Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 5589–5594 **5589**
DOI: 10.1021/ma1005765

Group Transfer Polymerization of *N*,*N*-Dimethylacrylamide Using Nobel Efficient System Consisting of Dialkylamino Silyl Enol Ether as an Initiator and Strong Brønsted Acid as an Organocatalyst

Keita Fuchise,[†] Ryosuke Sakai,[†] Toshifumi Satoh,[†] Shin-ichiro Sato,[†] Atsushi Narumi,[‡] Seigou Kawaguchi,[‡] and Toyoji Kakuchi*,[†]

[†]*Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan, and* [‡]*Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Jonan 4-3-16, Yonezawa 992-8510, Japan*

Received March 15, 2010; Revised Manuscript Received May 7, 2010

ABSTRACT: The combination of (*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene ((*Z*)-DATP) and Brønsted acid of trifluoromethanesulfonimide (Tf_2NH) was found to act as a highly efficient GTP initiating system for *N*,*N*-dimethylmethacrylamide (DMAA) at 0 °C. The Tf_2NH-catalyzed GTP of DMAA initiated by (*Z*)-DATP proceeded in a living manner to produce poly(*N*,*N*-dimethylacrylamide)s (PDMAA) with controlled molecular weights and narrow molecular weight distributions. The living nature was confirmed by kinetic measurements and a postpolymerization experiment. Furthermore, the MALDI-TOF MS analysis revealed that the molecular weight of the obtained PDMAA was in perfect agreement with that of PDMAA containing the (*Z*)-DATP initiator residue and the desilylated chain end, showing that the Tf_2NH-catalyzed GTP of DMAA proceeded without any side reactions. The obtained PDMAA was *r* diad rich and had up to 73% of *r* diad contents. Glass transition temperatures of PDMAA showed molecular weight dependence below 20 kg mol^{-1}.

Introduction

Controlled/living polymerization has been expanding its use involving a monomer, initiator, and end-capping agent and the polymerization concept with increasing demand for the precise synthesis of well-defined macromolecular architectures since the discovery of the living anionic polymerization of styrene in 1956 by Szwarc. For polar vinyl monomers, such as (meth)acrylates and (meth)acrylamides, the applicable scope in the controlled/living radical polymerization is generally broader than that for the anionic one. Although Ishizone et al. reported the living anionic polymerization of a series of *N*,*N*-dialkyl(meth)acrylamides,[1−7] the group transfer polymerization (GTP), which is one of the important forms in living anionic polymerization,[8−10] could not be used for *N*,*N*-dialkyl(meth)acrylamides. For example, Sogah and Webster et al. reported the GTP of *N*,*N*-dimethylacrylamide (DMAA)[11] and *N*,*N*-dimethylmethacrylamide[8] affording low molecular weight polymers with a relatively broad polydispersity index (> 1.43). Freitag et al. reported the GTP of *N*,*N*-diethylacrylamide producing the poly(*N*,*N*-diethylacrylamide) with the low polydispersities of 1.12−1.19 though the molecular weights were less than 3000.[12−14] Hence, the GTP of *N*,*N*-dialkyl(meth)acrylamide leading to well-defined polymers still remains a challenging task.

Recently, organocatalytic polymerization has turned into one of the common methods for preparing well-defined polymers, which began not only to improve well-established polymerization systems but also to provide polymer chemistry with new concepts and polymerization systems. For example, Hedrick et al. showed that the *N*-heterocyclic carbene (NHC) mediated ring-expansion polymerization of cyclic esters could lead to the spontaneous formation of cyclic polyesters with predictable molecular weights and narrow polydispersity indices.[15] Furthermore, Taton and coworkers showed a smart synthetic strategy for α,ω-hetero-end-functionalized poly(ethylene oxide) by using the zwitterionic ring-opening polymerization of ethylene oxide with NHC as the organocatalyst.[16] In the growing field of organocatalytic polymerizations, the organocatalyst was also found to be a new and facile GTP catalyst for (meth)acrylates; Taton et al. and Hedrick et al. independently reported that NHC successfully catalyzed the GTP of (meth)acrylates using 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS) as the initiator to produce well-defined homo- and block polymers.[17−19] In addition, we recently reported that trifluoromethanesulfonimide (Tf_2NH),[20−24] a very strong Brønsted acid, could promote the GTP of methyl methacrylate (MMA) using MTS as the initiator to afford the highly syndiotactic poly(methyl methacrylate) without any obvious side reactions.[25] Very importantly, the catalytic activity of Tf_2NH in the GTP process was significantly higher than the conventional Lewis acids, such as zinc halide and organic aluminum,[11] which showed the Tf_2NH-catalyzed GTP as a facile candidate for the living polymerization of *N*,*N*-dialkyl(meth)acrylamides by precise tuning of the polymerization system.

