Hydrogen-Bond-Assisted Syndiotactic-Specific Radical Polymerization of *N,N*-Dimethylacrylamide in the Presence of Tartrates

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INTRODUCTION

The development of stereospecific radical polymerization is one of the most important topics in the field of polymer synthesis and has attracted much attention. Stereocontrol of radical polymerization has been enabled for a wide range of monomers, such as methacrylates,[1-3] vinyl esters,[4] (meth)acrylamides,[5-15] and *N*-vinylamides.[16,17] Among them, radical polymerization of *N,N*-disubstituted acrylamides exhibited unique dependences of stereospecificity on the polymerization conditions such as the

1

N-substituents, temperature, and solvents.[6]

N,N-Dimethylacrylamide (DMAAm) tended to afford isotactic polymers, in particular in non-polar solvents such as toluene at low temperatures, whereas *N,N*-diphenylacrylamide provided syndiotactic polymers regardless of the solvents and temperature. Furthermore, the stereospecificity of DMAAm polymerization strongly depended on the solvents and temperature; syndiotactic-rich polymer with *racemo* (*r*) dyad = 58% was obtained in H_2O at 60°C, whereas isotactic polymer with *meso* (*m*) dyad = 72% was obtained in toluene at –78°C. The syndiotacticity of the former is the highest value among the radically prepared poly(DMAAm)s so far reported, although the syndiotacticity was much lower than those of poly(DMAAm)s prepared via anionic polymerizations.[18]
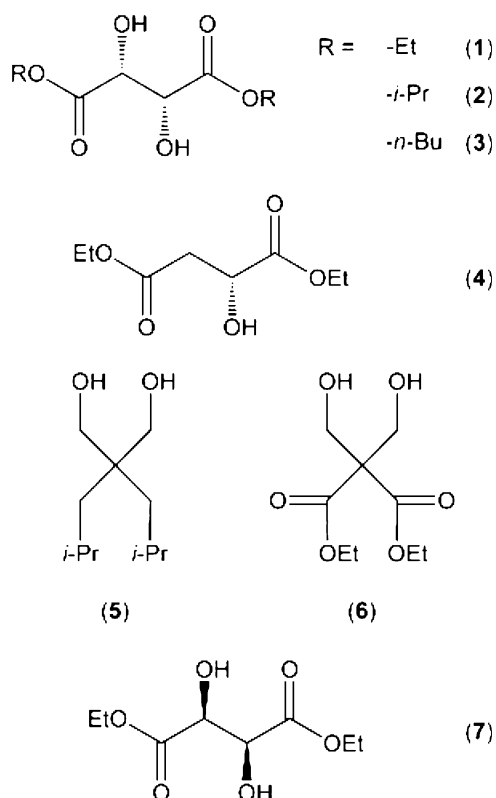
Recently, we found that a hydrogen-bonding interaction is available for controlling stereospecificity of radical polymerization of vinyl monomers, which have a mono-substituted amide group. For example, syndiotactic polymers were obtained by the radical polymerization of *N*-isopropylacrylamide (NIPAAm) in the presence of alkyl alcohols.[14(a)] NMR analysis revealed that the hydrogen-bonding interaction between the amide group of NIPAAm and alkyl alcohols played an important role for the induction of the syndiotactic-specificity. Furthermore, isotactic polymers were obtained by the radical polymerization of *N*-vinylacetamide (NVA) in the presence of tartrates, in which NVA and tartrates formed double hydrogen bonds between the carbonyl group of NVA and two hydroxyl groups of tartrates.[17]

Because DMAAm also has amide carbonyl group, it is expected that hydrogen-bond-assisted complex formation affects the stereospecificity of DMAAm polymerization. Thus, we started investigating the effect of hydrogen-bonding interaction on the stereospecificity of DMAAm polymerization and found that the addition of tartrates resulted in the significant induction of syndiotactic-specificity. Here, we report the preliminary results on the syndiotactic-specific radical polymerization of DMAAm in the presence of tartrates.

