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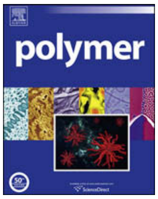

Metal-free isotactic-specific radical polymerization of *N*-alkylacrylamides with 3,5-dimethylpyridine *N*-oxide: The effect of the *N*-substituent and solvent on the isotactic specificity

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ABSTRACT

Radical polymerization of *N*-methylacrylamide (NMAAm), *N*-*n*-propylacrylamide, *N*-isopropylacrylamide (NIPAAm) and *N*-benzylacrylamide was investigated in $CHCl_3$, CH_2Cl_2 and CH_3CN, in the presence of 3,5-dimethylpyridine *N*-oxide (35DMPNO) to examine the effects of the *N*-substituent and the solvent on the isotactic specificity induced by 35DMPNO. With addition of 35DMPNO to radical polymerization of *N*-alkylacrylamides in $CHCl_3$, isotactic specificity was significantly induced in NIPAAm polymerization but only slightly induced in NMAAm polymerization. Furthermore, mixed solvents of CH_3CN and halomethanes such as $CHCl_3$ and CH_2Cl_2 enhanced the ability of 35DMPNO to induce isotactic specificity, and poly(NIPAAm) with 74% *meso* dyad was obtained.

1. Introduction

Development of stereospecific radical polymerization is a challenging topic in polymer synthesis and has attracted much attention. In the past decade particularly, stereocontrol of radical polymerization has been accomplished for a wide range of monomers such as methacrylates [1–5], vinyl esters [6,7], (meth)-acrylamides [8–23] and *N*-vinylamides [24–26]. Acrylamide derivatives have been extensively studied, and a wide range of stereospecific radical polymerizations of acrylamide derivatives have been achieved with stereo-controlling auxiliaries such as Lewis acids, Lewis bases and alcohols.

We have succeeded in synthesizing three types of stereoregular polymers by radical polymerization of acrylamide derivatives such as *N*-isopropylacrylamide (NIPAAm), utilizing only hydrogen bonding interaction without metal compounds, as follows. Addition of pyridine *N*-oxide (PNO) derivatives such as 3,5-dimethylpyridine *N*-oxide (35DMPNO) to NIPAAm polymerization in $CHCl_3$ at −60 °C gave poly(NIPAAm) with *meso* (*m*) dyad content 68% [16b]. Addition of hexamethylphosphoramide (HMPA) [14b] or 3-methyl-3-pentanol (3Me3PenOH) [17] to NIPAAm polymerization in toluene at −60 °C afforded poly(NIPAAm) with *racemo* (*r*) dyad content 70 or 71% [27]. Furthermore, addition of nonafluoro-*tert*-butanol instead of 3Me3PenOH varied the stereospecificity and formed heterotactic poly(NIPAAm) with 70% *mr* triad content [18b].

In previous papers [19,20] we reported significant effects of the *N*-substituent and the solvent on syndiotactic specificity, induced by HMPA or 3Me3PenOH, in radical polymerization of *N*-alkylacrylamides. In the present study we investigated radical polymerization of the *N*-alkylacrylamides, *N*-methylacrylamide (NMAAm), *N*-*n*-propylacrylamide (NNAAm), NIPAAm and *N*-benzylacrylamide (NBnAAm), in several solvents in the presence of 35DMPNO, to examine the effects of the *N*-substituent and the solvent on the isotactic specificity induced by 35DMPNO.

2. Experimental

2.1. Materials

NMAAm (supplied by Kohjin Co., Ltd) was fractionally distilled before use. NIPAAm (Tokyo Kasei Kogyo Co.) was recrystallized from hexane-toluene mixture. NNPAAm and NBnAAm were prepared according to a previous report [20]. Toluene was purified by washing with sulfuric acid, water and 5% aqueous NaOH, followed by fractional distillation. Chloroform, tetrahydrofuran (THF) and acetonitrile (Wako Co.) were fractionally distilled before use. Tri-*n*-butylborane (n-Bu_3B) as a THF solution ($1.0\ mol\,l^{-1}$), 35DMPNO (Aldrich Chemical Co.), dichloromethane and acetone (Wako Co.) were used without further purification.

