Triple Hydrogen Bonding for Stereospecific Radical Polymerization of a DAD Monomer and Simultaneous Control of Tacticity and Molecular Weight

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ABSTRACT: A triple hydrogen bonding interaction effectively controlled the stereochemistry during radical polymerization of acylamide derivatives. An acrylamide monomer, in which amide (proton donor site, D) and pyridine (proton acceptor site, A) moieties were arrayed in the DAD sequence, was polymerized in the presence of a cyclic imide as the ADA-type receptor in $CHCl_3$ to give syndiotactic polymers ($r = 72\%$) even at 60 °C while atactic polymers ($r = 43\%$) were obtained without the mediator. Furthermore, the simultaneous control of the tacticity and the molecular weights of the polymers were attained by RAFT polymerization in the presence of the mediator.

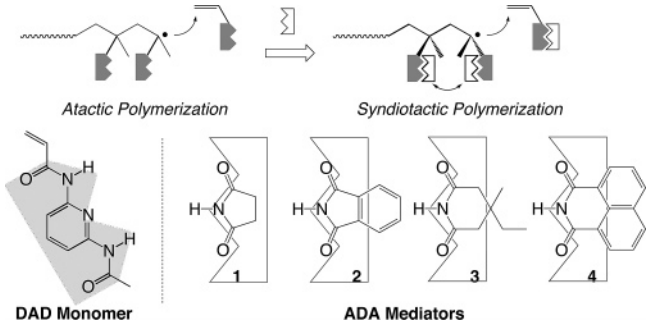
Introduction

Hydrogen bonding plays a crucial role in stabilizing the secondary and tertiary structures of natural macromolecules and even in the formation of well-designed natural small molecules. It is now exploited in bioinspired molecular recognition, self-assembly, host−guest chemistry, and supramolecular chemistry due to its moderate strength, reversibility, specificity, and directionality.[1] For synthetic macromolecules, a variety of supramolecular polymers have been prepared using multiple hydrogen bonding interactions between the designed arrays of the hydrogen donor and acceptor sites.[2] However, there have been few applications of such multiple interactions to catalysts or mediators that can control the primary structure of synthetic polymers during the polymerizations. In controlling the steric structure of vinyl polymers,[3] some specific solvents, such as bulky fluoro alcohols[4,5] and aprotic solvents,[6−9] which can form a single hydrogen bond with the polar substituents in the monomer units, were employed during radical polymerizations to give syndiotactic polymers only at a low temperature due to the weak interaction. For template polymerization, a high number of hydrogen bonding sites were put on the template polymer chains, whereas some special polymerization conditions are required for high stereospecificity.[10,11]

This paper describes the first efficient stereospecific radical polymerization mediated by multiple hydrogen bonding interactions of a low molecular weight mediator, which can work even at a high temperature (60 °C) to produce syndiotactic polymers ($r = 72\%$).

For the construction of an efficient triple hydrogen bonding interaction, the monomer was designed to have the arrays of a DAD sequence (D, proton donor; A, proton acceptor), in which amide and pyridine moieties were selected (Scheme 1). This compound has not been used as a monomer for any vinyl polymerizations although a similar divinyl acrylamide has often been available as a recognition site in molecular imprinted polymers.[12]

Scheme 1. Triple Hydrogen Bonding for Stereospecific Radical Polymerization of a DAD Monomer



Experimental Section

Materials. α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. 2,6-Diaminopyridine (Wako, >98%) was recrystallized from chloroform. Succinimide (**1**) (Kanto, >98%), phthalimide (**2**) (Wako, >99%), bemegride (3-ethyl-3-methylglutaridmide; **3**) (TCI, >98%), and 1,8-naphthalimide (**4**) (Wako, >97%) were used as received. Anhydrous tetrahydrofuran (THF) was purchased from Kanto (Japan) and used as received. Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[13]

Monomer Synthesis. The monomer was synthesized by the reaction of 2,6-aminopyridine with acetic anhydride followed by acryloyl chloride according to the synthesis of similar compounds.[14]

