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ARTICLE

Synthesis of AB Block and A_2B_2 and A_3B_3 Miktoarm Star-shaped Copolymers Using ω-End-functionalized Poly(methyl methacrylate) with A Hydroxyl Group Prepared by Organocatalyzed Group Transfer Polymerization

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The synthesis of miktoarm star-shaped polymers has been studied using various poly(methyl methacrylate)s (PMMAs) functionalized with a hydroxyl group, which were prepared by organocatalyzed group transfer polymerization (GTP) of methyl methacrylate, followed by Mukaiyama aldol-type termination of a silyl ketene acetal (SKA) moiety at the living PMMA end. To further elucidate this method, the effects of the employed catalysts, polymer chain length, and benzaldehyde derivatives on the ω-end-functionalization efficiency (%*F*) were investigated in detail. The electrophilic termination of the living PMMA end with benzaldehyde as the terminator produced a structurally defect-free ω-end-functionalized PMMA with a hydroxyl group (PMMA-OH). In addition, a two-arm PMMA with two hydroxyl groups ($PMMA_2$-OH_2) and a three-arm star-shaped PMMA with three hydroxyl groups ($PMMA_3$-OH_3), whose hydroxyl groups were located at the polymer chain centers, were prepared using terepthalaldehyde and benzene-1,3,5-tricarbaldehyde, respectively. The PMMA-OH, $PMMA_2$-OH_2, and $PMMA_3$-OH_3 obtained were then used as macroinitiators for the ring-opening polymerization (ROP) of D-lactide (DLA) to synthesize an AB block, A_2B_2 and A_3B_3 type miktoarm copolymers.

Introduction

A most significant advance in polymer chemistry in recent years has been based on employing concepts and tools in organic chemistry to construct complex macromolecular architectures at the molecular level.[1] Synthesis of new materials with improved properties and applications is still an intense and challenging area for polymer science and the advent of modern synthetic methods has paved the way for new opportunities in the preparation of well-defined polymeric materials.[2,3,4] Among these materials, end-functionalized polymers are receiving considerable attention due to their wide applications, such as compatibilizing agents for polymer processing, macromolecular surfactants, surface modifiers, and carriers in drug delivery systems.[5-8,9] In addition, they are used as precursors for preparing structurally complex macromolecular architectures and intelligent network structures.[10] To achieve the synthesis of end-functionalized polymers, polymer chemists have widely adopted various synthetic techniques typically employed in the synthesis of small organic molecules.[3]

End-functionalized polymers are mostly synthesized using controlled/living polymerizations methods, such as living radical and anionic polymerizations,[11-13,14] *i.e.*, the α-, ω-, and α,ω-end functionalization are achieved using functional initiators, terminators, and both, respectively. For quantitative α- and ω-end functionalization, quantitative initiation by functional initiators is required for the introduction of functional groups at the α-end of polymers, as well as to maintain the livingness of polymers prior to quantitative termination at the ω-end of polymers. For preparing the desired type of polymer main-chain and targeted end-functional groups, it is important to choose a suitable living polymerization method along with the functional initiators and terminators that are appropriately designed and synthesized in consideration of the selected living polymerization type.[10] Among the various living polymerizations, living anionic polymerization is a more credible method of introducing functional groups into the α-, ω-, and α,ω-ends of polymers compared to living radical polymerization method. Thus, we have focused on the group transfer polymerization (GTP) of acrylic monomers, one of the important

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living anionic polymerizations methods, which proceeds through numerous iterations of the Mukaiyama-Michael reaction between the propagating polymer chain end and a monomer.[16] During the GTP process, a silyl ketene acetal (SKA) group as the propagating end is one of the typical reactants for the Mukaiyama-Michael reaction with α,β-unsaturated ketones and the Mukaiyama aldol reaction with aldehydes. The α-end-functionalization by the GTP was reported using functional initiators that generally required the protection of the functional groups due to their high reactivity toward the SKA end groups of the polymers. For instance, α-end-functionalized poly(meth)acrylates with hydroxyl,[17] carboxylic acid,[17] cyanide,[17,18] alkylthio,[19,20] triphenylphosphonium,[19,20] and phenol [21] groups were prepared by the GTP using appropriately protected initiators.

