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Strong Brønsted Acid as a Highly Efficient Promoter for Group Transfer Polymerization of Methyl Methacrylate

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ABSTRACT: The Brønsted acid, trifluoromethanesulfonimide ($HNTf_2$), was revealed to act as a highly efficient activator for group transfer polymerization (GTP) of methyl methacrylate (MMA) at ambient temperature. The $HNTf_2$-catalyzed GTP of MMA initiated by 1-methoxy-1-trimethylsilyloxy-2-methyl-propene (MTS) proceeded in a living manner to produce poly(methyl methacrylate)s (PMMA) with controlled molecular weights and narrow molecular weight distributions. Kinetic measurement and post-polymerization experiment further supported that the polymerization proceeded in a living fashion. Furthermore, from the MALDI-TOF MS analysis, only one series of peaks was observed, which was in perfect agreement with the molecular weight of PMMA possessing the MTS initiator residue and the desilylated chain end, showing that the $HNTf_2$-catalyzed GTP of MMA proceeded without any side reactions. The syndiotacticity of the PMMA obtained by the $HNTf_2$-catalyzed GTP increased with the decreasing polymerization temperature; the syndiotactic (*rr*) triad content was 72% at 27 °C and 90% at −55 °C.

Introduction

Group transfer polymerization (GTP), a concept developed by Webster et al.,[1,2] is one of the most important living polymerization methods, and the GTP of (meth)acrylates generally guarantees an excellent molecular weight control even at room temperature.[3−8] Although the GTP process, the numerous iteration of the Mukaiyama−Michael reaction, can be catalyzed by both a Lewis base and Lewis acid, the most efficient GTP catalysts are typically Lewis bases, such as F_2^-,[3] HF_2^-,[3] CN^-,[9,10] N_3^-,[4] and RCO_2^-,[11−14] which are used in a catalytic amount such as a 0.1−1% catalyst loading based on the initiator.[1,2] On the other hand, the catalytic performance of a Lewis acid during the GTP is usually extremely low at a 10−20% catalyst loading based on the monomer requirements.[15] However, $HgI_2/(CH_3)_3SiI$,[16,17] $RAl(OAr)_2/(CH_3)_3SiI$,[18] and $B(C_6F_5)_3/CF_3SO_3Si(CH_3)_3$[19] were exceptionally effective for the acid-catalyzed GTP. In addition, the acid-catalyzed GTP has turned out to be a potentially promising synthetic strategy for stereospecific polymers with an excellent molecular weight control,[20,21] which is an important factor to determine the polymer properties such as the glass transition temperature and melting points. Although the acid-catalyzed GTP is thus expected to provide the simultaneous control of the molecular weight and stereoregularity, the lack of a suitable acid catalyst has prevented us from promoting the stereospecific living polymerization based on the GTP process. Hence, a more effective and versatile acid catalyst for the GTP has been required to overcome the low catalytic performance of the acid catalysis in the GTP process.

When we turn our attention to the recent development in the acid-catalyzed C−C bonding formation reaction, the novel concept of the transition from a Lewis acid to a strong Brønsted acid has been proposed in organic synthesis.[22−26] Yamamoto et al. have shown that the use of trifluoromethanesulfonimide ($HNTf_2$), one of the strong Brønsted acids, could catalyze the Mukaiyama reaction, the elementary GTP reaction, with an extremely high reactivity.[27,28] Very recently, List et al. achieved the asymmetric Mukaiyama aldol reaction using a chiral strong Brønsted acid with a high reactivity and high enantioselectivity.[29] In the $HNTf_2$-mediated reaction, $HNTf_2$ first reacted with organosilicon compounds to afford a strong Lewis acid of R_3SiNTf_2 that was a real catalytic species.[30] Although not only $HNTf_2$, but also CF_3SO_3H, are also well-known strong Brønsted acids, R_3SiNTf_2 is known to provide a higher catalytic performance than $CF_3SO_3SiR_3$.[30] In fact, the $CF_3SO_3SiR_3$-catalyzed GTP was found to lose livingness ($M_w/M_n = 2.35$) and could not produce the perfect conversion of a monomer.[19] Hence, we now aim to establish the acid-catalyzed GTP of methyl methacrylate (MMA) using $HNTf_2$, a strong Brønsted acid (Scheme 1). This article describes (1) the characterization and optimization of the $HNTf_2$-catalyzed GTP of MMA and (2) the mechanistic insight into the $HNTf_2$-catalyzed GTP of MMA.