We now report the living anionic polymerization of DMAA based on the GTP method using an organocatalyst, as shown in Scheme 1. We synthesized (*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene ((*Z*)-DATP) as a new GTP initiator and examined the initiating performance of (*Z*)-DATP and MTS for the polymerization of DMAA using Tf_2NH. This article describes (1) the characterization and optimization of the initiating systems, (2) the living nature of the Tf_2NH-catalyzed GTP of DMAA by varying the [DMAA]/[(*Z*)-DATP] ratios, kinetic study, postpolymerization, and mass spectral analysis of the obtained poly(*N*,*N*-dimethylacrylamide) (PDMAA), and (3)

---

*Corresponding author: Fax +81-11-706-6602; e-mail kakuchi@poly-bm.eng.hokudai.ac.jp.

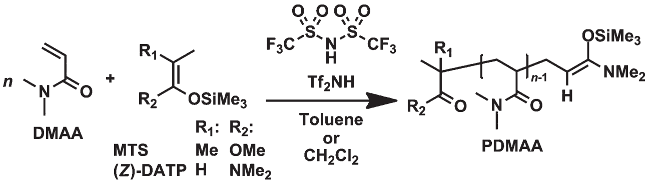
the detailed analyses of the tacticity and glass transition temperature of PDMAA.

Results and Discussion

Initiator for Tf_2NH-Catalyzed GTP of DMAA. First, we carried out the Tf_2NH-catalyzed GTP of DMAA using 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS) as the conventional GTP initiator in CH_2Cl_2 and toluene (Table 1, runs 1 and 2, respectively). The mechanism of the Tf_2NH-catalyzed GTP is described in our previous report.[25] Unexpectedly, the number-averaged-molecular weights (M_n) of the obtained polymers were 20.2 and 23.7 kg mol^{-1}, which were extremely higher than those previously prepared by the GTP method.[8,11−14] In particular, for the polymerization in CH_2Cl_2, the monomer was completely consumed after 2 h, and the molecular weight distribution (M_w/M_n) value of the obtained polymer was relatively low as 1.23 though the M_n value of the polymer was twice that of the theoretical value ($M_{n,theo}$) predicted from the monomer conversion and the initial concentration of the monomer, initiator, and Tf_2NH ($[M]_0$, $[I]_0$, and $[Tf_2NH]_0$, respectively).[26] These results obviously indicated that Tf_2NH was an effective catalyst for the polymerization of DMAA even using MTS as the initiator.

Thus, we designed and synthesized (*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene ((*Z*)-DATP) as the new GTP initiator because the rate of initiation should be greater than or equal to the rate of propagation for a living polymerization. As expected from the homology of the initiating species and growing species, the polymerization using (*Z*)-DATP smoothly proceeded in CH_2Cl_2 and toluene to afford well-defined PDMAAs with the low polydispersities of 1.08 and 1.11 (Table 1, runs 3 and 4, respectively). In addition, the M_ns were well-controlled as 12.7 kg mol^{-1} for CH_2Cl_2 and 11.9 kg mol^{-1} for toluene, which agreed with the $M_{n,theo}$ values of 10.2 and 10.5 kg mol^{-1}, respectively. These results strongly suggested that the structure of the initiator affected the initiation character of the Tf_2NH-catalyzed GTP of DMAA.

Scheme 1. GTP of *N*,*N*-Dimethylacrylamide (DMAA) Catalyzed by Tf_2NH



In order to directly show that the combination of (*Z*)-DATP and Tf_2NH was exceptionally effective for the GTP of DMAA, we next evaluated the combinations of (*Z*)-DATP and conventional GTP catalysts, such as zinc iodide (ZnI_2) as the Lewis acid and tris(dimethylamino)sulfonium bifluoride (TAS-HF_2) and tetra-*n*-butylammonium acetate (TBA-AcO) as the Lewis bases. All the polymerizations were carried out with $[DMAA]_0/[(Z)\text{-DATP}]_0/[catalyst]_0$ = 100/1/0.02 in toluene at 0 °C for 6 h. Table 2 summarizes the polymerization results. In clear contrast to the GTP of MMA,[11] the Lewis basic catalyst of TAS-HF_2 showed almost no catalytic activity toward the GTP of DMAA (conversion ∼ 0%, Table 2, run 11). Although the different Lewis basic GTP catalyst of TBA-AcO showed a fairly high monomer conversion (conversion = 57.0%, Table 2, run 12), the M_n of the obtained PDMAA (340 kg mol^{-1}) was extremely higher than that of $M_{n,theo}$ (5.75 kg mol^{-1}) and the M_w/M_n was as broad as 1.63, showing that Lewis basic catalysts insufficiently promoted the GTP of DMAA. In addition, ZnI_2, an active catalyst for the GTP of acrylate, also showed almost no catalytic activity (conversion ∼ 0%, Table 2, run 13). In clear contrast to these conventional GTP catalysts, Tf_2NH produced the perfect conversion of DMAA, obviously indicating that the new GTP initiating system comprised of (*Z*)-DATP and Tf_2NH was exceptionally effective for the GTP of DMAA as acrylamide derivative.