Step 1: Synthesis of *N*-(6-Aminopyridin-2-yl)acetamide. The monomer was synthesized by the reaction of 2,6-diaminopyridine and acetic anhydride. A solution of acetic anhydride (23 g; 0.23 mol) in dried THF (60 mL) was added dropwise with vigorous stirring to a solution of 2,6-diaminopyridine (29 g; 0.27 mol) and triethylamine (23 g; 0.23 mmol) in dried THF (350 mL). The temperature was maintained at 25−30 °C. The addition required 2 h and the stirring continued for 12 h. Water (400 mL) was added

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Table 1. Polymerization of a DAD Monomer in the Absence and Presence of ADA Imides (1−4) as a Mediator[a]

entry	mediator	*T*, °C	$[\text{mediator}]_0/[\text{M}]_0$	yield, %	M_n[b]	M_w/M_n[b]	*r*, %[c]
1	none	60	0	76	83 000	1.95	42.7
2	none	−40	0	68	50 000	2.02	44.4
3	**1**	60	1.0	65	151 000	2.65	52.7
4	**2**	60	1.0	66	141 000	2.42	54.8
5	**3**	60	1.0	91	96 000	1.84	54.3
6	**4**	60	1.0	50	50 000	2.02	71.5
7	**4**	60	0.25	85	73 000	2.68	52.4
8	**4**	60	0.50	81	68 000	2.65	59.4
9	**4**	60	0.70	74	75 000	3.58	67.2
10	**4**	60	1.5	64	46 500	2.15	72.4
11	**3**	60	4.0	85	73 000	2.38	54.5
12	**3**	−40	1.0	64	126 000	1.71	58.4

[a] DAD monomer: *N*-(6-acetamidopyridin-2-yl)acrylamide. **1**: succinimide. **2**: phthalimide. **3**: 3-ethyl-3-methylglutaridmide. **4**: 1,8-naphthalimide. Monomer/α,α-azobis(isobutyronitrile)/$CHCl_3$ = 100 mg/2.0 mg/2.0 mL, 14 h for 60 °C; Bu_3B + air, 42 h for −40 °C. [b] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography. [c] The content of racemo dyad (*r*) was determined by ^{1}H NMR spectroscopy.

into the solution and the THF was removed via rotary evaporator. The residual aqueous solution was set aside overnight, the crystals were collected, washed with water, dried under vacuum at 50 °C. Yield: 19.3 g (47.3%). ^{1}H NMR (DMSO-d_6), δ/ppm: 1.87 (s, 3H, CH_3CO), 5.56 (s, 2H, NH_2), 5.98−6.00 (d, 1H, C5−H of pyridinyl), 7.04−7.06 (d, 1H, C3−H of pyridinyl), 7.14−7.18 (t, 1H, C4−H of pyridinyl), 9.70 (s, 1H, CONH). ^{13}C NMR (DMSO-d_6), δ/ppm: 24.61 (CH_3), 101.25 (C3 of pyridinyl), 103.74 (C5 of pyridinyl), 139.29 (C4 of pyridinyl), 150.98 (C2 of pyridinyl), 158.87 (C6 of pyridinyl), 169.18 (C═O).