Results and Discussion

Evaluation and Optimization of the $HNTf_2$-Catalyzed Group Transfer Polymerization of MMA. In order to evaluate the availability of $HNTf_2$ as the acid catalyst for the GTP, we first carried out the polymerization of MMA using 1-methoxy-1-trimethylsilyloxy-2-methyl-propene (MTS) as the initiator in CH_2Cl_2 at various $[MTS]_0/[HNTf_2]_0$ ratios (Table 1, runs 1−4). Surprisingly, MMA was quantitatively consumed at the $[MTS]_0/[HNTf_2]_0$ value of 0.05, which critically differed from that of the GTP of MMA catalyzed by Lewis acid which failed because of its low reactivity. In addition, the polymerization homogeneously proceeded to afford PMMA, whose number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) estimated from SEC using PMMA calibrations were 13 500 and 1.04,

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respectively. The degree of polymerization of the obtained PMMA (DP = 135) was in reasonable correlation with that estimated from the initial ratio of $[MMA]_0/[MTS]_0$ ($DP_{theoretical}$ = 100). This distinct difference is discussed in a later section. In addition, the M_w/M_n value was extremely narrow, indicating that the polymerization occurred in a living fashion. Thus, these results clearly showed that the combination of the organosilane compound and $HNTf_2$ was available for the GTP of MMA. Importantly, just a 5% catalyst loading based on MTS could produce PMMA in high yield, which was in apparent contrast to the conventional Lewis acid-catalyzed GTP that required a 10−20% catalyst loading based on MMA.

To confirm that the polymerization system proceeded in a living fashion, we carried out the GTP of MMA using various ratios of the $[MMA]_0/[MTS]_0$ from 25 to 125 (runs 3 and 5−8). As a direct consequence of the living nature of the $HNTf_2$-catalyzed GTP of MMA, the resultant PMMAs had molecular weights predicted from the value of the $[MMA]_0/[MTS]_0$ (SEC traces of runs 3 and 5−8 are shown in Figure 1).

For further evidence of the living nature of the $HNTf_2$-catalyzed GTP of MMA, we carried out a kinetic investigation and postpolymerization experiments. The kinetic experiments showed a distinct first-order relationship between the reaction time and monomer conversion (Figure 2a). Furthermore, the molecular weight of the obtained PMMA linearly increased with the reaction time and reached complete conversion at 9 h (Figure 2b). In addition, the chain extension experiment produced a PMMA with a molecular weight (run 10) higher than the first PMMA sequence (run 9), showing that the chain end silyl group of the PMMA possessed the truly living nature (SEC traces of the chain extension experiment are shown in Figure 3).

In order to provide a detailed insight into the polymerization reaction, a MALDI-TOF MS measurement was carried out. From the MALDI-TOF MS analysis (Figure 4), only one series of peaks was observed, which was in perfect agreement with the molecular weight of PMMA possessing the MTS initiator residue and the desilylated chain end.

