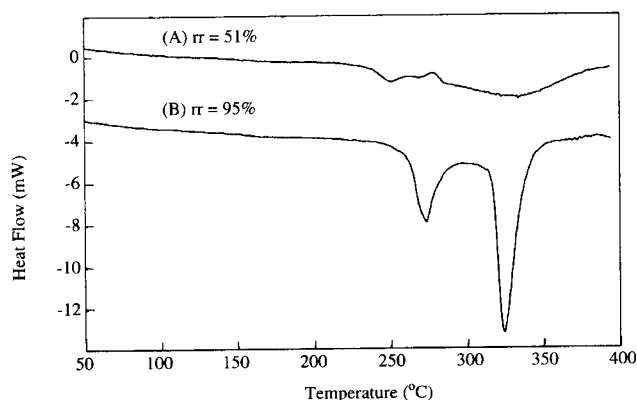

Figure 5. DSC curves of poly(N-MMAm)s: (A), run 9 in Table I; (B), run 5 in Table II [2nd heating run, heating rate: 10℃ min^{-1}, N_2 flow: 30 mL min^{-1}].

Table V. Statistical analysis of the carbonyl stereostructure of poly(N-MMAm)s

Conf.	run 2 in Table I		run 9 in Table I	
	Exp.[a]	Bernoullian[b] (P_m=0.17$_0$)	Exp.[a]	Bernoullian[b] (P_m=0.28$_7$)
mm	0.03$_0$	0.02$_9$	0.08$_0$	0.08$_2$
mr	0.28$_0$	0.28$_2$	0.41$_4$	0.41$_0$
rr	0.69$_0$	0.68$_9$	0.50$_6$	0.50$_8$
mrrm	0.02$_3$	0.02$_0$	0.04$_4$	0.04$_2$
mrrr	0.19$_0$	0.19$_4$	0.20$_6$	0.20$_8$
rrrr	}0.48$_0$	0.47$_5$ }0.48$_3$	0.25$_9$	0.25$_8$
mmrm		0.00$_8$	0.03$_3$	0.03$_4$
mmrr	}0.08$_5$	0.04$_0$ }0.08$_0$	}0.17$_1$	0.08$_4$ }0.16$_8$
mrmr		0.04$_0$		0.08$_4$
rmrr	0.19$_2$	0.19$_4$	0.21$_0$	0.20$_8$
mmmm	}0.02$_1$	0.00$_1$ }0.02$_1$	}0.04$_4$	0.00$_7$ }0.04$_9$
rmmr		0.02$_0$		0.04$_2$
mmmr	0.01$_2$	0.00$_8$	0.03$_3$	0.03$_4$

[a] Measured by 100 MHz ^{13}C NMR in D_2O at 60℃. [b] P_m=mm+ $mr/2$.

with different tacticities prepared in this study. Because the poly(N-MMAm) is hygroscopic, in the first heating run a broad endothermic peak was observed between 50 ℃ and 150℃ probably due to the evaporation of water. The hydrophilic poly(N-MMAm) samples seem to contain a significant amount of water even after drying under vacuum. The water in the samples was removed by heating the sample inside the instrument at 220℃ for 5 min before the second run. After this process, the sample was quickly quenched to 20℃, and the second heating run was performed. The thermal behavior of poly(N-MMAm) in the range of 20—400℃ was dependent on the tacticity of the sample. The poly(N-MMAm) with an *rr* content of 95% (run 5 in Table II) exhibited two sharp endothermic peaks at 275℃ and 325℃, which were as-

cribed to a melting transitions, whereas the poly(N-MMAm) with an *rr* content of 51% (run 9 in Table I) exhibited only broad, weak peaks around the corresponding temperatures. This implies that the morphology of the polymer changed from amorphous to a crystalline state due to the change in tacticity from *rr* = 51% to *rr* = 95%.

CONCLUSION

Radical polymerization of N-MMAm was carried out under various conditions. The stereochemistry of the polymerization was affected by solvent, temperature, and monomer concentration. By optimizing reaction condi-

tions, a polymer with *rr* triad content of 95% was obtained. The thermal properties of the polymers were found to be significantly influenced by the main-chain tacticity. The information obtained in this work would be useful in devising stereoregulation methods for radical polymerization of methacrylamide and other *N*-substituted methacrylamides. Some chiral poly(*N*-substituted methacrylamide)s obtained by radical polymerization have been used as chiral separation material which can resolve various types of pharmacologically important racemates including thalidomide.[16] Application of the stereoregulation methods that we developed here to this class of polymers could improve their resolution ability.

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