Step 2. Synthesis of *N*-(6-Acetamidopyridin-2-yl)acrylamide. A solution of of acryloyl chloride (2.7 g; 30 mmol) in dried THF (10 mL) was added dropwise with vigorous stirring to a solution of *N*-(6-aminopyridin-2-yl)acetamide (3.0 g; 20 mmol) and triethylamine (3.1 g; 31 mmol) in dried THF (45 mL). The temperature was maintained at 0 °C and gradually increased to room temperature after the addition. The addition required 1 h and the stirring continued for additional 12 h. Water (55 mL) was added into the solution and the THF was removed via rotary evaporator. The residual aqueous solution was put aside and the crystal was collected and washed with water. The crystals were dried and dissolved in ethanol before hexane was added (ethanol/hexane = 1/3, volume/volume). The insoluble part, if any, was removed by filtration and then the solvents were removed via rotary evaporation. The white crystals were dried under vacuum at 40 °C. Yield: 3.48 g (84.6%). ^{1}H NMR (DMSO-d_6), δ/ppm: 1.95 (s, 3H, CH_3CO), 5.61−5.64 (dd, 1H, trans H of CH_2═C, J^1 = 2 Hz, J^2 = 10 Hz), 6.12−6.17 (dd, 1H, cis H of CH_2═C), 6.47−6.54 (dd, 1H, CH_2═C*H*), 7.59−7.60 (d, 1H, C5−H of pyridinyl), 7.64 (d, 1H, C3−H of pyridinyl), 7.69 (d, 1H, C4−H of pyridinyl), 9.94 (s, 1H, C═CONH), 10.15 (s, 1H, CONH). ^{13}C NMR (DMSO-d_6), δ/ppm: 24.70 (CH_3), 109.84 (C5 of pyridinyl), 109.88 (C3 of pyridinyl), 128.28 (*C*H_2═CH), 132.06 (CH_2═*C*H), 140.48 (C4 of pyridinyl), 150.65 (C6 of pyridinyl), 150.94 (C2 of pyridinyl), 164.13 (CH_2═CH*C*O), 169.76 (CH_3*C*O).

Conventional Radical Polymerization. For a typical example, a degassed solution of monomer (100 mg; 0.49 mmol) in chloroform (2.0 mL) and AIBN (2.0 mg; 0.012 mmol) was prepared and dropped into a tube charged with 1 molar equivalent of 1,8-naphthalimide (**4**) (97 mg; 0.49 mmol) as a mediator (based on monomer) and sealed under nitrogen atmosphere, the tube was immersed in thermostatic oil bath at 60 °C for 14 h. The polymer was recovered by precipitation in diethyl ether and collection by centrifugation, and purification was carried out by repeating dissolution in DMF and precipitation in methanol, and finally dried under vacuum at 60 °C for 12 h. The gravimetrical polymer yield was 50%.

In the case of mediators other than **3**, dialysis against dimethyl sulfoxide (DMSO) (24 h) was carried out by using dialysis membrane (Spectra/Por, MWCO 3500) to remove the mediator before the above treatment. Polymer yields were measured gravimetrically while monomer conversions were determined by ^{1}H NMR analysis of the reaction solution. Polymerization at −40 °C was carried out with *n*-Bu_3B in the presence of a small amount of air.

RAFT Polymerization. A degassed mixture of a DAD monomer (0.70 g, 3.4 mmol), **4** (0.54 g, 2.7 mmol), CDB (4.6 mg, 0.017 mmol), and AIBN (2.8 mg, 0.017 mmol) in chloroform (5.6 mL) was prepared, then the solution was evenly charged in six glass tubes, and the tubes were sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. After the desired time, the solution was dropped into a large amount of diethyl ether and collected by centrifugation, washed with methanol, and finally dried under vacuum at 60 °C for 12 h. Monomer conversions were measured by using the vinyl protons in the ^{1}H NMR spectra of the reaction solution.

Measurements. The ^{1}H (400 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian Gemini 2000 spectrometer and a Varian INOVA 500 spectrometer, respectively. The diad tacticity of the polymer was determined by the area of the methyl carbon protons of the backbone, and the measurement was carried out at 170 °C in DMSO-d_6. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography (SEC) in DMF containing 100 mM LiCl at 40 °C on two polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-980 precision pump and a Jasco 930-RI detector. The columns were calibrated against 7 standard poly(methyl methacrylate) samples (Shodex; M_p = 1990−1950000; M_w/M_n = 1.02−1.09). Glass transition temperature (T_g) of the polymer was recorded on SSC-5200 differential scanning calorimetry (Seiko Instruments Inc.). Samples were first heated to 220 °C at 15°C/min, equilibrated at this temperature for 5 min, and cooled to 30 °C at 5 °C/min. After being held at this temperature for 5 min, the samples were then reheated to 220 °C at 10 °C/min. All T_g values were obtained from the second scan after removing the thermal history.