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2.2. Polymerization

A typical polymerization procedure was as follows. NNPAAm (0.628 g, 5.5 mmol) and 35DMPNO (1.35 g, 11 mmol) were dissolved in $CHCl_3$ to prepare 5 ml of solution with $[\text{monomer}]_0 = 1.1\ \text{mol l}^{-1}$ and $[\text{35DMPNO}]_0 = 2.2\ \text{mol l}^{-1}$. 4 ml of the solution was transferred to a glass ampoule and cooled to −60 °C. Polymerization was initiated by adding *n*-Bu_3B solution (0.44 ml) to the monomer solution under air [28]. Reaction was terminated after 48 h by adding a small amount of a solution of 2,6-di-*t*-butyl-4-methylphenol in THF at the polymerization temperature. The reaction mixture was poured into a large volume of diethyl ether, and the precipitated polymer collected by filtration or centrifugation then dried *in vacuo*. The polymer yield was determined gravimetrically.

2.3. Measurements

^1H NMR spectra were obtained using an EX-400 spectrometer (JEOL Ltd.) operated at 400 MHz. The tacticity of poly(NMAAm), poly(NIPAAm) and poly(NBnAAm) was determined from the ^1H NMR signals due to the methylene groups in the main chain, in deuterated dimethyl sulfoxide (DMSO-d_6) at 150 °C (Fig. 1). The tacticity of poly(NNPAAm) was determined from the ^1H NMR signals due to the methine groups in the main chain and one of the signals due to the in-chain methylene groups with *m* configuration, observed at lower magnetic field, in DMSO-d_6 at 150 °C. The modified analysis was needed for poly(NNPAAm) because the signal from the methylene groups in the side chain overlapped with the signals due to the in-chain methylene groups with *r* configuration, and with one of the signals due to those with *m* configuration, observed at higher magnetic field (Fig. 1b). Molecular weights and molecular weight distributions of the polymers were determined using size exclusion chromatography (SEC). The chromatograph was calibrated with Pullulan® standards for poly(NMAAm) and polystyrene standards for poly(NNPAAm), poly(NIPAAm) and poly(NBnAAm). SEC was performed with an HLC 8220 chromatograph (Tosoh Co.) at 40 °C with flow rate $0.35\ \text{ml min}^{-1}$. The polymer concentration was $1.0\ \text{mg ml}^{-1}$. Eluent and columns were chosen depending upon the polymer structure, as follows. Poly(NMAAm): H_2O containing NaCl ($1.0 \times 10^{-1}\ \text{mol l}^{-1}$) with Shodex OHpak column (SB-806M HQ, 8.0 mm ID × 300 mm long; Showa Denko); poly(NNPAAm), poly(NIPAAm) and poly(NBnAAm): dimethylformamide containing LiBr ($10\ \text{mmol l}^{-1}$) with TSK gel columns (SuperHM-M and SuperHM-H, both 6.5 mm ID × 150 mm long; Tosoh Co.).

