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ARTICLE

Synthesis of End-functionalized Poly(methyl methacrylate) by Organocatalyzed Group Transfer Polymerization Using Functional Silyl Ketene Acetals and α-Phenylacrylates

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The present study describes the α- and ω-end-functionalization of poly(methyl methacrylate)s (PMMAs) by the organocatalyzed group transfer polymerization (GTP) using both functional silyl ketene acetal (SKA) initiators and α-phenylacrylate terminators. The syntheses of structurally defect-free α-end-functionalized PMMAs with hydroxyl, ethynyl, vinyl, and norbornenyl groups (HO-PMMA, HC≡C-PMMA, H_2C=CH-PMMA, and NB-PMMA, respectively) were achieved by either the *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide-(Me_3SiNTf_2-) or *t*-Bu-P_4-catalyzed GTP of MMA using functional trimethyl SKAs (**1a**-**1d**). On the other hand, the ω-end-functionalized PMMAs with ethynyl, hydroxyl, vinyl, and bromo groups (PMMA-C≡CH, PMMA-OH, PMMA-CH=CH_2, and PMMA-Br, respectively) were for the first time obtained by the Me_3SiNTf_2-catalyzed GTP of MMA followed by a termination reaction using functional α-phenylacylates (**2a**-**2d**). All the polymerizations produced end-functionalized PMMAs with controlled molar masses, narrow dispersities, and defect-free polymer structures as designed. The quantitative incorporation of functionalities into the α- or ω-end of the PMMAs was confirmed by the ^{1}H NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements.

Introduction

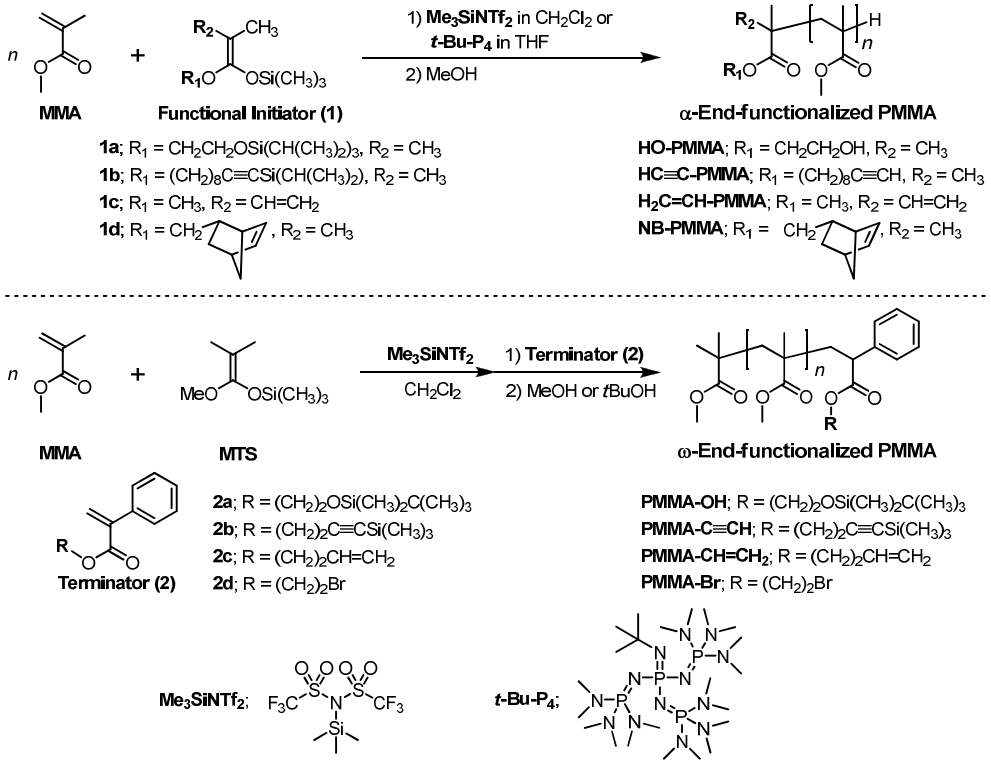
Group transfer polymerization (GTP) as a controlled/living polymerization method was reported more than 30 years ago, as to practically settle the industrial issues of the super-low polymerization temperature required by the anionic polymerization of (meth)acrylates. In principle, the initiation and propagation reactions of GTP are originally rooted in the Mukaiyama-Michael reaction.[1-3] As an indispensable ingredient during the GTP process, a silyl ketene acetal (SKA) with a moderate reactivity was innovatively utilized to replace the extremely reactive lithium enolate as the active center of the anionic polymerization of (meth)acrylates, so that the propagating end of the enolate almost or completely existed in a neutral trialkylsilylated form, mainly depending on the solvent used and the mechanism through which the polymerization undergoes. For precisely this reason, a conventional catalyst of either a nucleophilic anion, such as $SiMe_3F_2^-$,[1, 4-5] HF_2^-,[1, 4-6] or CN^-,[1, 4, 6-7] or a transition metal compound, such as ZnX_2 (X = Cl, Br, and I) [6, 8], was required to activate the SKA for enhancing its nucleophilicity or to activate the carbonyl moiety in the (meth)acrylate for enhancing the electrophilicity of the double bond, thus causing promotion of the repetitive Mukaiyama-Michael reactions between the SKA at polymer end and the monomer. Since Webster first proposed and demonstrated the concept of GTP, many efforts have been devoted to investigating the applicable monomers and catalysts, their optimal combinations, and the applications in the synthesis of well-defined polymers. Overall, the controlled polymerization of methacrylates had been significantly achieved by the GTP using a conventional nucleophilic anion, while that of acrylates was only to some extent realized by the GTP using a conventional transition metal compound.