EXPERIMENTAL

Materials

DMAAm (Tokyo Kasei Kogyo Co.) was fractionally distilled. Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH; this was followed by fractional distillation. Methanol (MeOH) was distilled before use. Dehydrated tetrahydrofuran (THF), dehydrated chloroform (Kanto Chemical Co.), tri-*n*-butylborane (*n*-Bu$_3$B) as a THF solution (1.0M) (Aldrich Chemical Co.), *t*-butyl alcohol (*t*-BuOH), 3-methyl-3-pentanol (3Me3PenOH), diethyl L-tartrate (L-EtTar) (**1**), diisopropyl L-tartrate (L-iPrTar) (**2**), di-*n*-butyl L-tartrate (L-BuTar) (**3**), diethyl D-tartrate (D-EtTar) (**7**), diethyl D-malate (D-EtMal) (**4**), 2,2-diisobutyl-1,3-propanediol (**5**) (Tokyo Kasei Kogyo Co.), and diethyl bis(hydroxymethyl)malonate (**6**) (Wako Co.) were commercially obtained and used without further purification for polymerization reactions.

OH O
RO—...—OR R = -Et (1)
O OH   -i-Pr (2)
            -n-Bu (3)

O
EtO—...—OEt (4)
O OH

OH OH   OH OH
                O=   =O
i-Pr i-Pr   OEt OEt
  (5)   (6)

OH O
EtO—...—OEt (7)
O OH

Polymerization

Typical polymerization procedure is as follows; DMAAm (0.261 g, 2.64 mmol) was dissolved in toluene to prepare a 5 mL solution (0.528 mol/L). Four milliliter of the solution was transferred to the glass ampoule and cooled at –60°C. The polymerization was initiated by adding n-Bu$_3$B solution (0.21 mL) into the monomer solution.[19] After 24h, the reaction was terminated with a small amount of THF solution of 2,6-di-t-butyl-4-methylphenol at –60°C. The polymerization mixture was poured into a large amount of diethyl ether, and the precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

The ^{1}H NMR spectra were measured on an EX-400 spectrometer (JEOL Ltd.) operated at 400MHz. The tacticities of the poly(DMAAm)s were determined from ^{1}H NMR signals due to methylene group in chain, measured in deuterated dimethyl sulfoxide (DMSO-d_6) at 150°C (Figure 1). The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) (HLC 8220 instrument (Tosoh Co.)) equipped with TSK gels (SuperHM-M and SuperHM-H (Tosoh Co.)) using dimethylformamide (LiBr 10 mmol/L) as an eluent at 40°C ([polymer] = 1.0 mg/mL, flow rate = 0.35 mL/min). The SEC chromatogram was calibrated with standard polystyrene samples.

<Figure 1>

RESULTS AND DISCUSSION

First, we carried out radical polymerization of DMAAm in toluene at –60°C in the absence or presence of fourfold amounts of alcohol compounds, such as MeOH, *tert*-BuOH, and 3Me3PenOH, which significantly induced syndiotactic-specificity in the radical polymerization of NIPAAm, (Table 1, Runs 1-4).[14(a)] Slight increases in syndiotacticity were observed by the addition of alcohol compounds, whereas isotactic poly(DMAAm) (*m* = 70%) was obtained in the absence of alcohols (Figure 1(a)), as reported in the literature.[6] However, the syndiotacticities of the poly(DMAAm)s prepared in the presence of alcohols were comparable to that of poly(DMAAm) (*r* = 43%)

5

prepared in 2-propanol at –78°C,[6] suggesting that the added alcohols worked as just one

component of mixed solvents.

<Table 1>

Then, we examined the effect of tartrates (**1**-**3**), which significantly induced

isotactic-specificity in the radical polymerization of NVA,[17] on the stereospecificity of

DMAAm polymerization (Table 1, Runs 5-7). Significant increases (up to 36%) in

syndiotacticity were observed by the addition of twofold amounts of tartrates, regardless

of ester groups. Further, the syndiotacticities were higher than that of poly(DMAAm) (*r*

= 58%) prepared in H_2O at 60°C (Figure 1(b)). Thus, it appeared that the added tartrates

worked as the stereocontrolling auxiliaries also in the DMAAm polymerizations. It

should be noted that the induced stereospecificity was not isotactic but syndiotactic,

although the reason is not clear at this time. Monool compound D-EtMal (**4**), of which

the structure is similar to L-EtTar, afforded poly(DMAAm) having almost the same

syndiotacticity as those prepared in the presence of alkyl alcohols (Table 1, Run 8). Thus,

it is assumed that diol structure is essential to induce the syndiotactic-specificity in

DMAAm polymerization.

DMAAm polymerizations were carried out in the presence of twofold amounts

of 1,3-diols, such as **5** and **6**, to examine the effect of relative positions of two hydroxyl

groups (Table 1, Runs 9 and 10). The syndiotacticities of the obtained poly(DMAAm)s

were slightly higher than those in the presence of alkyl alcohols, but much lower than

those in the presence of tartrates. Thus, it is important that two hydroxyl groups are adjacent.