Controlled/Living Characteristics for Tf_2NH-Catalyzed GTP of DMAA. In order to characterize the controlled/living nature of the GTP of DMAA, we first carried out the polymerizations using various ratios of $[DMAA]_0/[(Z)\text{-}DATP]_0$ from 25 to 400 (Table 1, runs 4−8). Figure 1 shows the SEC traces of the obtained PDMAAs. Their M_ns increased from 3.24 to 53.9 kg mol^{-1}, which agreed with the $M_{n,theo}$ values predicted from the $[DMAA]_0/[(Z)\text{-}DATP]_0$.

Table 2. GTP of DMAA Using (*Z*)-DATP and Various Catalysts in Toluene at 0 °C for 6 h[a]

run	catalyst	conv (%)[b]	$M_{n,theo}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	M_w/M_n[e]
11	TAS−HF_2	0			
12	TBA−AcO	57.0	5.75	340	1.63
13	ZnI_2	0			
14	Tf_2NH	>99	10.2[f]	12.1	1.09

[a] $[M]_0$ = 0.50 mol L^{-1}; $[M]_0/[I]_0/[cat.]_0$ = 100/1/0.02. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $[M]_0/[I]_0$ × conversion × (MW of DMAA) + (MW of (*Z*)-DATP). [d] Determined by SEC in DMF containing 0.01 mol L^{-1} LiBr using a multiangle laser light scattering detector. [e] Determined by SEC in DMF containing 0.01 mol L^{-1} LiBr using polystyrene standards with an RI detector. [f] Calculated from the equation described in ref 26.

Table 1. Group Transfer Polymerization (GTP) of *N*,*N*-Dimethylacryamide (DMAA) Using Tf_2NH at 0 °C[a]

run	initiator	solvent	$[M]_0/[I]_0/[Tf_2NH]_0$	time (h)	conv (%)[b]	$M_{n,theo}$ (kg mol^{-1})[c]	M_n (kg mol^{-1})[d]	M_w/M_n[e]
1	MTS	CH_2Cl_2	100/1/0.02	2	>99	10.2	20.2	1.24
2	MTS	toluene	100/1/0.05	3	34.3	3.68	23.7	1.76
3	(*Z*)-DATP	CH_2Cl_2	100/1/0.02	1	>99	10.2	12.7	1.08
4	(*Z*)-DATP	toluene	100/1/0.05	3	>99	10.5	11.9	1.11
5	(*Z*)-DATP	toluene	25/1/0.05	3	>99	2.71	3.24	1.16
6	(*Z*)-DATP	toluene	50/1/0.05	3	>99	5.32	6.10	1.12
7[f]	(*Z*)-DATP	toluene	200/1/0.05	5	>99	21.0	23.5	1.06
8[g]	(*Z*)-DATP	toluene	400/1/0.05	9	>99	41.8	53.9	1.07
9	(*Z*)-DATP	toluene	50/1/0.05	3	>99	5.32	5.63	1.20
10[h]	(*Z*)-DATP	toluene	50/1/0.05	4	>99	10.5	11.0	1.14

[a] $[M]_0$ = 0.50 mol L^{-1}. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from the equation described in ref 26. [d] Determined by SEC in DMF containing 0.01 mol L^{-1} LiBr using a multiangle laser light scattering detector. [e] Determined by SEC in DMF containing 0.01 mol L^{-1} LiBr using polystyrene standards with an RI detector. [f] $[M]_0$ = 0.80 mol L^{-1}. [g] $[M]_0$ = 2.0 mol L^{-1}. [h] Postpolymerization after run 9.

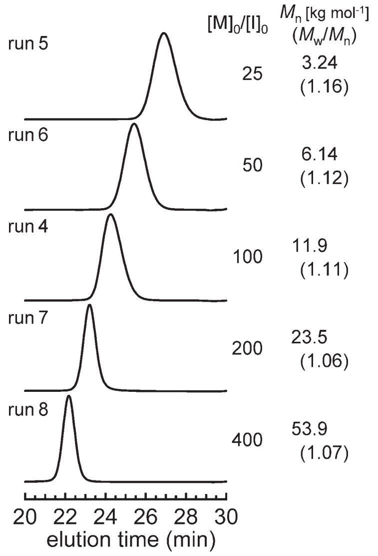


Figure 1. SEC traces of the PDMAA polymerized with different monomer to initiator ratios ($[M]_0/[I]_0$) (runs 4−8) (eluent, DMF containing 0.01 mol L^{-1} LiBr; flow rate, 1.0 mL min^{-1}).