The recent progress in GTP has been basically related to the application of organocatalysts in this field since 2007.[9] The creative use of organocatalysts has largely improved the livingness of GTP because the basic organocatalysts used, on the one hand, can in a great sense suppress side reactions due to its low nucleophilicity, and the acidic organocatalysts used, on the other hand, significantly enhance the Lewis acidity of the catalyst. For instance, Taton et al. and Waymouth et al. reported that *N*-heterocyclic carbene (NHC) efficiently catalyzed the GTP of both methyl methacrylate (MMA) and *tert*-butyl acrylate in a controlled/living fashion.[10,11] Furthermore, Taton et al. reported the synthesis of block copolymers composed of methacrylates, acrylates, *N,N*-dimethylacrlamide, and methacrylonitrile by the same NHC-catalyzed GTP method,[12,13] which can be hardly achieved by the GTP using a conventional catalyst. Chen et al. reported that

triphenylmethyl tetrakis(pentafluorophenyl)borane promoted the oxidative GTP of alkyl (meth)acrylates, α-methylene-γ-butyrolactone, and γ-methyl-α-methylene-γ-butyrolactone.[14-17] We have also reported the controlled/living GTP using highly strong organic acids and bases as catalysts and appropriate ketene silyl acetals as initiators;[18-23] *e.g.*, trifluoromethanesulfonimide ($HNTf_2$), Me_3SiNTf_2, and the phosphazene base of *t*-Bu-P_4 for methyl methacrylate (MMA) using 1-methoxy-1-trimethylsilyloxy-2-methyl-1-propene (MTS), Me_3SiNTf_2 and 1-[bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene ($C_6F_5CHTf_2$) for methyl acrylate (MA) and *n*-butyl acrylate (*n*BA) using 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene, and $HNTf_2$ for *N,N*-dimethylacrylamide using (*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene.

This study aims at the synthesis of end-functionalized poly(methyl methacrylate) (PMMA) by the organocatalyzed GTP method. It is well known that the synthesis of end-functionalized polymers by the controlled/living polymerizations can be achieved using either functional initiators or terminators, or both. For the GTP using functional initiating agents, Sogah et al. and Bandermann et al. reported the GTPs of MMA initiated by hydroxyl- and cyanide-functionalized SKAs.[6,24] Reetz et al. and Shen et al. reported the GTPs of acrylates using alkylthiosilane and triphenylphosphonium-containing SKAs, which correspondingly produced the hydroxyl- and triphenylphosphonium-terminated polyacrylates.[6,25-31] For the GTP using functional terminating agents, Quirk et al. and Sivaram et al. reported the synthesis of end-functionalized PMMAs with hydroxyl and amino groups using methyl-2-phenylpropenoate and benzaldehyde derivatives, respectively.[27,32,33] Nevertheless, these results based on the GTP using conventional catalysts were insufficient and needed to be improved in terms of the precise polymer synthesis and end-functionalization efficiency (%*F*), and the synthesis of the end-functionalized polyacrylates and polyacrylamides are still remaining tasks for the GTP chemistry. Recently, we reported that α, ω, and α, ω-end-functionalized poly(*n*-butyl acrylate)s (P*n*BAs) were precisely synthesized by the Me_3SiNTf_2-catalyzed GTP using functional triisopropyl SKA initiators and α-phenylacrylate terminators,[34] which afforded quantitative %*F*s. Some functionalities, such as the ethynyl and norbornenyl groups, had been for the first time introduced to the α and ω-ends of P*n*BA in the GTP field. We now report the precise syntheses of α-end-functionalized PMMAs by the Me_3SiNTf_2- and *t*-Bu-P_4-catalyzed GTP using various functional trimethyl SKA initiators (**1a-1d**) and ω-end-functionalized PMMAs using functional α-phenylacrylate terminators (**2a-2d**). It should be highly emphasized that the end-functionalization of PMMA is rather different from that of previously reported P*n*BA because the designed trimethyl SKA initiators for PMMA synthesis have much higher reactivity than those of triisopropyl SKA initiators for P*n*BA synthesis and they are inappropriate for acrylic polymer synthesis; on the other hand, for ω-end-functionalization, the reactivity of the living center at PMMA ω-end is low and totally different from that of a living polyacrylate end, as shown in Scheme 1, which would change the possibility and efficiency of ω-end-functionalization.

Scheme 1. Synthesis of α- and ω-end-functionalized poly(methyl methacrylate) by the organocatalytic GTP using functional silyl ketene acetal initiators and α-phenylacrylate terminators



Experimental Section

Materials. Dichloromethane (CH_2Cl_2, > 99.5%; water content, < 0.001%), toluene (> 99.5%; water content, < 0.001%), tetrahydrofuran (THF, > 99.5%; water content, < 0.001%), *n*-butyllithium (*n*-BuLi, 1.6 mol L^{-1} in *n*-hexane), imidazole (> 98.0%), and triethylamine (> 99.0%) were purchased from Kanto Chemicals Co., Inc. Methyl methacrylate (MMA, > 99.8%), *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2, > 95.0%), isobutyryl chloride (> 98.0%), methyl tiglate (> 98.0%), 9-decyn-1-ol (> 94.0%), *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$), 4-(dimethylamino)pyridine (DMAP, > 99.0%), diisopropylamine (DIPA, > 99.0%), chlorotriisopropylsilane ($^iPr_3SiCl$, > 98.0%), chlorotrimethylsilane (Me_3SiCl, > 98.0%), and sodium hydride (55wt%, dispersion in liquid paraffin) were purchased from Tokyo Kasei Kogyo Co., Ltd. (1*R*, 2*S*, 4*R*)-5-Norbornene-2-carboxylic acid (97%), tetrabutylammonium fluoride (TBAF, 1.0 mol L^{-1} in THF), sodium trifluoroacetate (98%), and DowEX® marathon® MSC (H) ion-exchange resin were purchased from the Sigma-Aldrich Chemicals Co. MMA, methyl tiglate, DIPA, and CH_2Cl_2 were distilled over CaH_2 and degassed by three freeze-pump-thaw cycles prior to use. Me_3SiCl was distilled without using any drying agent and degassed by three freeze-pump-thaw cycles prior to use. Toluene and THF were distilled from sodium benzophenone ketyl. The functional initiators, 1-(2-triisopropylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene (**1a**), 1-(10-trimethylsilyldec-9-yn-1-yloxy)-1-trimethylsiloxy-2-methyl-1-propene (**1b**), 1-methoxy-1-trimethylsiloxy-2-methyl-1,3-butadiene (**1c**), and 1-((1*S*,4*S*)-norborn-5-en-2-ylmethoxy)-1-trimethylsiloxy-2-metylprop-1-ene (**1d**), were synthesized according to a previously reported procedure.[34] The synthetic details of **1a-1d** are described in the Supporting Information (SI). The functional terminators, 2-(*tert*-butyldimethylsiloxy)ethyl 2-phenylacrylate (**2a**), 4-trimethylsilyl-3-butynyl 2-phenylacrylate (**2b**), 3-butenyl 2-phenylacrylate (**2c**), and 2-bromoethyl 2-phenylacrylate (**2d**) were used as reported.[34] All other chemicals were purchased from available suppliers and used without purification.