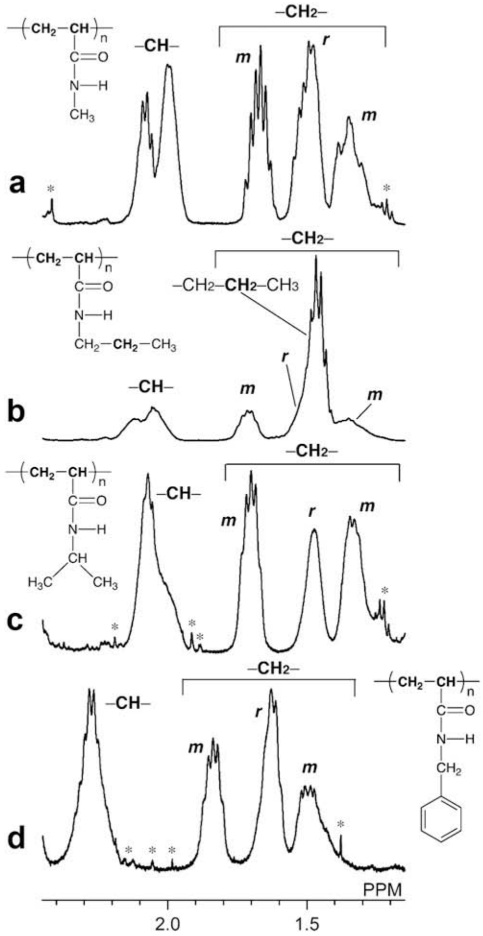

Fig. 1. Expanded scale ^1H NMR spectra of (a) poly(NMAAm) with $m = 58\%$ (Table 4, run 10), (b) poly(NNPAAm) with $m = 56\%$ (Table 1, run 16), (c) poly(NIPAAm) with $m = 74\%$ (Table 5, run 6), and (d) poly(NBnAAm) with $m = 58\%$ (Table 1, run 32), as measured in DMSO-d_6 at 150 °C.

3. Results and discussion

3.1. Radical polymerization of N-alkylacrylamides in $CHCl_3$ in the presence or absence of 35DMPNO

Radical polymerization of *N*-alkylacrylamides in $CHCl_3$ at low temperatures for 48 h was carried out in the presence or absence of 35DMPNO (Table 1). In the absence of 35DMPNO, polymer was obtained almost quantitatively at temperatures above −40 °C, regardless of the *N*-substituents of the monomers used (Table 1, runs 1–4, 9–12, 17–20, 25–28). Addition of 35DMPNO drastically reduced polymer yield, number average molecular weight and M_w/M_n of the polymers obtained (Table 1, runs 5–8, 13–16, 21–24, 29–32) [29,30]. This is probably because of the synergistic effect of initiator efficiency reduced by complex formation between *n*-Bu_3B and 35DMPNO, and monomer reactivity reduced by complex formation between monomers and 35DMPNO, as reported previously [16b].

In the absence of 35DMPNO, *r* dyad content increased slightly as the bulkiness of the *N*-substituent of the monomer increased, as observed for radical polymerization of *N*-alkylacrylamides in toluene at low temperatures [20]. Addition of 35DMPNO increased the *m* dyad content of the resultant polymers. Fig. 2 shows the increase in *m* dyad content with addition of 35DMPNO to the radical polymerization system at −60 or 0 °C. The isotactic specificity induced by 35DMPNO depended significantly on the bulkiness of the *N*-substituent of the monomer [31]. A similar tendency was observed in radical polymerization of *N*-alkylacrylamides in toluene in the presence of HMPA, although HMPA induced syndiotactic specificity to a greater extent in NNPAAm polymerization than in NIPAAm polymerization at −60 °C [20]. It should be noted that both 35DMPNO (Table 1, runs 5–8) and HMPA [20] hardly affected the stereospecificity of radical polymerization of NMAAm. NMAAm polymerization is discussed in more detail later.

3.2. Solvent effect on the isotactic specificity in radical polymerization of NIPAAm in the presence of 35DMPNO

In a previous paper [16], we proposed a mechanism for the isotactic specificity induced by PNO derivatives, in which formation of a hydrogen bonding-assisted complex plays a key role. Thus, radical polymerization of NIPAAm in the presence or absence of 35DMPNO was carried out in several solvents at −60 °C to examine the solvent effect on isotactic specificity (Table 2). Half the amount

Table 1
Radical polymerization of *N*-alkylacrylamides in $CHCl_3$ at low temperatures for 48 h in the presence or absence of 35DMPNO.