Results and Discussion

1. Radical Polymerization of the DAD Monomer in the Presence of ADA Additives: Control of Tacticity. A conventional radical polymerization of the DAD monomer was carried out with AIBN in $CHCl_3$ at 60 °C to give atactic polymers (*r* = 42.7%) (entry 1 in Table 1), in which the tacticity was calculated by the integration of the main-chain *meso*- and *rac*-methylene proton peaks at 1.4−1.9 ppm in ^{1}H NMR spectra (Figure 1A). The tacticity was almost atactic similarly to other acrylamide polymers obtained in conventional radical polymerizations,[15] in which the growing sp^2-like planar carbon radical species lacks the stereospecific chain growth if no other factors are available. The monomer was soluble in $CHCl_3$, but the resulting polymer was precipitated during the polymerization due to the low solubility in $CHCl_3$.

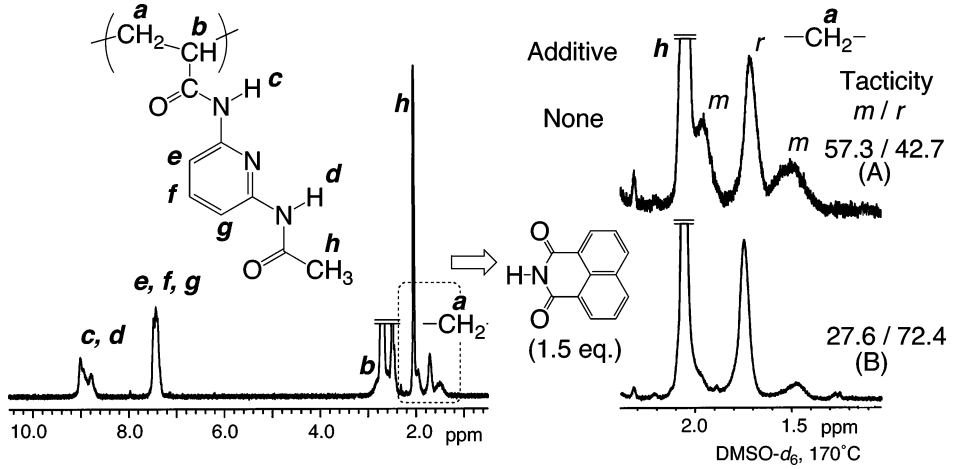

Figure 1. ^{1}H NMR spectra (400 MHz, DMSO-d_6, 170 °C) of the polymer prepared with α,α-azobis(isobutyronitrile) (AIBN) in $CHCl_3$ at 60 °C (entry 1, Table 1 in the main text; racemo dyad (r) = 42.7%) (A) and with AIBN/1,8-naphthalimide (**4**) in $CHCl_3$ at 60 °C (entry 10, Table 1 in the main text; r = 72.4%) (B).

Decreasing the polymerization temperature to −40 °C increased the syndiotacticity slightly (r = 44.4%) but did not significantly influence the tacticity (entry 2). Little changes of the tacticity by the polymerization temperatures were also observed in radical polymerizations of the other vinyl monomers, such as vinyl acetate, acrylamide, *N*-isopropylacrylamide,[4,5,15] in normal solvents without additives while the fraction of syndiotactic diads increases with decreasing temperatures in radical polymerizations of other 1,1-disubsituted monomers, such as methyl methacryalte.[5,16] ^{1}H NMR analysis of the monomer solution showed almost no dependence of the chemical shifts on the monomer concentration, indicating no significant intermolecular self-association of the monomer.

A series of cyclic imides (**1**−**4**) were then added to the polymerization as the ADA-type receptors for possible control of the stereospecificity. The addition of an equimolar amount of these imides did not disturb the polymerization in terms of the yields and molecular weights, but affected the stereochemistry of the polymer chains. With **1**−**3**, the diad syndiotacticity (r) increased to 53−55% (entries 3−5). A further increase was observed with the increasing bulkiness of the imides; the r value increased to 71.5% with **4** even at 60 °C (entry 6). The increased syndiotacticity was due to the increased bulkiness of the monomer units via the strong hydrogen bonding interaction with the mediators, which results in increased steric hindrance on the propagation.