D-EtTar (**7**) exhibited the syndiotactic-specificity comparable with the enantiomer **1** (Table 1, Runs 5 and 11). Unexpectedly, the induced syndiotactic-specificity decreased by mixing equimolar amounts of **1** and **7** (Table 1, Run 12). These results indicate that the induced syndiotactic-specificity also depends on the enantiomeric excess of the added tartrates, although the reason is not clear at this time.[20]

The solvent effect was also investigated in the presence of **3**. An opposite effect on syndiotacticity of the obtained poly(DMAAm)s was observed in the absence and presence of **3**; the syndiotacticity tended to decrease (increase) in the absence (presence) of **3**, as the polarity of the solvent used decreased. This result strongly suggests that hydrogen-bonding interaction played an important role to induce the syndiotactic-specificity also in the present polymerization systems.

All the alcohol compounds examined in this paper increased the polymer yields. Interestingly, significant increases in molecular weight were observed, only when tartrates, except for *rac*-EtTar, were added. This tendency suggests that chiral tartrates not only induced the syndiotactic-specificity but also accelerated the polymerization reaction, probably through the hydrogen-bonding interactions with the DMAAm monomer and/or the propagating chain-end.

CONCLUSIONS

We succeeded in inducing syndiotactic-specificity and accelerating reaction by adding

chiral tartrates into radical polymerization of DMAAm. To the best of our knowledge, this is the first example of syndiotactic-specific radical polymerization of DMAAm. Further work is now under way to examine the effect of tartrates in more details and to reveal the structure of the hydrogen-bond-assisted complex. The mechanism of the present polymerization system will be reported in the near future.

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20. The ^{13}C NMR signal due to carbonyl carbon of DMAAm monomer (0.25 mol/L), measured in toluene-d_8 at –60°C, exhibited almost the same downfield shift with the addition of equimolar amounts of L-EtTar (0.25 mol/L) and *rac*-EtTar (0.25 mol/L). This result indicates that there are no predominant interactions between the added tartrates.

Table 1. Radical polymerization of DMAAm for 24h at –60°C in the absence or presence of alcohol compounds[a]

Run	Added alcohol	Solvent	Yield %	Tacticity / %[b] m	r	M_n[c] x 10^4	M_w[c] / M_n
1	None	Toluene	56	70	30	2.21	1.6
2	MeOH	Toluene	88	61	39	2.36	1.6
3[d]	t-BuOH	Toluene	>99	62	38	2.21	1.9
4	3Me3PenOH	Toluene	>99	58	42	2.28	2.1
5[d]	L-EtTar (**1**)	Toluene	>99	37	63	7.70	3.0
6[d]	L-iPrTar (**2**)	Toluene	>99	35	65	7.38	2.7
7[d]	L-BuTar (**3**)	Toluene	>99	34	66	6.73	3.2
8	D-EtMal (**4**)	Toluene	>99	59	41	1.88	1.9
9[d]	**5**	Toluene	85	55	45	2.60	2.0
10[d]	**6**	Toluene	>99	54	46	2.40	3.2
11	D-EtTar (**7**)	Toluene	>99	36	64	7.44	2.6
12[e]	rac-EtTar	Toluene	>99	44	56	2.52	2.2
13	None	THF	33	60	40	1.48	1.5
14[d]	L-BuTar (**3**)	THF	>99	49	51	1.90	2.0
15[d]	None	CHCl$_3$	25	70	30	1.75	1.5
16	L-BuTar (**3**)	CHCl$_3$	92	59	41	3.18	1.7

a. [DMAAm]$_0$ = 0.5 mol/L, [R-OH]$_0$ = 2.0 mol/L (Runs 2-4 and 8), [HO-R-OH]$_0$ = 1.0 mol/L (Runs 5-7, 9-13, 15, and 17), [n-Bu$_3$B]$_0$ = 0.05 mol/L.

b. Determined by ^{1}H NMR signals due to methylene group.

c. Determined by SEC (polystyrene standards).

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. [L-EtTar]$_0$ = 0.5 mol/L, [D-EtTar]$_0$ = 0.5 mol/L.

Figure 1. ^{1}H NMR spectra of the main-chain methylene groups of the poly(DMAAm)s prepared in toluene at –60 °C in the (a) absence or (b) presence of L-BuTar (3) (Table 1, Runs 1 and 7), as measured in DMSO-d_6 at 150 °C.

13