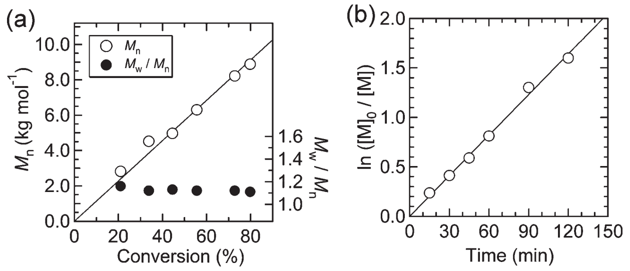


Figure 2. (a) Dependence of molecular weight (M_n) and polydispersity (M_w/M_n) on the monomer conversion and (b) kinetic plots for the polymerization of DMAA ($[DMAA]_0$ = 0.50 mol L^{-1}; $[DMAA]_0/[(Z)\text{-DATP}]_0/[Tf_2NH]_0$ = 100/1/0.02; solvent, toluene; temperature, 0 °C).

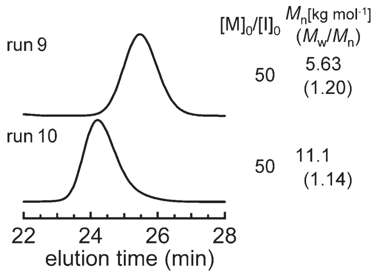


Figure 3. SEC traces of the PDMAA obtained by the first polymerization (run 9) and following postpolymerization (run 10) (eluent, DMF containing 0.01 mol L^{-1} of LiBr; flow rate, 1.0 mL min^{-1}).

Furthermore, all the M_w/M_n values were as low as 1.06−1.16, which strongly indicated that the Tf_2NH-catalyzed GTP of DMAA proceeded in a living manner. In addition, we confirmed the living nature on the basis of the kinetic study for the Tf_2NH-catalyzed GTP of DMAA. As shown in Figure 2a, the molecular weight of the obtained PDMAA linearly increased from 2.82 to 8.88 kg mol^{-1} with the reaction time, and the M_w/M_n values of the obtained PDMAAs were in the range of 1.09−1.16. The kinetic plots shown in Figure 2b proved the distinct first-order relationship between the reaction time and the monomer conversion. Finally, the chain extension experiment also proved the living nature of the Tf_2NH-catalyzed GTP of DMAA. Figure 3 shows SEC traces for the chain extension experiment. A PDMAA with M_n = 5.63 kg mol^{-1} and M_w/M_n = 1.20 was first prepared by the perfect conversion of 50 equiv of DMAA using $[(Z)\text{-DATP}]_0/[Tf_2NH]_0$ = 1/0.05. The polymerization was further continued by the subsequent addition of 50 equiv of DMAA to afford a PDMAA with M_n = 11.1 kg mol^{-1} and M_w/M_n = 1.14, indicating that the chain end group of the growing PDMAA possessed a truly living nature. Thus, the Tf_2NH-catalyzed GTP of DMAA was revealed to possess a living nature and produced a well-defined PDMAA at 0 °C.

In order to provide a detailed insight into the polymerization reaction, a MALDI-TOF MS measurement for the obtained PDMAA was carried out. The results are summarized in Figure 4. Only one series of peaks was observed as shown in Figure 4a,b. The difference in the m/z values among each molecular ion peak was just 99.1, which corresponded to the molecular weight of DMAA as a monomer unit. An expanded molecular ion peak in the obtained MS spectrum is shown in Figure 4c. The pattern of the observed isotopic distribution of the molecular ion peak was in a good agreement with the theoretical isotopic distribution of PDMAA cationized by sodium ions which consists of 39 repeating units, a residue of (Z)-DATP, and the desilylated terminating end (molecular formula: $C_{200}H_{362}O_{40}N_{40}Na$). These results indicated that Tf_2NH-promoted GTP proceeded in a living fashion without any side reactions, such as a back-biting reaction.[19,27] Thus, we first realized the living polymerization of acrylamide through the GTP process by using the strong Brønsted acid, Tf_2NH, as a good promoter of the polymerization.