Measurements. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by a JEOL JNM-A400II. The polymerization solution was prepared in an MBRAUN stainless steel glove-box 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 glove-box were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. Size exclusion chromatography (SEC) measurements for the end-functionalized PMMAs were performed at 40 °C using a Jasco GPC-900 system equipped with a reflective index (RI) detector and two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min^{-1}. The molar mass ($M_{n,SEC}$) and dispersity (M_w/M_n) of the resulting PMMA were determined by the SEC based on PMMA standards with their M_w (M_w/M_n)s of 1.25 × 10^3 kg mol^{-1} (1.07), 6.59 × 10^2 kg mol^{-1} (1.02), 3.003 × 10^2 kg mol^{-1} (1.02), 1.385 × 10^2 kg mol^{-1} (1.05), 60.15 kg mol^{-1} (1.03), 30.53 kg mol^{-1} (1.02), and 11.55 kg mol^{-1} (1.04), 4.90 kg mol^{-1} (1.10), 2.87 kg mol^{-1} (1.06), and 1.43 kg mol^{-1} (1.15). 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 200-500 shots were summed. The spectra were externally calibrated using narrow-dispersed polystyrene as a linear calibration. Samples for the MALDI-TOF MS measurements of the end-functionalized PMMAs were prepared by mixing the polymer (10 mg mL^{-1}, 30 μL), the matrix (1,8-dihydroxy-9-(10*H*)-anthracenone (20 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 30 μL) in THF.

Synthesis of α-End-functionalized PMMA by Me_3SiNTf_2-catalyzed GTP of MMA using Functional Initiators (1a-1d). A typical procedure is as follows: a stock solution of Me_3SiNTf_2 (20 μL, 2.0 μmol, 0.10 mol L^{-1}) was added to the mixtrue of MMA (200 mg, 2.00 mmol) and **1a** (16.0 μL, 40.0 μmol) in CH_2Cl_2 (1.75 mL) under an argon atmosphere at room temperature. After stirring for 4 h, a small amount of methanol was added to quench the polymerization. The crude product was purified by reprecipitation into *n*-hexane to give $^iPr_3SiO$-PMMA as a white solid. The deprotection of the triisopropylsilyl group was implemented for 2 days at room temperature by adding TBAF (0.80 mL (0.80 mmol), 1.0 mol L^{-1} in THF) to a solution of $^iPr_3SiO$-PMMA (180 mg (28.1 μmol), $M_{n,SEC}$ = 6,400 g mol^{-1}, and M_w/M_n = 1.04) in THF (4.0 mL) and methanol (0.1 mL). The mixture was then diluted with THF and passed through a short column of silica gel. The polymer was purified by reprecipitation into *n*-hexane to give HO-PMMA as a white solid; yield, 130 mg (72%). $M_{n,SEC}$ = 5,900 g mol^{-1}, and M_w/M_n = 1.04. The GTPs of MMA using **1b**-**1d** were carried out by a similar method.

Synthesis of ω-End-functionalized PMMA by Me_3SiNTf_2-catalyzed GTP of MMA uisng Functional Terminators (2a-2d). The above described polymerization procedure is applied to the mixture of MMA (0.200 g, 2.00 mmol), MTS (16.2 μl, 80.0 μmol), and Me_3SiNTf_2 (40.0 μl (4.00 μmol), 0.100 mol L^{-1} in CH_2Cl_2) in CH_2Cl_2 (1.73 mL). After 2 h polymerization, **2a** (109 mg, 0.4 mmol) was added and the entire mixture was further stirred for 24 h. The polymer was purified by reprecipitation into *n*-hexane to give the PMMA-C≡$CSiMe_3$ as a white solid; yield, 190 mg (95%), $M_{n,SEC}$ = 3,460 g mol^{-1}, and M_w/M_n = 1.07. The GTPs of MMA using **2b**-**2d** as terminators were carried out by the same method.