Table 1. GTP of MMA Using Strong Brønsted Acid of $HNTf_2$[a]

run	$[M]_0/[I]_0/[cat.]_0$	time (h)	conv[b] (%)	$M_{n,theor}$[c]	$M_{n,SEC}$[d]	M_w/M_n[d]
1	100/1/0.005	24	0	nd	nd	nd
2	100/1/0.01	24	0	nd	nd	nd
3	100/1/0.05	24	>99	10100	13500	1.04
4	100/1/0.1	24	>99	10100	12800	1.04
5	25/1/0.05	24	>99	2610	3860	1.08
6	50/1/0.05	24	>99	5110	6740	1.06
7	75/1/0.05	24	>99	7610	11200	1.04
8	125/1/0.05	24	>99	12600	17000	1.04
9	50/1/0.05	6	>99	5110	6950	1.06
10	50 + 50/1/0.05	6 + 12	>99	10100	13400	1.06

[a] [M] = 1.0 mol L^{-1}; solvent, CH_2Cl_2; temperature, 27 °C. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0) \times$ conv $\times$ (MW of MMA) + (MW of MTS). [d] Determined by SEC in THF using PMMA standards.

This result means that this strong Brønsted acid-mediated GTP proceeded in a living manner without any side reactions, such as a backbiting reaction. Thus, the strong Brønsted acid, $HNTf_2$, could overcome the low reactivity of the conventional Lewis acid catalyst used in the GTP.

Stereocontrol and Mechanistic Aspect of the $HNTf_2$-Catalyzed Group Transfer Polymerization of MMA. As a

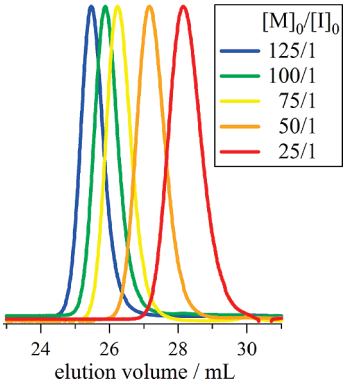


Figure 1. SEC traces of the PMMA (runs 3 and 5−8) (eluent, THF; flow rate, 1.0 mL min^{-1}).

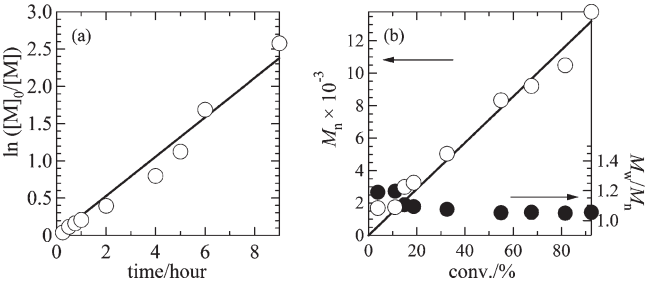


Figure 2. (a) Kinetic plots for the polymerization of MMA and (b) dependence of molecular weight (M_n) and polydispersity (M_w/M_n) on the monomer conversion (conv).

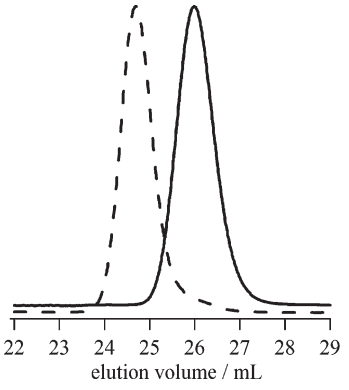
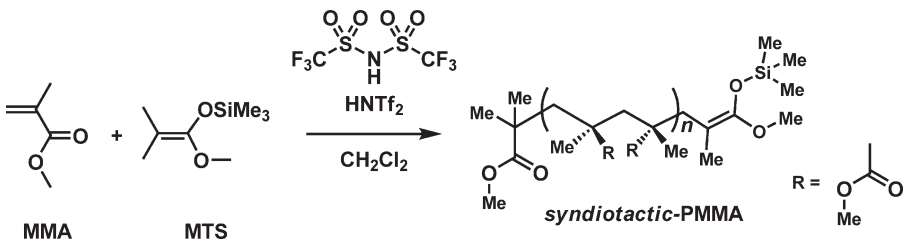


Figure 3. SEC traces of first PMMA sequence (solid line) and postpolymerization (dashed line) (eluent, THF; flow rate, 1.0 mL min^{-1}).