Stereoregularity and Thermal Property of PDMAA. The stereoregularity of a polymer, one of the important structural factors, affects the polymer properties, such as the melting temperature, glass transition temperature, and mechanical strength. It is interesting to study the tacticity of PDMAAs synthesized by the GTP method in comparison to those prepared using other polymerization methods. Figure 5 shows the ^1H and ^{13}C NMR spectra of PDMAAs synthesized using (Z)-DATP as the initiator and Tf_2NH as the

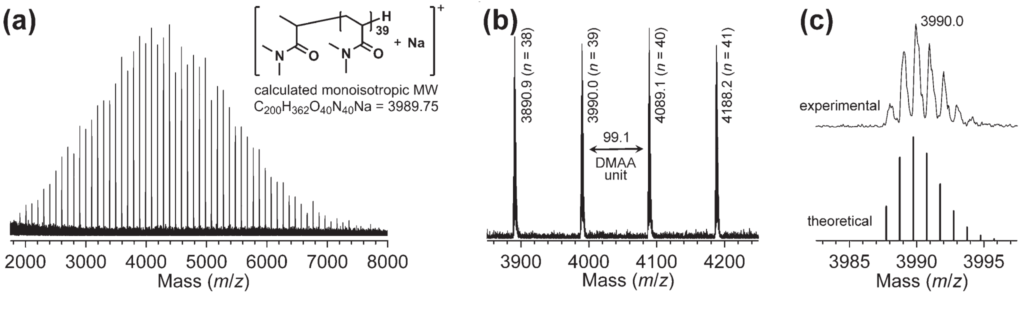


Figure 4. MALDI-TOF MS spectra in reflector mode of the obtained PDMAA ($[M]_0/[I]_0/[Tf_2NH]_0$ = 100/1/0.02, conversion = 44.5%, M_n = 4.97 kg mol^{-1}, M_w/M_n = 1.13).

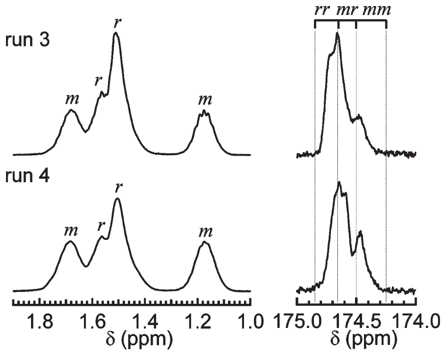


Figure 5. ^{1}H NMR spectra measured in DMSO-d_6 at 150 °C (left) and ^{13}C NMR spectra measured in $CDCl_3$ at 50 °C (right) of the PDMAAs (runs 3 and 4).

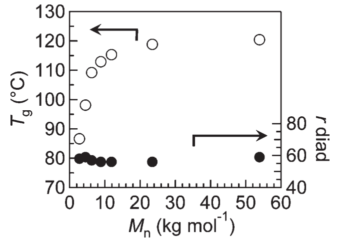


Figure 6. Plots of the glass transition temperature (T_g) and *r* diad content for PDMAA as a function of the number-averaged molecular weight (M_n).

catalyst. The diad tacticity (*m*/*r*) of PDMAA was determined from the resonances of the main-chain methylene protons appearing between 1 and 2 ppm in the ^{1}H NMR spectra measured in DMSO-d_6 at 150 °C and the triad tacticity from the resonances of the carbonyl carbon appearing around 175 ppm in the ^{13}C NMR spectra measured in $CDCl_3$ at 50 °C.[1−3,28,29] The *m*/*r* values of the PDMAAs polymerized at 0 °C in CH_2Cl_2 and toluene (Table 1, runs 3 and 4) were 35/65 and 44/56, respectively, and those at −78 °C in CH_2Cl_2 and toluene were 27/73 and 38/62, respectively. These results indicated that the Tf_2NH-catalyzed GTP of DMAA produced the *r* diad rich PDMAA in a polar solvent or at a lower temperature. This tendency of tacticity change with temperature differed from that for the conventional radical polymerization, in which the content of the *m* diad of the resultant PDMAA increased with the decreasing polymerization temperature.[29,30]

Despite the importance of the glass transition temperature (T_g) in polymer science, detailed characterization of the T_g of PDMAA has scarcely been reported.[31−35] We take into account that PDMAA synthesized by Tf_2NH-catalyzed GTP of DMAA could produce an ideal model polymer; in other words, PDMAA synthesized by Tf_2NH-catalyzed GTP of DMAA possessed no initiator and terminator residues. Hence, we finally focused on the characterization of the T_g for PDMAAs with various molecular weights. A typical DSC trace for PDMAA is shown in the Supporting Information. The step in the baseline is assignable to a glass transition. The glass transition temperature was defined as the inflection point in the step and was determined from the minimum of the first derivative of the curve. Figure 6 lists the T_gs of PDMAA with different molecular weights. Basically, the T_g of PDMAA has been known to be around 120 °C.[32,33] Figure 6 shows the plots of the T_gs as a function of the M_n, indicating that the T_gs increased with the increasing M_n values. Importantly, the T_g for the PDMAA possessed a molecular weight dependence below 20 kg mol^{-1} (Figure 6). Thus, using Tf_2NH-catalyzed GTP of DMAA, precise characterization of the glass transition temperature for PDMAA was successfully achieved.