Results and discussion

Synthesis of Hydroxyl, Ethynyl, Vinyl, and Norbornenyl α-End-functionalized PMMA. The functional trimethylsilyl ketene acetals (**1a-1d**) were synthesized by a conventional method using lithium diisopropylamide (LDA). Their synthetic details are rather similar to those for synthesizing functional triisopropylsilyl ketene acetals in our previous study.[34] **1a**, **1b**, and **1d** were prepared by reacting their precursors of the functional isobutyrates with LDA followed by Me_3SiCl, while **1c** was synthesized by treating methyl tiglate with LDA and then Me_3SiCl. All the functional initiators

Table 1. Synthesis of hydroxyl, ethynyl, vinyl, and norbornenyl □-end-functionalized PMMAs using **1a**, **1b**, **1c**, and **1d** [a]

Run	Initiator (I)	Catalyst	$[MMA]_0/[I]_0$	Time (h)	$M_{n,calcd}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	M_w/M_n [c]
1	**1a**	Me_3SiNTf_2	25	2	2,700	3,300	1.08
2	**1a**	Me_3SiNTf_2	50	4	5,100	5,900	1.04
3	**1a**	Me_3SiNTf_2	100	16	10,100	10,200	1.03
4	**1a**	*t*-Bu-P_4	200	1	20,300	22,300	1.07
5	**1a**	*t*-Bu-P_4	400	1	40,300	48,400	1.18
6	**1b**	Me_3SiNTf_2	25	2	2,700	3,800	1.07
7	**1b**	Me_3SiNTf_2	50	5	5,200	6,500	1.04
8	**1b**	Me_3SiNTf_2	100	18	10,200	11,900	1.02
9	**1b**	*t*-Bu-P_4	200	1	20,300	22,300	1.07
10	**1b**	*t*-Bu-P_4	400	1	40,300	49,200	1.12
11	**1c**	Me_3SiNTf_2	25	4	2,600	4,500	1.08
12	**1c**	Me_3SiNTf_2	50	17	5,100	7,800	1.06
13	**1c**	Me_3SiNTf_2	100	19	10,000	13,900	1.05
14	**1c**	*t*-Bu-P_4	200	1	20,100	25,100	1.14
15	**1c**	*t*-Bu-P_4	400	1	40,100	42,200	1.22
16	**1d**	Me_3SiNTf_2	25	2	2,700	3,400	1.08
17	**1d**	Me_3SiNTf_2	50	5	5,200	6,000	1.04
18	**1d**	Me_3SiNTf_2	100	18	10,200	11,800	1.03
19	**1d**	*t*-Bu-P_4	200	1	20,200	20,300	1.05
20	**1d**	*t*-Bu-P_4	400	1	40,200	40,700	1.13

[a] Argon atmosphere; solvent, CH_2Cl_2 (Me_3SiNTf_2) or THF (*t*-Bu-P_4); $[MMA]_0$ = 1.0 mol L^{-1}; $[Me_3SiNTf_2]_0/[I]_0$ = 0.05 or $[t\text{-Bu-}P_4]_0/[I]_0$ = 0.01; temperature, room temp.; monomer conversion determined by ^{1}H NMR in $CDCl_3$, > 99 %. [b] Calculated by $[MMA]_0/[I]_0$ × conv. × (M. W. of MMA: 100.12) + (M. W. of initiator residue: **1a** = 132.16, **1b** = 224.34, , **1c** = 114.14, and **1d** = 194.27). [c] Determined by SEC in THF using PMMA standards.

were purified by distillation under reduced pressure and stored under an argon atmosphere prior to use. The group transfer polymerization (GTP) of methyl methacrylate (MMA) using **1a**, **1b**, **1c**, and **1d** as initiators was carried out to synthesize the hydroxyl, ethynyl, vinyl, and norbornenyl α-end-functionalized poly(methyl methacrylate)s (HO-PMMA, HC≡C-PMMA, H_2C=CH-PMMA, and NB-PMMA), respectively. We previously reported that Me_3SiNTf_2 was a significant catalyst for the synthesis of the low molar mass PMMA,[18] while *t*-Bu-P_4 was more favorable for the synthesis of the high molar mass PMMA.[22] Me_3SiNTf_2 and *t*-Bu-P_4 were thus correspondingly utilized in this study to realize the synthesis of both the low and high molar mass α-end-functionalized PMMAs. Table 1 summarizes the results of the polymerizations. All the polymerizations of MMA, either using Me_3SiNTf_2 or *t*-Bu-P_4, proceeded in quantitative monomer conversion manner within the fixed polymerization time. The α-end-functionalized PMMAs prepared with **1a** and **1b** were treated by tetra-*n*-butylammonium fluoride (TBAF) in order to remove the trialkylsilyl protection moieties. The Me_3SiNTf_2-catalyzed GTPs of MMA at the low initial $[MMA]_0/[I]_0$ ratios of 25, 50, and 100 (Runs 1-3, 6-8, 11-13, and 16-18) were well controlled no matter which initiator was used, i.e., the molar mass of each α-end-functionalized PMMA estimated by SEC ($M_{n,SEC}$) was in good agreement with its calculated value ($M_{n,calcd}$); all the dispersities (M_w/M_n) were narrower than 1.08; and the SEC traces of all polymer products in Figure 1 showed unimodal and extremely narrow dispersities. On the other hand, the *t*-Bu-P_4-catalyzed GTPs of MMA at the relatively high initial $[MMA]_0/[I]_0$ ratios of 200 and 400 (Runs 4-5, 9-10, 14-15, and 19-20) produced α-end-functionalized PMMAs with their $M_{n,SEC}$s ranging from 20,000 to 50,000 g mol^{-1} though the M_w/M_ns were slightly greater than those prepared by Me_3SiNTf_2.

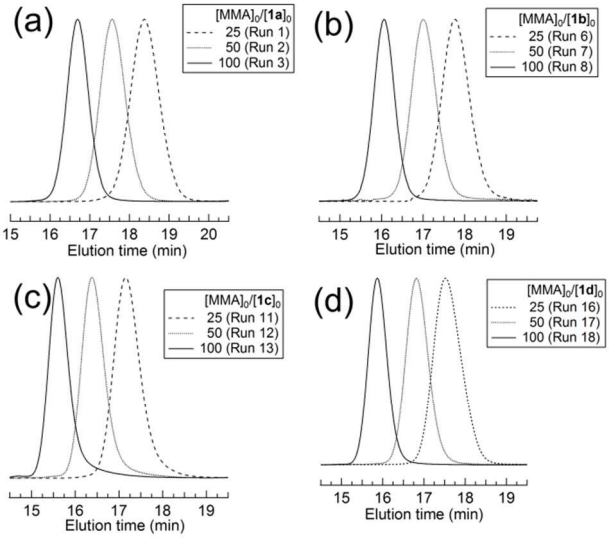


Figure 1. SEC traces of (a) HO-PMMA (Runs 1-3), (b) HC≡C-PMMA (Runs 6-8), (c) H_2C=CH-PMMA (Runs 11-13), and (d) NB-PMMA (Runs 16-18) synthesized by Me_3SiNTf_2-catalyzed GTP.