Run	Monomer	Temp. (°C)	$[35DMPNO]_0$ ($mol\,l^{-1}$)	Yield (%)	Dyad[a] (%)		$10^{-4}M_n$[b]	M_w/M_n[b]
					m	*r*		
1[c]	NMAAm	0	0.0	>99	48	52	0.89	5.1
2[c]	NMAAm	−20	0.0	>99	46	54	1.39	4.8
3[c]	NMAAm	−40	0.0	>99	47	53	1.31	4.5
4[c]	NMAAm	−60	0.0	84	48	52	1.93	3.9
5	NMAAm	0	2.0	11	50	50	0.10	2.6
6	NMAAm	−20	2.0	23	50	50	0.14	3.2
7	NMAAm	−40	2.0	25	50	50	0.27	3.4
8[c]	NMAAm	−60	2.0	14	51	49	0.54	4.6
9	NNPAAm	0	0.0	>99	46	54	1.51	1.9
10	NNPAAm	−20	0.0	99	45	55	1.78	1.7
11	NNPAAm	−40	0.0	>99	46	54	1.70	1.8
12	NNPAAm	−60	0.0	79	47	53	2.24	1.8
13	NNPAAm	0	2.0	15	50	50	0.54	1.2
14	NNPAAm	−20	2.0	13	52	48	0.68	1.3
15	NNPAAm	−40	2.0	20	54	46	0.91	1.4
16[c]	NNPAAm	−60	2.0	57	56	44	1.52	1.6
17[d]	NIPAAm	0	0.0	>99	45	55	0.98	1.4
18[d]	NIPAAm	−20	0.0	>99	46	54	1.33	1.5
19[c,d]	NIPAAm	−40	0.0	96	47	53	1.26	1.6
20[c,d]	NIPAAm	−60	0.0	26	46	54	1.69	1.6
21[d]	NIPAAm	0	2.0	5	54	46	0.72	1.3
22[d]	NIPAAm	−20	2.0	5	60	40	0.93	1.2
23[d]	NIPAAm	−40	2.0	20	65	35	0.99	1.2
24[c,d]	NIPAAm	−60	2.0	40	68	32	0.94	1.3
25	NBnAAm	0	0.0	98	43	57	1.38	1.9
26	NBnAAm	−20	0.0	96	44	56	1.64	2.0
27	NBnAAm	−40	0.0	93	43	57	1.78	2.0
28	NBnAAm	−60	0.0	89	42	58	2.40	1.8
29	NBnAAm	0	2.0	13	51	49	0.77	1.3
30	NBnAAm	−20	2.0	22	55	45	0.92	1.4
31	NBnAAm	−40	2.0	11	57	43	1.48	1.5
32[c]	NBnAAm	−60	2.0	2	58	42	nd[e]	nd[e]

$[M]_0 = 1.0\ mol\,l^{-1}$, $[n\text{-}Bu_3B]_0 = 1.0 \times 10^{-1}\ mol\,l^{-1}$.

[a] Determined by ^1H NMR.

[b] Determined by SEC (Pullulan® standards for poly(NMAAm), polystyrene standards for poly(NNPAAm), poly(NIPAAm) and poly(NBnAAm)).

[c] Monomer, polymer or both were precipitated during the polymerization reaction.

[d] Taken from Ref. [16b].

[e] Not determined.

of 35DMPNO relative to NIPAAm was added because of the poor solubility of 35DMPNO in less polar solvents, particularly toluene. The monomer, polymer or both precipitated during the polymerization reaction, regardless of the polarity of the solvent used.

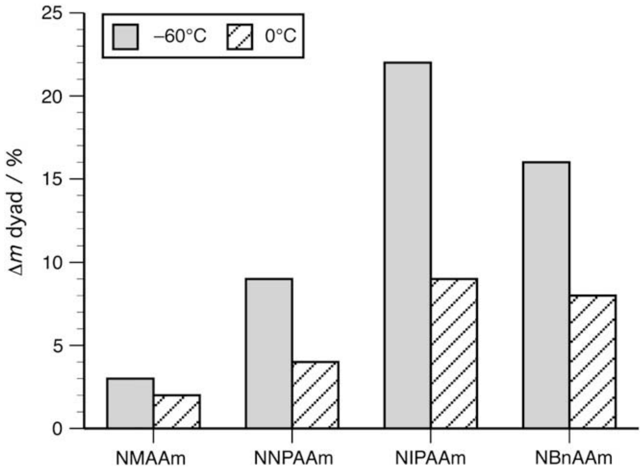

Fig. 2. Increased *m* dyad (Δ*m*) content in poly(*N*-alkylacrylamide)s by adding 35DMPNO to the polymerization in $CHCl_3$ at −60 or 0 °C.