This is similar to the solvent-mediated syndiospecific radial polymerizations of methacrylates, (meth)acrylamides, and vinyl acetate (VAc) in bulky fluoro alcohol[4,5] or amide solvents,[6−8] in which a single hydrogen bond is responsible for the induction, while the triple hydrogen bonding is highly effective in terms of the temperature and the amount of the solvents/mediators. For example, addition of the same volume of a bulky fluoro alcohol [$(CF_3)_3COH$] to VAc ([$(CF_3)_3COH]_0$ = 50 vol %) resulted in only a slight increase of the racemo diad from 53.4% to 55.9% at 60 °C though a higher syndiotacticity was attained by lowering the temperature to −78 °C (r = 67.5%).[4] Further addition of the solvent at −78 °C ([$(CF_3)_3COH]_0$ = 80 vol %) increased the r content (r = 72.2%). A similar result was obtained for *N*-isopropylacrylamide radical polymerization, in which the r content increased only slightly from 55% to 59% at 60 °C on addition of equimolar amount of a bulky aprotic solvent, such as hexamethylphosphoramide, while a higher r content (65%) was obtained at a lower temperature (−60 °C).[7] With increasing the solvent ([HMPA]$_0$/[NIPAM]$_0$ = 2.0) at −60 °C, the r content reached 70%. Such significant dependences of the tacticities on the solvent amount and the temperature are due to the relatively low association constants between the monomers and the solvents (K = 10^1−10^2 L/mol at room temperature).[4,7]

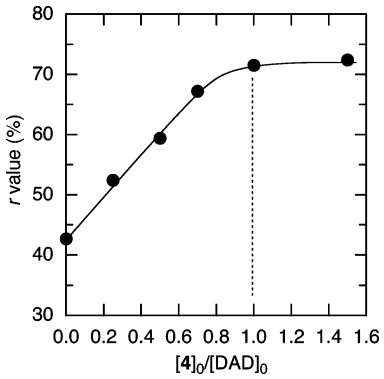

Figure 2. Dependence of racemo dyad (r) values of the obtained polymer on [1,8-naphthalimide (**4**)]$_0$/[M]$_0$ during the radical polymerization at varying the concentrations of **4** in $CDCl_3$ at 60 °C (M/α,α-azobis(isobutyronitrile)/$CHCl_3$ = 100 mg/2.0 mg/2.0 mL).

The concentration of **4** was then changed to examine its effects on the tacticity. On increasing the amount of **4** (entries 1 and 6−9), the syndiotacticity increased almost linearly, reached 70% in the presence of equimolar amount of **4**, and became almost constant even on further addition of **4** (1.5 equiv) (Figure 2). A similar dependence was observed for a less bulky mediator (**3**), in which the r content reached 55% on addition of equimolar amount of **3** (entry 5) and did not change significantly on the further addition (4 equiv; entry 11). On decreasing the temperature, the r value increased slightly to 58% (entry 12) while the effect was smaller than those in the solvent-mediated syndiospecific radical polymerizations mentioned above. These results suggest that the added ADA-mediators coordinate efficiently and strongly to the DAD arrays in the monomer units at 1:1 molar ratio to induce stereospecific chain growth even at high temperature. However, the linear increase of the tacticity with increasing amounts of the mediator up to 1:1 molar ratio indicates that the mediators cannot work catalytically due to the strong association constant with the monomer, unlike lanthanide triflates, which work catalytically during the isospecific radial polymerization of (meth)acrylamides via multisite coordination.[15]