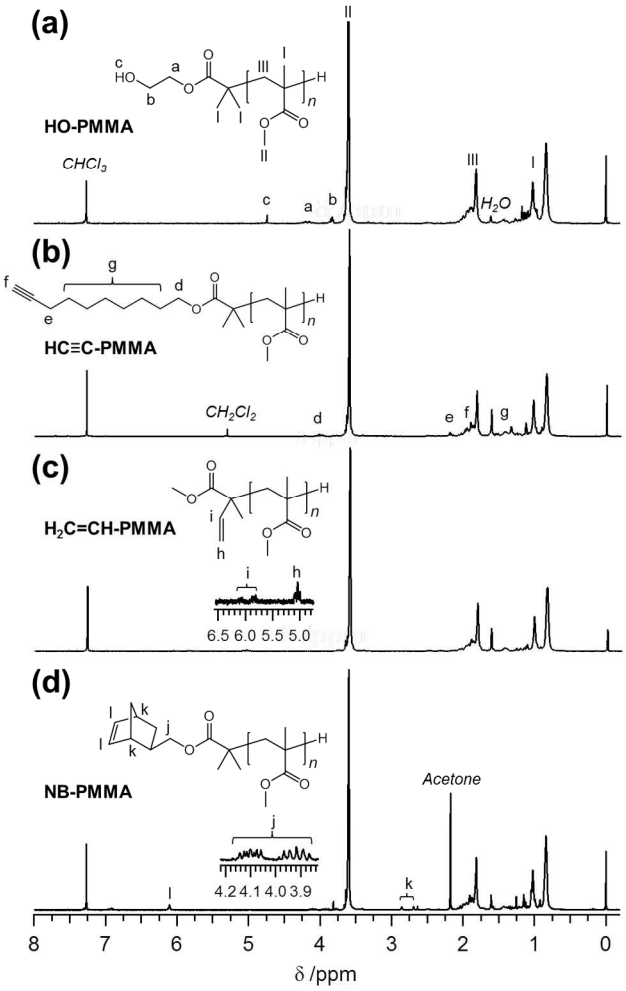


Figure 2. ^{1}H NMR spectra of (a) HO-PMMA (Run 1, $M_{n,SEC}$ = 3,300 g mol^{-1}, M_w/M_n = 1.08), (b) HC≡C-PMMA (Run 6, $M_{n,SEC}$ = 3,800 g mol^{-1}, M_w/M_n = 1.07), (c) H_2C=C-PMMA, (Run 11, $M_{n,SEC}$ = 4,500 g mol^{-1}, M_w/M_n = 1.08), and (d) NB-PMMA, (Run 16, $M_{n,SEC}$ = 3,400 g mol^{-1}, M_w/M_n = 1.08).

The introduction of hydroxyl, ethynyl, vinyl, and norbornenyl functionalities to the α-end of PMMA was initially investigated by ^{1}H NMR measurements, as shown in Figure 2. The characteristic signals were clearly observed around 3.80 - 4.30 ppm due to the -C*H*$_2$O$_2$C- protons of the residues of **1a**, **1b**, and **1d** at the α-ends of PMMAs, while those appeared at 4.95 - 5.15 ppm and 5.75 - 6.15 ppm for the vinyl protons derived from the residue of **1c**, together with those from the PMMA main chain at 3.62 ppm, 2.10-1.75 ppm, and 1.02 ppm. In order to clarify the chemical constitution of the resulting α-end-functionalized PMMAs, the matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) measurements for each type of α-end-functionalized PMMA were implemented using a low molar mass polymer, as shown in Figures 3(a)-(d). For each of the MALDI-TOF MS spectra of (a) HO-PMMA, (b) HC≡C-PMMA, and (c) H_2C=CH-PMMA, only one population of molecular ion peaks was observed. The interval between two neighboring molecular ion peaks was ca. 100.02, which was very consistent with the exact molar mass of the repeating MMA unit (M.W. = 100.05). In addition, the *m*/*z* values of the observed molecular ion peaks for each α-end-functionalized PMMA corresponded to their calculated molar masses when the α-end possessed an initiator residue; for example, the observed values of 2656.71 (a), 2748.01 (b), and 2638.14 (c) agreed with the calculated values of 2656.38, 2748.48, and 2638.37 for the sodium-cationized 25-mer structures of $[HO(CH_2)_2O_2CCMe_2\text{-}(MMA)_{25}\text{-}H + Na]^+$, $[HC{\equiv}C(CH_2)_8O_2CCMe_2\text{-}(MMA)_{25}\text{-}H + Na]^+$, and $[MeO_2CCMe(HC{=}CH_2)\text{-}(MMA)_{25}\text{-}H + Na]^+$, respectively. On the contrary, the MALDI-TOF MS spectrum of NB-PMMA showed two populations of molecular ion peaks. The values of the molecular ion peaks in the main population corresponded to the calculated molar mass values of the sodium-cationized NB-PMMA, $[NBCH_2O_2CCMe_2\text{-}(MMA)_n\text{-}H + Na]^+$. Those of the sub population, on the other hand, were assigned to the sodium-cationized structure of $[H_2C{=}CHCH_2O_2CCMe_2\text{-}(MMA)_n\text{-}H + Na]^+$, which was regenerated during the cationization process due to the retro Diels-Alder reaction. The α-end-functionalization efficiency (%*F*) of the obtained PMMAs, which was directly estimated from the MALDI-TOF MS measurements, was determined to be quantitative (> 99%), which indicated the quantitative introduction of functionalities to the α-end of PMMA using the functional initiators.