Table 2
Radical polymerization of NIPAAm in various solvents at −60 °C for 48 h in the presence or absence of 35DMPNO.

Run	Solvent	$[35DMPNO]_0$ ($mol\,l^{-1}$)	Yield (%)	Dyad[a] (%)		$10^{-4}M_n$[b]	M_w/M_n[b]
				m	*r*		
1	Toluene	0.0	72	47	53	1.93	2.8
2	Toluene	0.5	68	52	48	0.96	1.2
3	$CHCl_3$	0.0	26	46	54	1.69	1.6
4	$CHCl_3$	0.5	84	55	45	1.86	1.4
5	THF	0.0	52	50	50	1.75	1.7
6	THF	0.5	8	50	50	nd[c]	nd[c]
7	CH_2Cl_2	0.0	39	49	51	3.64	1.8
8	CH_2Cl_2	0.5	4	63	37	nd[c]	nd[c]
9	Acetone	0.0	10	55	45	1.66	1.6
10	Acetone	0.5	2	59	41	nd[c]	nd[c]

$[M]_0 = 1.0\ mol\,l^{-1}$, $[n\text{-}Bu_3B]_0 = 1.0 \times 10^{-1}\ mol\,l^{-1}$.

[a] Determined by ^1H NMR signals due to methylene group.

[b] Determined by SEC (polystyrene standards).

[c] Not determined.

No clear dependence of the induced isotactic specificity on polarity of the solvents was observed. Of the solvents examined, halomethanes ($CHCl_3$ and CH_2Cl_2) allowed moderately significant induction of isotactic specificity. In particular, a greater increase was observed in CH_2Cl_2 (14%) than in $CHCl_3$ (9%), although CH_2Cl_2 is more polar than $CHCl_3$. Taking into account that halomethanes can form hydrogen bonds with Lewis bases [32,33], it is suggested that moderately polar and hydrogen bond donor solvents should be suitable for inducing significant isotactic specificity. This is probably because such solvents inhibit formation of self-associates of 35DMPNO [34], resulting in enhancement of the ability of 35DMPNO to induce isotactic specificity.

3.2.1. *Radical polymerization of NIPAAm in CH_2Cl_2 at low temperatures in the presence or absence of 35DMPNO*

NIPAAm polymerization in CH_2Cl_2 in the presence or absence of 35DMPNO was carried out in more detail (Table 3). In the absence of 35DMPNO polymer was obtained almost quantitatively, except at −60 °C (Table 3, runs 1–4). Addition of 35DMPNO drastically reduced the polymer yield at higher temperatures (Table 3, runs 5–6). However, polymer was obtained at moderate yield at lower temperatures even in the presence of 35DMPNO (Table 3, runs 7–8). These results correspond with those for NIPAAm polymerization in $CHCl_3$ in the presence of 35DMPNO [16]. The *m* dyad content of the polymers was comparable with that obtained in $CHCl_3$ (cf. Table 1).

Table 3
Radical polymerization of NIPAAm in CH_2Cl_2 at low temperatures for 48 h in the presence or absence of 35DMPNO.

Run	Temp. (°C)	$[35DMPNO]_0$ ($mol\,l^{-1}$)	Yield (%)	Dyad[a] (%)		$10^{-4}M_n$[b]	M_w/M_n[b]
				m	*r*		
1	0	0.0	96	44	56	2.16	1.5
2	−20	0.0	99	44	56	2.94	1.5
3	−40	0.0	92	47	53	4.07	1.5
4[c]	−60	0.0	39	49	51	3.64	1.6
5	0	2.0	2	56	44	nd[d]	nd[d]
6	−20	2.0	3	62	38	nd[d]	nd[d]
7[c]	−40	2.0	29	66	34	0.96	1.3
8[c]	−60	2.0	32	68	32	1.07	1.4
9	−60	0.25	90	58	42	3.95	1.8
10[c]	−60	0.50	4	63	37	nd[d]	nd[d]
11[c]	−60	1.0	7	66	34	nd[d]	nd[d]
12[c]	−60	1.5	14	67	33	nd[d]	nd[d]

$[M]_0 = 1.0\ mol\,l^{-1}$, $[n\text{-}Bu_3B]_0 = 1.0 \times 10^{-1}\ mol\,l^{-1}$.