Scheme 1. Schematic Representation of $HNTf_2$-Mediated Group Transfer Polymerization of MMA



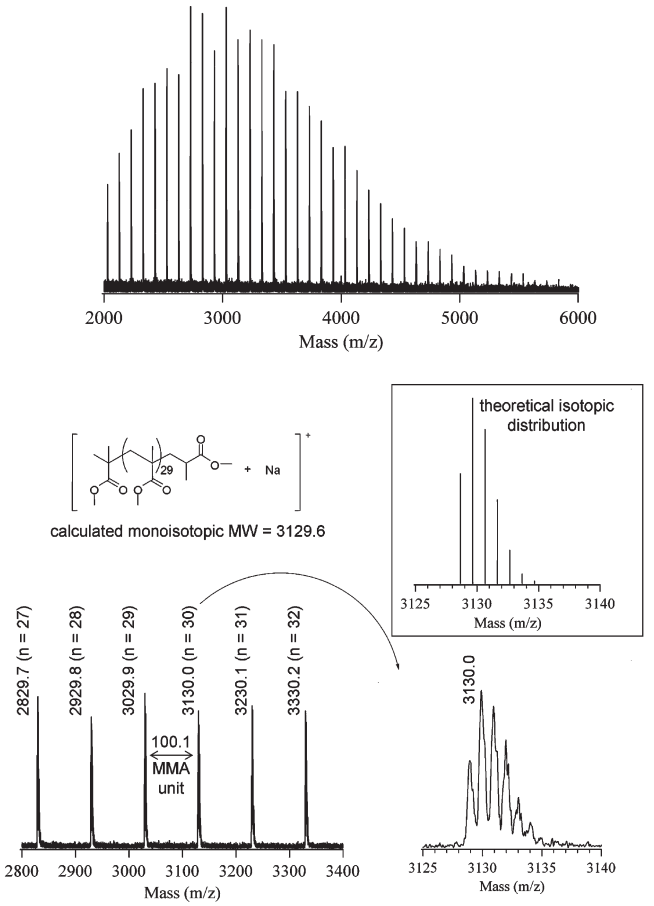


Figure 4. MALDI-TOF MS spectra at reflector mode of the obtained PMMA ($[M]_0/[I]_0/[cat.]_0 = 100/1/0.05$, conversion = 18.8%, $M_{n,SEC}$ = 3250, $M_w/M_n = 1.09$).

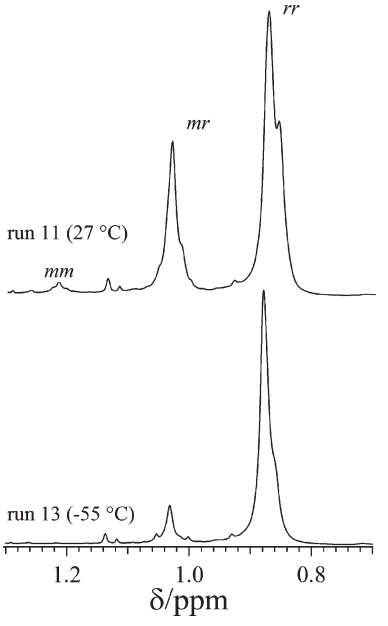


Figure 5. ^{1}H NMR spectra of the PMMAs in $CDCl_3$ at 50 °C (runs 11 and 13).