Conclusions

Tf_2NH, a strong Brønsted acid, was revealed to act as a good promoter for the GTP of the acrylamide derivative. The GTP initiating system comprised of (*Z*)-DATP and Tf_2NH could provide a PDMAA with a higher molecular weight than that of any polyacrylamide derivatives synthesized previously by the GTP technique. As a direct consequence of the homology of the initiating and growing species, (*Z*)-DATP showed an excellent initiating efficiency and polymerization control as the GTP initiator when compared to the conventional initiator of MTS. In addition, the living character of the GTP of DMAA by the combination of (*Z*)-DATP and Tf_2NH was strongly confirmed by the postpolymerization experiment and MALDI-TOF MS measurement. To the best of our knowledge, this report showed the first reliable demonstration of the living polymerization of the acrylamide monomer through the GTP process.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMAA), *n*-butyllithium (1.6 mol L^{-1} in hexane), dry dichloromethane (CH_2Cl_2, >99.5%; water content <0.001%), dry acetonitrile (MeCN, >99.5%; water content <0.002%), tetrahydrofuran (THF), toluene, 2-propanol, and pyridine were purchased from Kanto Chemicals Co., Inc. DMAA was dried over CaH_2 and distilled two times under reduced pressure. CH_2Cl_2 was distilled from CaH_2 and degassed by three freeze−pump−thaw cycles. THF and toluene were distilled from sodium benzophenone ketyl. 1-Methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS), diisopropylamine, *N*,*N*-dimethylpropionamide, chlorotrimethylsilane, and *trans*-3-indoleacrylic acid were purchased from Tokyo Kasei Kogyo Co., Ltd. MTS was purified by fractional distillation under argon. Diisopropylamine, *N*,*N*-dimethylpropionamide, and chlorotrimethylsilane were dried over CaH_2 followed by distillation. Tf_2NH, tris(dimethylamino)sulfonium difluorotrimethylsilicate (TAS-$SiMe_3F_2$), tetra-*n*-butylammonium acetate (TBA-AcO), and sodium trifluoroacetate were available from the Sigma-Aldrich Chemicals Co. and used as received. Zinc iodide (ZnI_2) was purchased from Junsei Chemical Co., Ltd., and used as received. Insulin (bovine) was purchased from TAKARA BIO, Inc., and used as received. Tris(dimethylamino)sulfonium bifluoride (TAS-HF_2) was prepared according to the method reported by Webster and co-workers from TAS-$SiMe_3F_2$.[8] All other chemicals were purchased from various suppliers and used without purification.

Measurements. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400II and JEOL-ECP400. The preparation of the polymerization solution was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2 < 1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. The characterizations for the molecular weights of PDMAA were performed by size exclusion chromatography (SEC) (pump: Jasco PU-2080 Plus, degasser: Jasco 2080-53, column oven: Jasco CO-2065 Plus, temperature of the column oven: 40 °C) using DMF containing 10 mmol L^{-1} LiBr as the eluent and at the flow rate of 1.0 mL min^{-1} at room temperature (25 °C). The SEC was equipped with three columns (Shodex KD806 M × 2; size: 8 mm × 300 mm, average bead size: 5 μm, exclusion limit: 2×10^7 and Shodex OHpak SB-8025HQ; size: 8 mm × 300 mm, particle size: 6 μm, exclusion limit: 1×10^4), an refractive index detector (RI: Shodex RI-71), and a multiangle laser light scattering detector (MALLS; Wyatt Technology DAWN-DSP, wavelength λ = 632.8 nm). The weight-averaged-molecular weight (M_w) of PDMAA was determined by the MALLS. The polydispersity index (M_w/M_n) was determined by the RI based on polystyrene standards with the $M_n(M_w/M_n)$s of 2.18×10^3 g mol^{-1} (1.08), 4.76×10^3 g mol^{-1} (1.08), 8.00×10^3 g mol^{-1} (1.05), 1.58×10^4 g mol^{-1} (1.05), 4.12×10^4 g mol^{-1} (1.07), 1.10×10^5 g mol^{-1} (1.04), and 2.28×10^6 g mol^{-1} (1.02). The number-averaged-molecular weight (M_n) of PDMAA was calculated from $M_w/(M_w/M_n)$. The Rayleigh ratio $R(90)$ at a scattered angle of 90° was based on that of pure toluene at a wavelength of 632.8 nm at 25 °C. The corrections for the sensitivity of 17 detectors at angles of other than 90° and the dead volume of each detector were performed using the scattering intensities of 0.30 wt % DMF containing 10 mmol L^{-1} LiBr solution of a polystyrene standard with $M_w = 4.41 \times 10^4$ g mol^{-1} and $M_w/M_n = 1.07$. The polymer sample solutions with a mass concentration (C_p) of about 5×10^{-4} g mL^{-1} were injected using a sample loop of 100 μL to the SEC columns and diluted 10$-$10^3 times lower than the original C_p in the columns during the separation. Thus, the concentration effect on the M_w value can be ignored.