[a] Determined by ^1H NMR signals due to methylene group.

[b] Determined by SEC (polystyrene standards).

[c] Monomer, polymer or both were precipitated during the polymerization reaction.

[d] Not determined.

NIPAAm polymerization in CH_2Cl_2 was carried out at −60 °C in the presence of various amounts of 35DMPNO (Table 3, runs 4, 8–12). The polymer yield drastically decreased when half or an equimolar amount of 35DMPNO was added. A similar tendency was observed in NIPAAm polymerization in $CHCl_3$ [16], but was enhanced in CH_2Cl_2. Fig. 3 shows the relationship between the $[35DMPNO]_0/[NIPAAm]_0$ ratio and the *m* dyad content of the polymers obtained. The relationship observed in $CHCl_3$ is also plotted. Significant increase in *m* dyad content of the polymers obtained in CH_2Cl_2 was found at lower $[35DMPNO]_0/[NIPAAm]_0$ ratios, although no difference was found at higher $[35DMPNO]_0/[NIPAAm]_0$ ratios between CH_2Cl_2 and $CHCl_3$ solvents. This result reconfirms that CH_2Cl_2 is a better solvent than $CHCl_3$ for inducing isotactic specificity with a smaller amount of 35DMPNO.

3.2.2. Radical polymerization of NIPAAm in CH_3CN at low temperatures in the presence or absence of 35DMPNO

In a previous paper [19] we reported that the *m* dyad content of poly(NIPAAm) increased with increase in polarity of the solvent used, even in the absence of stereo-controlling auxiliaries. For instance, poly(NIPAAm) with $m = 57\%$ was obtained by polymerization in CH_3CN at −40 °C. Furthermore, CH_3CN can form hydrogen bonds to Lewis bases [35] as well as $CHCl_3$ and CH_2Cl_2. Thus we conducted NIPAAm polymerization in CH_3CN in the presence of 35DMPNO (Table 4, runs 1–8), expecting further improvement of the induced isotactic specificity.

Polymer was obtained almost quantitatively in the absence of 35DMPNO (Table 4, runs 1–4), although polymerization at −60 °C proceeded heterogeneously from the beginning of polymerization. The *m* dyad content gradually increased with decreasing polymerization temperature, as reported previously [19]. Addition of 35DMPNO decreased polymer yield, particularly at higher temperatures (Table 4, runs 5–6). The polymer yield decreased again at −60 °C even in the presence of 35DMPNO (Table 4, run 8), because of the heterogeneous nature of the polymerization system. The *m* dyad content of the polymer obtained at 0 °C was higher than was obtained in $CHCl_3$ or CH_2Cl_2, and reached 68% at −40 °C. Taking into account that the temperature must be lowered to −60 °C to obtain poly(NIPAAm) with $m = 68\%$ by polymerization in $CHCl_3$ or CH_2Cl_2, it is suggested that CH_3CN is a much better solvent than $CHCl_3$ and CH_2Cl_2 for the present system.