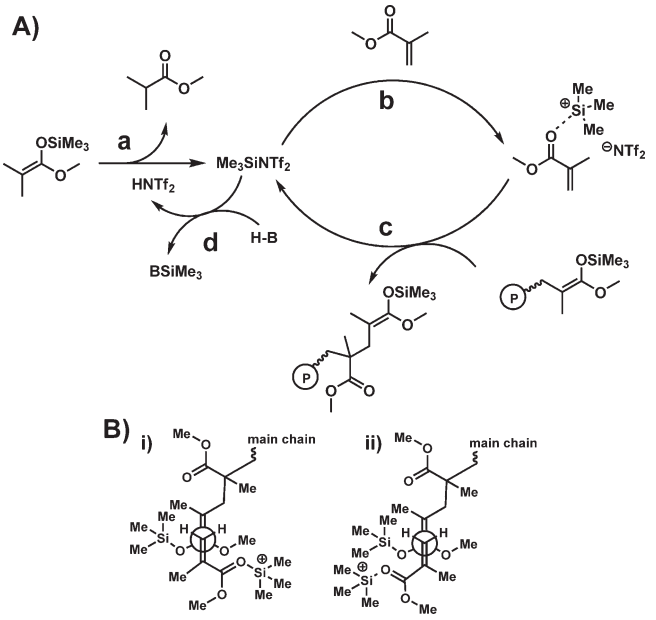
direct advantage of the acid-catalyzed GTP, the produced PMMA was expected to possess a syndiotactic stereoregularity in the polymer backbone (vide supra). The stereoregularity of the obtained PMMA was determined by ^{1}H NMR measurements (Figure 5).[31−33] Table 2 shows the polymerization results and the stereoregularities of the obtained PMMAs synthesized at 27, −40, and −55 °C. As expected, the stereoregularity of the obtained PMMA was syndiotactic even at room temperature (27 °C, *mm*/*mr*/*rr* = 1/27/72). Furthermore, by decreasing the temperature, a higher composition of the syndiotactic sequence was obtained. Importantly, the syndiotactic PMMA obtained at −55 °C showed almost the same stereocontrol as that obtained using *t*-BuLi/AlR_3 at −78 °C,[34] which was one of the most established synthetic pathways for the syndiotactic PMMA except for the transition-metal-catalyzed systems. Thus, we succeeded in synthesizing the sydiotactic PMMA without the aid of transition metals.

Table 2. Stereoregularity of PMMAs Obtained Using Strong Brønsted Acid of $HNTf_2$[a]

run	time (h)	temp (°C)	$M_{n,SEC}$[b]	M_w/M_n[b]	conv[c] (%)	tacticity[d] (%) *mm*	*mr*	*rr*
11	9	27	13800	1.05	92.4	1	27	72
12	72	−40	13300	1.03	97.3	0	13	87
13	168	−55	14000	1.04	>99	0	10	90

[a] [M] = 1.0 mol L^{-1}; solvent, CH_2Cl_2. [b] Determined by SEC in THF using PMMA standards. [c] Determined by ^{1}H NMR spectra in $CDCl_3$. [d] Determined by ^{1}H NMR spectra in $CDCl_3$ at 50 °C.

Scheme 2. Proposed Mechanism (upper) and the Speculation (lower) of the Syndiotactic Control of the Strong Brønsted Acid-Catalyzed Group Transfer Polymerization of Methyl Methacrylate



We next focused on the mechanistic aspects of the living polymerization for the $HNTf_2$-mediated GTP of MMA, as shown in Scheme 2A. We assumed a polymerization mechanism based on the analogy of the principle estimated for the strong Brønsted acid-catalyzed Mukaiyama aldol reaction reported by Yamamoto et al. and List et al.[27−29] First, MTS reacted with $HNTf_2$ to generate the catalytic species of Me_3SiNTf_2 (step a). Furthermore, the $HNTf_2$-mediated reaction is well-known to possess a "self-repair" mechanism (step d), which further consumed MTS to regenerate the catalytic Me_3SiNTf_2 due to the presence of an extremely low amount of impurities. Because the initiator MTS was thus partly consumed in steps a and d, the obtained PMMA always showed a higher molecular weight than that estimated from the initial ratio of $[MMA]_0/[MTS]_0$ (Tables 1 and 2).