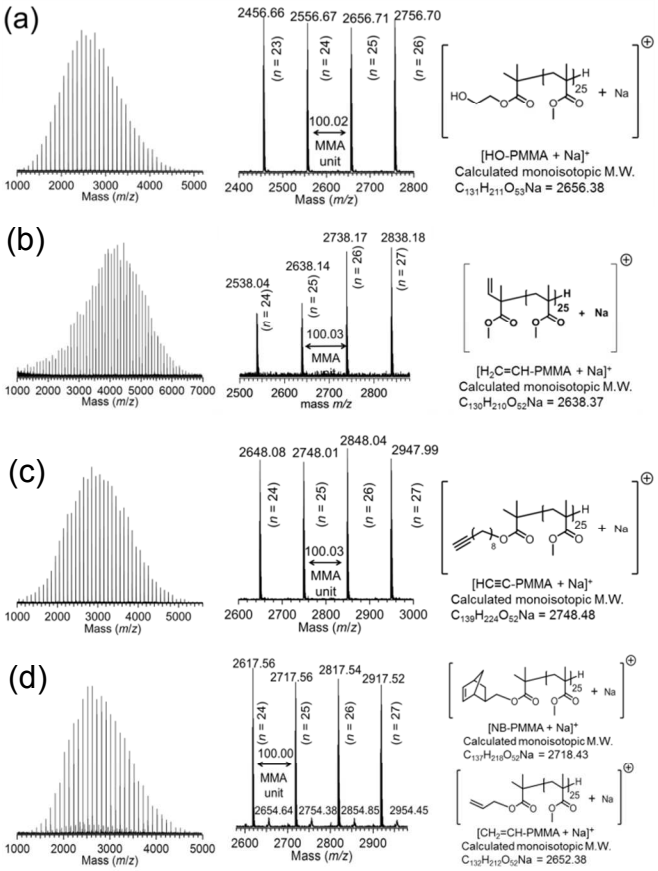


Figure 3. MALDI-TOF MS spectra of (a) HO-PMMA (Run 1, $M_{n,SEC}$ = 3,300 g mol^{-1}, M_w/M_n = 1.08), (b) HC≡C-PMMA (Run 6, $M_{n,SEC}$ = 3,800 g mol^{-1}, M_w/M_n = 1.07), (c) H_2C=CH-PMMA, (Run 11, $M_{n,SEC}$ = 4,500 g mol^{-1}, M_w/M_n = 1.08), and (d) NB-PMMA, (Run 16, $M_{n,SEC}$ = 3,400 g mol^{-1}, M_w/M_n = 1.08).

Synthesis of Hydroxyl, Ethynyl, Vinyl, and Bromo ω-End-functionalized PMMA. In addition to the α-end-functionalization, the ω-end-functionalization of PMMA by the Me_3SiNTf_2-catalyzed GTP using functional terminators was also attempted. In order to find a suitable terminator, five potential candidates, methyl α-phenylacrylate (αPhA-Me), dimethyl itaconate (DMI), bezaldehyde (BA), ethyl ethylacrylate (EEA), and *N*,*N*-dimethyl methacrylamide (DMMAm), were initially used to investigate their suitability, as shown in Scheme 2. Followed by the quantitative polymerization of 25 equiv. MMA, the termination reaction was carried out for 24 h with the addition of an excessive quantity of a terminator. Table 2 summarizes the polymerization and ω-end-functionalization results. All the polymerizations (Runs 21-25) produced well-defined PMMAs with the targeted molar mass and extremely narrow dispersity. For the %*F*, a quantitative value (> 99%) was only achieved when αPhA-Me was used (Run 21). High %*F*s of 92.1% and 78.6% were also attained with DMI (Run 22) and BA (Run 23), respectively. On the contrary, only the moderate %*F* of 46.9% was obtained using EEA (Run 24) and absolutely no end-functionalized product was obtained using DMMAm (Run 25). The termination behavior using these potential terminators was further investigated by MALDI-TOF MS measurements, as shown in Figure S1. The MALDI-TOF MS spectrum of the αPhA-Me terminated PMMA only showed one population of molecular ion peaks. In addition, the value of each ion peak could be perfectly assigned to a PMMA possessing a MTS residue at the α-end, a specified degree of polymerization (DP) of MMA, and a reacted αPhA-Me residue at the ω-end, strongly suggesting the quantitative ω-end-functionalization by αPhA-Me. When using DMI, the MALDI-TOF MS spectrum exhibited three populations of molecular ion peaks. The two main populations of ion peaks corresponded to the ω-end-functionalized products with DMI, in which one population was attributed to the desilylated DMI ω-end-functionalized products and the other was the silylated ones. The sub ion peaks were assigned to the hydrogen ω-end-functionalized PMMA products, which were obtained after quenching by alcohol. Obviously, no DMI functionality was bonded to their ω-ends at all for the PMMA products due to the sub ion peaks. When using BA, a similar ion peak distribution to that of DMI was observed in its MALDI-TOF MS spectrum. Different from DMI and BA, termination using EEA resulted in three types of products, i.e., the products with ω-end-functionalized by EEA, two EEAs, and hydrogen. The targeted product with ω-end-functionalized by EEA only had a 46.9% content. In the case when using DMMAm, only the ion peaks of the hydrogen ω-end-functionalized PMMAs were observed in its MALDI-TOF MS spectrum, indicating that DMMAm could not react with the living propagation end of PMMA at all. It seems that the %*F* was significantly dependent on the chemical structure of the used terminator. For instance, αPhA-Me with an electron-delocalized phenyl group at the α position was highly favorable for the electrophilic reaction with the living PMMA chain end of a SKA moiety as the active center. DMI and EEA with electron-donating alkyl groups at the α position, on the other hand, showed a less efficient electrophilicity toward the SKA group at the PMMA chain end. DMMAm with a low monomer reactivity did not react with the SKA group at all.