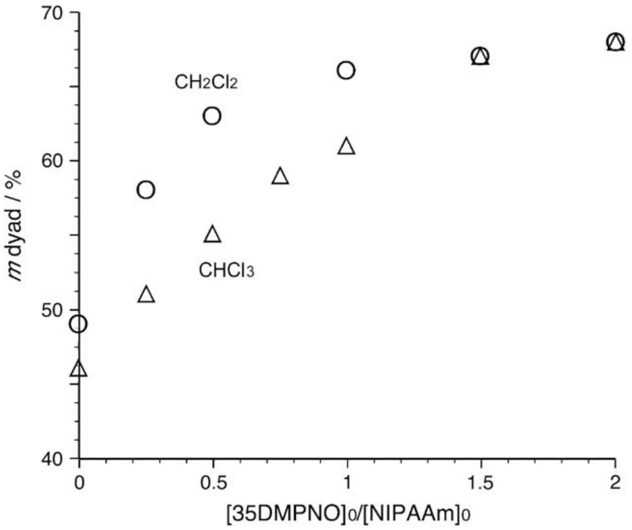

Fig. 3. Relationship between the $[35DMPNO]_0/[NIPAAm]_0$ ratio and *m* dyad content of poly(NIPAAm) prepared in $CHCl_3$ or CH_2Cl_2 at −60 °C.

Table 4
Radical polymerization of *N*-alkylacrylamides in CH_3CN at low temperatures for 48 h in the presence or absence of 35DMPNO.

Run	Monomer	Temp. (°C)	$[35DMPNO]_0$ (mol l^{-1})	Yield (%)	Dyad[a] (%)		$10^{-4}M_n$[b]	M_w/M_n[b]
					m	*r*		
1	NIPAAm	0	0.0	96	49	51	1.90	1.5
2	NIPAAm	−20	0.0	98	53	47	2.04	1.6
3	NIPAAm	−40	0.0	>99	57	43	2.09	1.6
4[c]	NIPAAm	−60	0.0	82	59	41	1.22	1.8
5[c]	NIPAAm	0	2.0	1	60	40	nd[d]	nd[d]
6[c]	NIPAAm	−20	2.0	4	63	37	nd[d]	nd[d]
7[c]	NIPAAm	−40	2.0	26	68	32	0.88	1.3
8[c]	NIPAAm	−60	2.0	5	68	32	nd[d]	nd[d]
9[c]	NMAAm	−60	2.0	87	53	47	4.75	8.2
10[c]	NMAAm	−60	2.0	31	58	42	1.40	5.2

$[M]_0 = 1.0$ mol l^{-1}, $[n\text{-}Bu_3B]_0 = 1.0 \times 10^{-1}$ mol l^{-1}.

[a] Determined by ^1H NMR signals due to methylene group.

[b] Determined by SEC (Pullulan® standards for poly(NMAAm), polystyrene standards for poly(NIPAAm)).

[c] Monomer, polymer or both were precipitated during the polymerization reaction.

[d] Not determined.

3.2.3. Radical polymerization of NIPAAm in mixed solvent at low temperatures in the presence or absence of 35DMPNO

If polymerization in CH_3CN at −60 °C could proceed homogeneously, further improvement in the isotactic-specificity induced by 35DMPNO would be expected. Thus we conducted NIPAAm polymerization in mixed solvents ($CH_3CN + CHCl_3$ or $CH_3CN + CH_2Cl_2$) at −60 °C in the presence or absence of a twofold amount of 35DMPNO (Table 5).

Despite the expectation to the contrary, radical polymerization in the mixed solvent proceeded heterogeneously, regardless of the presence of 35DMPNO. In the absence of 35DMPNO, however, the *m* dyad content of the polymers obtained in mixed solvents containing 50–67 vol% of CH_3CN (Table 5, runs 2–3, 10–11) was higher than that in either CH_3CN or halomethane alone. The implication is that a mixed solvent significantly affects the stereospecificity even

Table 5
Radical polymerization of NIPAAm in mixed solvent (CH_3CN+halomethane) at −60 °C for 48 h in the presence or absence of 35DMPNO.