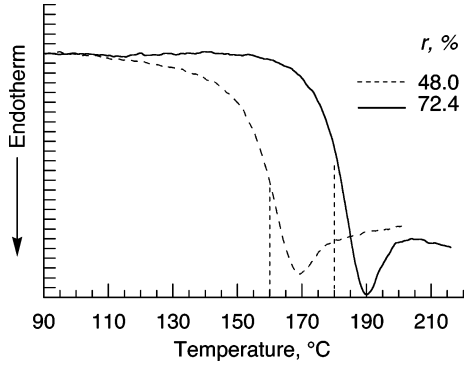

Figure 3. Differential scanning calorimetry curves of the atactic [racemo dyad (r) = 48.0%, the number-average molecular weight (M_n) = 131,000, the weight-average molecular weight (M_w)/M_n = 3.57; the glass transition temperature (T_g) = 160 °C] and syndiotactic (r = 72.4%, M_n = 47,000, M_w/M_n = 2.15; T_g = 180 °C) polymers.

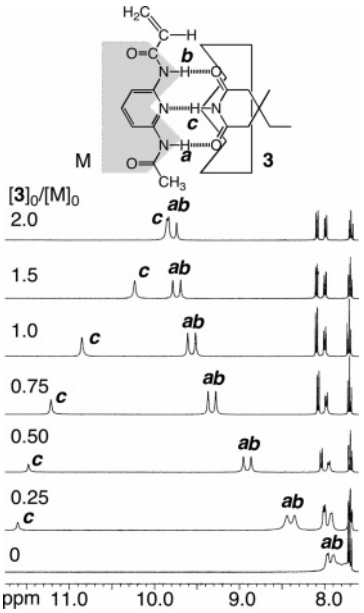

Figure 4. ^{1}H NMR spectra of the mixture of the monomer and 3-ethyl-3-methylglutaridmide (**3**) by varying the concentration of **3** in $CDCl_3$ at 23 °C: $[M]_0$ = 100 mM; $[\mathbf{3}]_0$ = 0 (A), 25 (B), 50 (C), 75 (D), 100 (E), and 150 (F) mM.

We then analyzed the thermal properties of the polymers, which usually depend on the tacticity of the polymers. Even the atactic polymers (r = 48.0%, M_n = 131,000, M_w/M_n = 3.57) had a relatively high glass transition temperature (T_g = 160 °C) due to the presence of the aromatic group in the substituents (Figure 3). The syndiotactic polymers (r = 72.4%, M_n = 47 000, M_w/M_n = 2.15) were more thermally stable (T_g = 180 °C) than the atactic polymers similar to a series of poly(NIPMA) with different tacticities.[8]

To confirm the hydrogen bonding interaction between the DAD monomer and the ADA additive, the mixture of the monomer and **3**, which gave the homogeneous $CHCl_3$ solution at any mixing ratios, was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ at 23 °C. Upon the addition of **3** into the monomer solution, both the amide protons (*a* and *b)* in the monomer shifted downfield (Figure 4) and almost reached a constant (Figure 5A). The imide proton (*c*) of **3** shifted upfield with increasing amount of **3**. This indicates that the multiple hydrogen bonding interactions occurred between the monomer and **3** in $CHCl_3$ as expected. The stoichiometry of the interactions was then evaluated by Job's method by varying the concentration of these components (Figure 5B). This shows the formation of

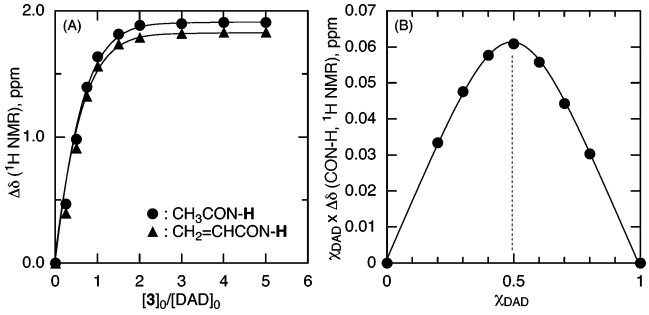

Figure 5. Changes in the amide proton chemical shifts of the monomer in the presence of 3-ethyl-3-methylglutaridmide (**3**) ($[M]_0$ = 100 mM) (A) and Job plots for the association of the monomer with **3** from the changes in chemical shift (ppm) of the acetamide proton of the monomer ($[M]_0$ + $[\mathbf{3}]_0$ = 50 mM) (B) in $CDCl_3$ at 23 °C.