The specific refractive index increment (dn/dc) was measured using a differential refractometer (Otsuka Electronics DRM-1021, wavelength λ = 632.8 nm) at 25 °C. The solutions of PDMAA ($M_w = 1.12 \times 10^4$ g mol^{-1}) in DMF containing 10 mmol L^{-1} LiBr with the C_p of 1.0$-$5.0 mg mL^{-1} were prepared by a gravimetric method according to the literature.[36] The measured values were plotted as a function of the sample concentrations; the least-squares method was applied, providing the dn/dc of 0.0786 mL mg^{-1}, and this value was used for the M_w determinations of all the PDMAA samples.

The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106$-$107 W cm^{-2}) operating at 3 Hz was used to produce the laser desorption, and 200 shots were summed. The spectra were externally calibrated using insulin (bovine) with a linear calibration. Samples for the MALDI-TOF MS were prepared by mixing the polymer (1.5 mg mL^{-1}, 10 μL), the matrix (*trans*-3-indoleacrylic acid, 10 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 10 μL) in THF.

The glass transition temperature (T_g) of the polymers was measured by differential scanning calorimetry (DSC) on a Bruker AXS TG-DTA 3100SA equipped with a Bruker AXS CU9440. The samples were first heated to 180 °C at the heating rate of 20 °C min^{-1}, equilibrated at this temperature for 4 min, and then cooled to 0 °C at the cooling rate of 10 °C min^{-1}. After being held at this temperature for 4 min, the samples were reheated to 360 °C at the heating late of 10 °C min^{-1}. All the T_g values were obtained from the second scan after removing the thermal history.

Synthesis of (*Z*)-DATP. To a solution of diisopropylamine (26.7 mL, 190 mmol) in THF (170 mL) was dropwise added *n*-butyllithium (121 mL, 1.57 mol L^{-1} in hexane, 190 mmol) at 0 °C under an argon atmosphere, and the mixture was stirred for 30 min at 0 °C. *N*,*N*-Dimethylpropionamide (18.8 mL, 173 mmol) was added to the solution of lithium diisopropylamide at 0 °C, and the reaction mixture was stirred for 1 h at 0 °C. Trimethylsilyl chloride (32.8 mL, 260 mmol) was then added to the reaction mixture at 0 °C. After stirring for 1 h at 0 °C, the entire mixture was filtered and the filtrate was distilled under reduced pressure. The reaction was repeated once again because the purity of the product was 85%. The product of the first reaction (10.4 mL) was added to a solution of lithium diisopropylamide prepared from diisopropylamine (1.71 mL, 12.2 mmol) and *n*-butyllithium (7.77 mL, 1.57 mol L^{-1} in hexane, 12.2 mmol) in THF (54 mL). After stirring for 1 h at 0 °C, trimethylsilyl chloride (2.05 mL, 16.2 mmol) was added. The reaction mixture was directly distilled from the reaction container under reduced pressure to give (*Z*)-DATP as a colorless liquid with a purity of 99%. The stereochemistry of the product was determined by a NOESY measurement as the *Z*-isomer, and the measured spectrum is shown in the Supporting Information (Figure S1). Yield: 6.86 g (22.9%); bp: 68$-$70 °C/54 mmHg. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.19 (s, 9H, $-$Si(CH_3)$_3$), 1.52 (d, J = 6.59 Hz, 3H, $=$CH$-$CH_3), 2.46 (s, 6H, $-$N(CH_3)$_2$), 3.65 (q, J = 6.59 Hz, 1H, $=$C$H$$-CH_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 0.2, 10.9, 40.5, 80.5, 154.7.

Polymerization of DMAA. A typical procedure for the polymerization is as follows: to a solution of DMAA (0.991 g, 10.0 mmol) and (*Z*)-DATP (20.5 μL, 0.10 mmol) in toluene (18.91 mL) was added a stock solution (20 μL, 2.0 μmol) of Tf$_2$NH in CH$_2$Cl$_2$ (0.10 mol L^{-1}) at 0 °C. The polymerization was quenched after 3 h by the addition of a small amount of 2-propanol and pyridine. Aliquots were removed from the reaction mixture to determine the conversion of DMAA from the ^{1}H NMR spectrum. The reaction mixture was dialyzed using a cellophane tube (Spectra/Por 6 Membrane; MWCO: 1000) in methanol and freeze-dried from water to provide the polymer as a white solid. When the molecular weight of the obtained polymer was predicted to be near the cutoff molecular weight of the cellophane tube, reprecipitation from ethanol into hexane was carried out instead of dialysis as an intermediate procedure for the purification of the obtained polymer. Yield: 953 mg (96.2%); M_n = 11.9 kg mol^{-1}, M_w/M_n = 1.11. The polymerization using TBA$-$AcO as a catalyst was carried out using the same procedure. On the other hand, DMAA was added to a solution of (*Z*)-DATP and a catalyst in toluene to start the polymerizations using TAS$-$HF$_2$ or ZnI$_2$ as the catalyst.