Scheme 2. Potential terminators for the Me_3SiNTf_2-catalyzed GTP of MMA

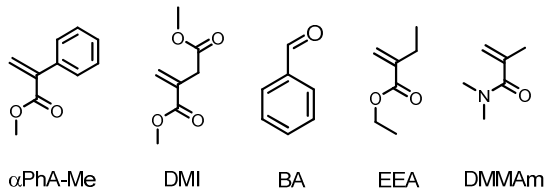


Table 2. Termination reaction using αPhA-Me, DMI, BA, EEA, and DMMAm followed by Me_3SiNTf_2-catalyzed GTP of MMA [a]

Run	Terminator (T)	$[T]_0/[I]_0$	$M_{n,SEC}$ [b]	M_w/M_n [b]	%*F* [c]
21	αPhA-Me	5	3,470	1.07	>99
22	DMI	5	3,350	1.07	92.1
23	BA	5	3,440	1.09	78.6
24	EEA	10	3,540	1.07	46.9
25	DMMAm	5	3,100	1.08	0

[a] Ar atmosphere; $[M]_0$ = 1.0 mol L^{-1}; Initiator, MTS; Catalyst, Me_3SiNTf_2; $[M]_0/[I]_0/[Cat.]_0$ = 25/1/0.05; solvent, CH_2Cl_2; polymerization time, 2 h; termination time, 24 h; polymerization temperature, room temp.; MMA conversion determined by ^1H NMR in $CDCl_3$, > 99%. [b] Determined by SEC in THF using PMMA standards. [c] End-functionalization efficiency estimated by intensity of ion peaks in MALDI-TOF MS spectrum.

Since αPhA-Me was the most efficient terminator for the Me_3SiNTf_2-catalyzed GTP of MMA, four functional α-phenylacrylates, **2a**-**2d**, were correspondingly used for synthesizing the ethynyl, hydroxyl, vinyl, and bromo ω-end-functionalized PMMAs (PMMA-C≡CH, PMMA-OH, PMMA-CH=CH_2, and PMMA-Br). After a 2 h polymerization of MMA in CH_2Cl_2, the termination reaction was further carried out for 24 h by adding an excessive amount of a terminator to the polymerization mixture. All the polymerizations (Runs 26-29) had a quantitative monomer conversion and produced PMMAs with the targeted molar mass around 3,000 g mol^{-1} and dispersity narrower than 1.07. The %*F*, as estimated by the ^1H NMR measurements, was >99% no matter which functional α-phenylacrylate was used. The existence of these functionalities at the ω-end of PMMA was confirmed by ^1H NMR and MALDI-TOF MS measurements. As shown in the ^1H NMR spectra (Figure S2), the characteristic signals belonging to the residues of **2a**-**2d** were simultaneously observed at 0.11 - 0.15, 4.01 - 4.15, and 7.18 ~ 7.33 ppm due to the $Si(CH_3)_3$, -CH_2O_2C-, and aromatic *H* of **2a**, at 4.03 - 4.08 and 7.17 ~ 7.32 ppm due to the -CH_2O_2C- and aromatic *H* of **2b**, at 3.99 - 4.15, 5.65 - 5.82, 4.94 - 5.10, and 7.22 ~ 7.42 ppm due to the -CH_2O_2C-, -CH=CH_2, -C*H*=CH_2, and aromatic *H* of **2c**, and at 4.26 - 4.47 and 7.23 ~ 7.40 ppm due to the -CH_2O_2C- and aromatic *H* of **2d**, respectively, together with the proton signals of the PMMA main chain at 0.77 - 1.25, 1.76 - 2.09, and 3.54 - 3.69 ppm. In the MALDI-TOF MS spectra shown in Figure 4, each of the spectra showed only one population of ion peaks with the interval between two neighboring ion peaks being around 100.05 (exact molar mass of MMA unit). In

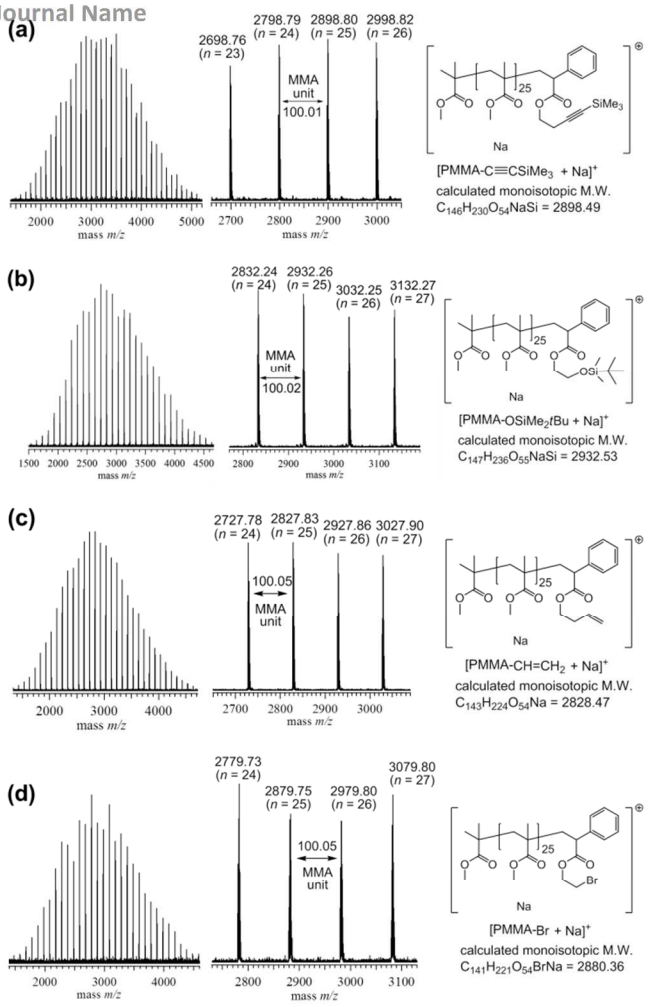


Figure 3. MALDI-TOF MS spectra of (a) PMMA-C≡CSiMe$_3$ (Run 26, $M_{n,SEC}$ = 3,460; M_w/M_n = 1.07), (b) PMMA-OSiMe$_2$*t*Bu (Run 27, $M_{n,SEC}$ = 3,250; M_w/M_n = 1.06), (c) PMMA-CH=CH$_2$ (Run 28, $M_{n,SEC}$ = 3,730; M_w/M_n = 1.07), and (d) PMMA-Br (Run 29, $M_{n,SEC}$ = 3,690; M_w/M_n = 1.07).