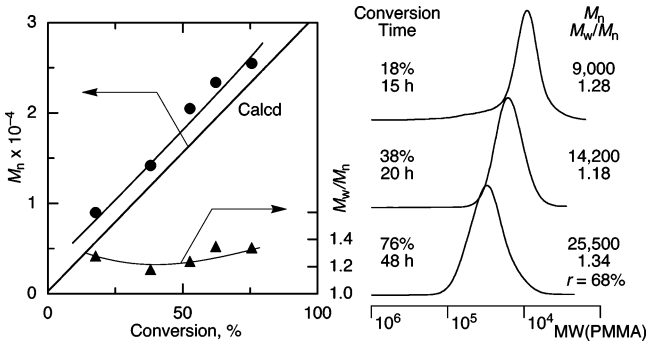

Figure 6. Reversible addition fragmentation chain-transfer (RAFT) polymerization in the presence of 1,8-naphthalimide (**4**) in $CHCl_3$ at 60 °C. $[M]_0/[\mathbf{4}]_0/[\alpha,\alpha$-azobis(isobutyronitrile)$]_0$/[cumyl dithiobenzoate]$_0$ = 244/195/1.0/1.6 mM.

a 1:1 complex between the monomer and the mediator. The binding constant (K) calculated from the data in Figure 5B is 654 L/mol, a reasonable value for the triple hydrogen bonding between similar combinations under similar conditions.[11] Thus, the strong triple hydrogen bonding interaction should also exist in the radical polymerization to work for controlling the reaction. Such strong hydrogen bonding as well as the bulkiness of the additive is requisite for the stereospecific radical polymerization though such a detailed analysis was not possible for **4** due to its low solubility.

2. Stereospecific Living Radical Polymerization for the Simultaneous Control of Molecular Weights and Tacticity. A further study was directed for the simultaneous control of the tacticity and the molecular weight.[9,17−24] The reversible addition fragmentation chain-transfer (RAFT) polymerization of the DAD monomer was thus carried out with AIBN in the presence of a RAFT agent (CDB)[13,25] and **4** in $CHCl_3$ at 60 °C ($[M]_0/[\mathbf{4}]_0/[AIBN]_0/[CDB]_0$ = 244/195/1.0/1.6 mM; $[\mathbf{4}]_0/[M]_0$ = 0.8).

The polymerization proceeded smoothly with a slight induction period to reach a 76% monomer conversion in 48 h. The number-average molecular weight (M_n) of the obtained polymers increased in direct proportion to the monomer conversion and agreed well with the calculated values assuming that one polymer chain is generated from one molecule of the RAFT agent (Figure 6), and the molecular weight distributions were narrow throughout the reactions (M_w/M_n = 1.1−1.3). The polymer obtained in a combination with the RAFT system also showed a high syndiotacticity (r = 68.0%), which was a reasonable value for the polymer obtained in the presence of 0.8 equiv of **4** to the monomer (see Figure 2). Thus, the triple hydrogen bonding interaction can efficiently function even during the RAFT polymerization to produce polymers with

controlled molecular weights and a high stereospecificity even at a relatively high temperature.

Conclusion. In conclusion, we have demonstrated that the triple hydrogen bonding interaction is highly effective for controlling the stereochemistry during radical polymerization even at high temperature, where the reported solvent-mediated syndiospecific radical polymerizations did not efficiently work due to the relatively weak single hydrogen bonding interactions. Although this study showed the first but only one effective example based on the triple hydrogen bonding interaction for a specific combination of the DAD monomer and the ADA additive, this may lead to developing organic catalysts that can produce excellent polymer materials without the contamination of metal catalyst residues and would also allow further control of the polymerization with better hydrogen bonding interactions based on the significantly developing supramolecular chemistry.

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