Me_3SiNTf_2 then coordinated with MMA to increase the electrophilicity of MMA (step b). Finally, the silyl enolate species attacked MMA (step c) to propagate the PMMA chain, which released the catalyst. A similar mechanism was proposed for trityl tetrakis(pentafluorophenyl)borate-catalyzed GTP of MMA reported by Chen and co-workers.[20,21] Finally, we focused on the mechanistic aspects of the stereospecific polymerization for the $HNTf_2$-mediated GTP of MMA, as shown in Scheme 2B. The steric repulsion between the chain end of PMMA and the incoming monomer was expected to significantly increase (ii) because the carbonyl group of the incoming MMA was expected to coordinate with Me_3SiNTf_2. This steric demand (i) led to the syndiotactic regularity in the PMMA main chain.

Conclusions

Thus, the strong Brønsted acid turned out to be a superior catalyst for the GTP system when compared to conventional Lewis acids, which could easily produce a highly stereocontrolled PMMA with a predictable molecular weight and narrow polydispersity without the aid of heavy metals. To the best of our knowledge, this is the first demonstration of the strong Brønsted acid of $HNTf_2$-catalyzed precise polymer synthesis, which leads to the new concept in synthetic polymer chemistry.

Experimental Section

Materials. Dichloromethane (> 99.5%; water content, < 0.001%) was purchased from the Kanto Chemical Co., Inc., and distilled under an argon atmosphere over CaH_2 and stored under an argon atmosphere. The trifluoromethanesulfonimide ($HNTf_2$) was available from the Sigma-Aldrich Chemicals Co. and used as received. The 1-methoxy-1-trimethylsilyloxy-2-methylpropene (MTS) and methyl methacrylate (MMA) were purchased from the Tokyo Kasei Kogyo Co., Ltd., and used after distillation under reduced pressure (no drying agent for MTS and CaH_2 as drying agent for MMA). For the determination of the stereoregularity of the obtained PMMA, the obtained PMMA was purified using preparative SEC.

Instruments. The ^1H and ^{13}C NMR spectra were recorded using JEOL JNM-A400II and JEOL-ECP-400 instruments. The preparation of 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 size exclusion chromatography (SEC) was performed at 40 °C in THF (1.0 mL min^{-1}) using a Jasco GPC-900 system equipped with set of Waters Ultrastyragel 7 mm columns (linear, 7.8 mm × 300 mm) and two Shodex KF-804 L columns (linear, 8 mm × 300 mm). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a poly(methyl methacrylate) calibration. The preparative SEC was performed in $CHCl_3$ (3.5 mL min^{-1}) at 23 °C using a JAI LC-9201 equipped with a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7×10^4) and a JAI RI-50s refractive index detector. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm nitrogen laser (3 nm pulse width). Two hundred shots were accumulated for the spectra at a 25 kV acceleration voltage at the reflector mode and calibrated using insulin (TAKARA BIO, Inc.) as the internal standard. Samples for the MALDI-TOF MS were prepared by mixing the polymer (10 mg mL^{-1}, 30 μL), the matrix (1,8-dihiydroxy-9(10*H*)-anthracenone, 30 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 30 μL) in THF.

Polymerization of MMA. A typical procedure for the polymerization is as follows: To a CH_2Cl_2 solution (4.2 mL) of MMA (0.50 mL, 4.7 mmol) and MTS (9.5 μL, 47 μmol) was added a CH_2Cl_2 stock solution (24 μL) of $HNTf_2$ (670 μg, 2.4 μmol). The polymerization was quenched after 24 h by the addition of a small amount of methanol. Before the addition of methanol, we gathered a portion of polymerization mixtures for determining the MMA conversion that was directly determined from the ^1H NMR measurements of a portion of polymerization mixtures. The polymer was isolated by reprecipitation from CH_2Cl_2 into hexane. Yield: 430 mg (92.0%); SEC (RI): $M_n = 13\,500$ g mol^{-1}, $M_w/M_n = 1.04$.

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