addition, no matter which functional α-phenylacrylate was used, the *m*/*z* value of each ion peak perfectly corresponded to the polymer product which was composed of an MTS residue at the α-end, specified MMA units in the main chain, and a reacted residue of a functional α-phenylacrylate at the ω-end. For instance, the determined *m*/*z* values of the sodium-cationized 25-mer PMMA-C≡CSiMe$_3$, PMMA-OSiMe$_2$*t*Bu, PMMA-C=CH$_2$, and PMMA-Br were 2898.80, 2932.26, 2827.83, and 2879.75, respectively, which fairly agreed with their theoretical monoisotopic molar masses of 2898.49, 2932.53, 2828.47, and 2880.36, respectively, when they had the predicted sodium-cationized 25-mer structures of [MeO$_2$CCMe$_2$-MMA$_{25}$-CH$_2$CHPhCCO$_2$(CH$_2$)$_2$C≡CSiMe$_3$ + Na]$^+$, [MeO$_2$CCMe$_2$-MMA$_{25}$-CH$_2$CHPhCCO$_2$(CH$_2$)$_2$OSiMe$_2$*t*Bu + Na]$^+$, [MeO$_2$CCMe$_2$-MMA$_{25}$-CH$_2$CHPhCCO$_2$(CH$_2$)$_2$CH=CH$_2$ + Na]$^+$, and [MeO$_2$CCMe$_2$-MMA$_{25}$-CH$_2$CHPhCCO$_2$(CH$_2$)$_2$Br + Na]$^+$, respectively. These results provided definitive proof to support the fact that the functional α-phenylacrylate was stoichiometrically bonded to the PMMA ω-end after the termination reaction.

Table 3. Synthesis of ω-end-functionalized PMMAs by Me$_3$SiNTf$_2$-catalyzed GTP of MMA using functional α-phenylacylates (**2a**-**ad**) [a]

Run	Terminator (T)	$M_{n,cald.}$ [b]	$M_{n,SEC}$ [c]	M_w/M_n [c]	%F [d]
26	**2a**	2,900	3,460	1.07	>99
27 [e]	**2b**	2,930	3,250	1.06	>99
28	**2c**	2,830	3,730	1.07	>99
29	**2d**	2,880	3,690	1.07	>99

[a] Ar atmosphere; $[M]_0$ = 1.0 mol L^{-1}; $[MMA]_0/[MTS]_0/[Me_3SiNTf_2]_0$ = 25/1/0.05; $[T]_0/[MTS]_0$ = 5; Solvent, CH_2Cl_2; polymerization temperature, room temp.; polymerization time, 2 h; termination time, 24 h; MMA conversion (conv.) determined by ^{1}H NMR in $CDCl_3$, > 99%. [b] Calculated by $M_{n,cald} = [MMA]_0/[I]_0 \times$ conv. × (M. W. of MMA: 100.12) + (M. W. of initiator residue: 101.12) + (M. W. of terminator residue: **2a** = 272.41, **2b** = 306.47, , **2c** = 202.25, and **2d** = 255.11) × %F. [c] Determined by SEC in THF using PMMA standards. [d] End-functionalization efficiency determined by ^{1}H NMR in acetone-d_6. [e] Terminated by ^{t}BuOH instead of MeOH.

Conclusion

The α-end-functionalized PMMAs with hydroxyl, ethynyl, vinyl, and norbornenyl groups were obtained with targeted molar masses up to 50,000 g mol^{-1}, dispersities narrower than 1.22, and defect-free polymer structures by either the Me$_3$SiNTf$_2$- or *t*-Bu-P$_4$-catalyzed GTPs using newly designed functional SKAs as the initiators. The quantitative ω-end-functionalization of PMMA by the Me$_3$SiNTf$_2$-catalyzed GTP, on the other hand, succeeded for the first time using α-phenylacrylate terminators. The quantitative incorporation of ethynyl, hydroxyl, vinyl, norbornenyl, and bromo functionalities into either the α- or ω-end of PMMA was significantly supported by the MALDI-TOF MS measurements. This study provides a facile method for end-functionalization by the organocatalyzed GTP procedure. These reactive functionalities at the polymer ends are of great significance to do further chemical conversions into other functional moieties, such as bioactive peptides and fluorescent dyes, and to serve as polymeric precursors for constructing polymethacrylate-based complicated polymer architectures, such as block copolymers, star-shaped polymers, and graft copolymers.

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† Electronic Supplementary Information (ESI) available: The synthetic details of functional isobutyrates, ^{1}H NMR and MALDI-TOF MS spectra of the end-functionalized PMMAs are available. See DOI: 10.1039/b000000x/

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For Table of Contents Graphical Abstract Use Only

Synthesis of End-functionalized Poly(methyl methacrylate) by Organocatalyzed Group Transfer Polymerization Using Functional Silyl Ketene Acetals and α-Phenylacrylates

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The α and ω-end-functionalization of poly(methyl methacrylate) by organocatalyzed group transfer polymerization was achieved using functional silyl ketene acetal initiators and α-Phenylacrylate terminators.