Run	Solvent	$[35DMPNO]_0$ (mol l^{-1})	Yield (%)	Dyad[a] (%)		$10^{-4}M_n$[b]	M_w/M_n[b]
				m	*r*		
	<CH_3CN–$CHCl_3$> CH_3CN (vol%)						
1	33	0.0	98	58	42	3.11	1.7
2[c]	50	0.0	96	61	39	2.38	1.9
3	67	0.0	>99	62	38	1.49	1.9
4	100	0.0	82	59	41	1.98	1.8
5	33	2.0	2	72	28	nd[d]	nd[d]
6	50	2.0	3	74	26	nd[d]	nd[d]
7	67	2.0	8	74	26	nd[d]	nd[d]
8	100	2.0	4	68	32	nd[d]	nd[d]
	<CH_3CN–CH_2Cl_2> CH_3CN (vol%)						
9	33	0.0	49	57	43	2.90	2.4
10	50	0.0	87	60	40	2.57	2.0
11	67	0.0	32	60	40	2.22	1.8
12	100	0.0	82	59	41	1.98	1.8
13	33	2.0	13	72	28	0.71	1.4
14	50	2.0	5	74	26	nd[d]	nd[d]
15	67	2.0	4	73	27	nd[d]	nd[d]
16	100	2.0	4	68	32	nd[d]	nd[d]

$[M]_0 = 1.0$ mol l^{-1}, $[n\text{-}Bu_3B]_0 = 1.0 \times 10^{-1}$ mol l^{-1}.

[a] Determined by ^1H NMR signals due to methylene group.

[b] Determined by SEC (polystyrene standards).

[c] Polymerization proceeded homogeneously.

[d] Not determined.

in a heterogeneous system. A similar tendency was observed in the presence of 35DMPNO. The *m* dyad content of the polymers reached 74%, although the polymer yield was drastically reduced (Table 5, runs 6–7, 14). To the best of our knowledge, the *m* dyad content (74%) is the highest that has been found for poly(NIPAAm) prepared radically under metal-free conditions.

3.3. Radical polymerization of NMAAm in CH_3CN at −60 °C in the presence or absence of 35DMPNO

As noted above, stereospecificity in the radical polymerization of NMAAm is hardly affected by the addition of Lewis base stereocontrolling auxiliaries such as 35DMPNO and HMPA. It is known that the stereospecificity of radical polymerization of less bulky acrylates, such as methyl and ethyl acrylates, is scarcely affected by polymerization temperature [36]. However, for more bulky acrylates such as isopropyl, *tert*-butyl and trimethylsilyl acrylates, the stereospecificity varied slightly with polymerization temperature. In addition, syndiotactic specificity gradually increased with decrease in the polymerization temperature [37]. These results suggest that it should be difficult to control the stereospecificity of radical polymerization of NMAAm with methyl group as an *N*-substituent as well as methyl acrylate. In fact, there have been no reports of stereospecific polymerization of NMAAm, except for syndiotactic-specific radical polymerization of NMAAm in the presence of alkyl alcohol [20].

Thus, we attempted to induce isotactic specificity in radical polymerization of NMAAm by employing 35DMPNO as an additive and CH_3CN as solvent (Table 4, runs 9–10). Only the use of CH_3CN as a solvent slightly increased the *m* dyad content of the polymer obtained, even in the absence of 35DMPNO (53%). Addition of 35DMPNO further increased the *m* dyad content up to 58%, although the value is much lower than that for poly(NIPAAm) prepared under corresponding conditions. However, to the best of our knowledge, the *m* dyad content is the highest so far reported for poly(NMAAm).

4. Conclusions

The effects of the *N*-substituent and solvent on the isotactic specificity induced by 35DMPNO, in the radical polymerization of *N*-alkylacrylamides, were investigated. The isotactic specificity was significantly induced in NIPAAm polymerization, whereas only slight induction was observed for NMAAm, suggesting that the bulkiness of the *N*-substituent influenced the induced isotactic specificity. Furthermore, use of $CHCl_3$, CH_2Cl_2, or CH_3CN as solvent gave more efficient induction of isotactic specificity in NIPAAm polymerization than in the less polar toluene, suggesting that moderately polar and hydrogen donor solvents should be suitable for the present polymerization system. By mixing CH_3CN with halomethanes such as $CHCl_3$ and CH_2Cl_2, the isotactic specificity was further improved, and as a result poly(NIPAAm) with $m = 74\%$ was obtained. To the best of our knowledge, that *m* dyad content is the highest that has been observed for poly(NIPAAm) prepared radically under metal-free conditions.

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