Postpolymerization of DMAA. The polymerization of DMAA in toluene at 0 °C was carried out with $[M]_0/[I]_0/[Tf_2NH]_0 = 50/1/0.05$ using the typical procedure for 3 h. Subsequently, the postpolymerization was started by adding 50 equiv of DMAA to the reaction mixture after aliquots were removed from the reaction mixture for determining the conversion of DMAA and the M_n value of the product. After 4 h, the postpolymerization was quenched by adding a small amount of 2-propanol and pyridine. Following purification, the products were same as the typical polymerization of DMAA.

Acknowledgment. We gratefully acknowledge the Global COE Program (Catalysis as the Basis for Innovation in Materials Science) of the Ministry of Education, Culture, Sports, Science and Technology, and Mistubishi Chemical Corporation for their financial support.

Supporting Information Available: NOESY spectrum of (*Z*)-DATP and representative DSC trace of PDMAA. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* **1999**, *32*, 6466–6477.

(2) Kobayashi, M.; Ishizone, T.; Nakahama, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4677–4685.

(3) Kobayashi, M.; Ishizone, T.; Nakahama, S. *Macromolecules* **2000**, *33*, 4411–4416.

(4) Ishizone, T.; Ito, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4328–4332.

(5) Ito, M.; Ishizone, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4832–4845.

(6) Suzuki, T.; Kusakabe, J.; Ishizone, T. *Macromolecules* **2008**, *41*, 1929–1936.

(7) Suzuki, T.; Kusakabe, J.-i.; Kitazawa, K.; Nakagawa, T.; Kawauchi, S.; Ishizone, T. *Macromolecules* **2010**, *43*, 107–116.

(8) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.

(9) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855–2860.

(10) Webster, O. W. *Adv. Polym. Sci.* **2004**, *167*, 1–34.

(11) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473–1488.

(12) Eggert, M.; Freitag, R. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 803–813.

(13) Freitag, R.; Baltes, T.; Eggert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 3019–3030.

(14) Baltes, T.; Garret-Flaudy, F.; Freitag, R. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2977–2989.

(15) Jeong, W.-H.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.

(16) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *J. Am. Chem. Soc.* **2009**, *131*, 3201–3209.

(17) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 5390–5393.

(18) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399–7404.

(19) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5996–6005.

(20) Foropoulos, J.; Desmarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723.

(21) Ishihara, K.; Hiraiwa, Y.; Yamamoto, H. *Synlett* **2001**, 1851–1854.

(22) Hiraiwa, Y.; Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **2006**, *2006*, 1837–1844.

(23) Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744–5758.

(24) Yamamoto, H. *Tetrahedron* **2007**, *63*, 8377–8412.

(25) Kakuchi, R.; Chiba, K.; Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747–8750.

(26) Theoretical molecular weight ($M_{n,theo}$) of PDMAA obtained from Tf_2NH-catalyzed GTP was calculated by the following equation: $M_{n,theo} = [M]_0/([I]_0 - [Tf_2NH]_0) \times \text{conv} \times (\text{MW of DMAA}) + (\text{MW of initiator residue})$. According to the proposed mechanism of polymerization described in ref 25, the silyl enol ether for the initiator must be consumed by the reaction with Tf_2NH to produce the real catalyst, Tf_2NSiMe_3. Thus, $[Tf_2NH]_0$ was subtracted from $[I]_0$ in the equation to obtain the effective concentration of the initiator for the polymerization.

(27) Müller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 87–104.

(28) Bulai, A.; Jimeno, M. L.; Alencar de Queiroz, A.-A.; Gallardo, A.; San Román, J. *Macromolecules* **1996**, *29*, 3240–3246.

(29) Liu, W. H.; Nakano, T.; Okamoto, Y. *Polym. J.* **2000**, *32*, 771–777.

(30) Hirano, T.; Masuda, S.; Nasu, S.; Ute, K.; Sato, T. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1192–1203.

(31) Krause, S.; Gormley, J. J.; Roman, N.; Shetter, J. A.; Watanabe, W. H. *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 3573–3586.

(32) Mohajer, Y.; Wilkes, G. L.; Gia, H.; McGrath, J. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1980**, *21*, 229–230.

(33) Xie, X.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 1746–1752.

(34) Bolig, A. D.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2004**, *126*, 4897–4906.

(35) Mariott, W. R.; Chen, E. Y. X. *Macromolecules* **2005**, *38*, 6822–6832.

(36) Kikuchi, M.; Lien, L. T. N.; Narumi, A.; Jinbo, Y.; Izumi, Y.; Nagai, K.; Kawaguchi, S. *Macromolecules* **2008**, *41*, 6564–6572.