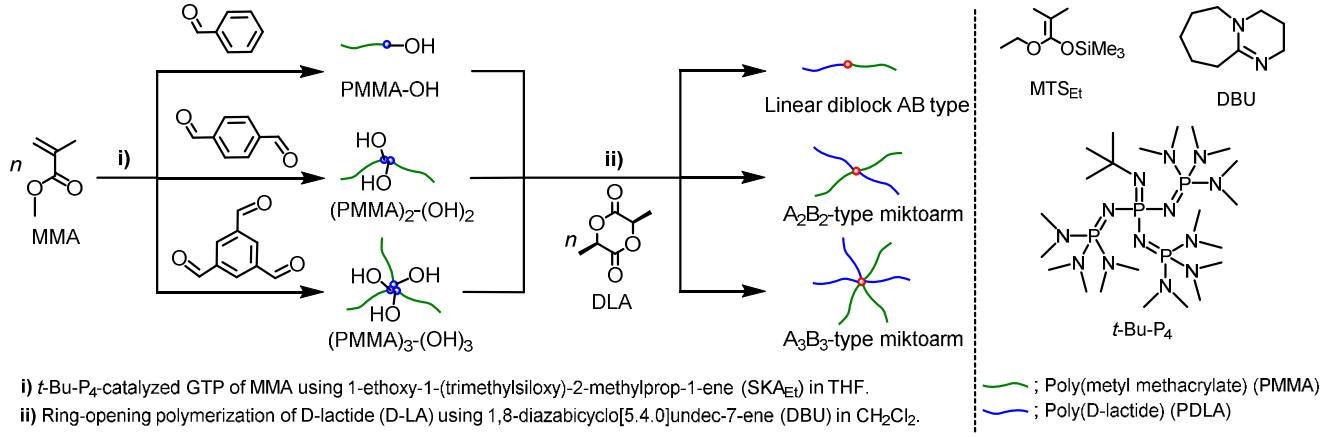
On the contrary, the ω-end-functionalization by the GTP has not been sufficiently realized even though various types of terminators have been examined. For example, Sogah et al. synthesized end-functionalized PMMAs with the bromo and vinylphenyl groups by the termination reaction using bromine/*N*-bromosuccinimide and 4-(bromomethyl)styrene, respectively.[22-24] Webster et al. reported the synthesis of the ω-end-functionalized PMMAs with the phosphonate group using diethyl vinylphosphonate and bis(trymethylilyl) vinylphosphonate as terminating agents.[25] Quirk et al. and Sivaram et al. reported the synthesis of the ω-end-functionalized PMMAs with the hydroxyl and amino groups using methyl-2-phenylpropenoate and benzaldehyde derivatives, respectively.[10,26] Nevertheless, these GTPs using conventional catalysts were hardly controlled to produce well defined polymers, resulting in the fact that their ω-end-functionalization efficiency turned out to be poor because these catalysts gives a low cyclic fraction due to back-biting reactions and needed to be improved.

The recent utilization of organocatalysts for GTP has made significant progress in the improvement of the livingness of polymerization.[27-36] The living nature of organocatalyzed GTP is advantageous for ω-end-functionalization; for example, we recently reported the quantitative ω-end-functionalization of poly(*n*-butyl acrylate) and PMMA by organic Lewis acid-catalyzed GTP using α-phenyacrylate derivatives as the terminators.[35,36] Basic organocatalysts have not yet been examined though. As a part of our studies aimed at exploring the scope of organocatalysts and improving the GTP process, we now report (1) a detailed study of the termination reaction of the living chain ends of PMMA prepared by the *t*-BuP_4-catalyzed GTP method with benzaldehydes as terminators. (2) The synthesis of the ω-end-functionalized PMMA with a hydroxyl group, a two-arm PMMA with two hydroxyl groups, and a three-arm PMMAs with three hydroxyl groups, and (3) the convenient synthesis of AB block and A_2B_2 and A_3B_3 miktoarm star-shaped copolymers using the PMMAs with the hydroxyl groups for the ring-opening polymerization of D-lactide, as shown in Scheme 1.

Experimental Section

Materials. Methyl methacrylate (MMA, >99.8%), benzaldehyde (PhCHO, >98%), *p*-anisaldehyde (*p*-MeO-PhCHO, >99%), *p*-fluorobenzaldehyde (*p*-F-PhCHO, >97%), *p*-trifluoromethylbenzaldehyde (*p*-CF_3-PhCHO, 95%), *p*-phenylbenzaldehyde (*p*-Ph-PhCHO, >95%), *p*-allyloxybenzaldehyde (*p*-CH_2=$CHCH_2O$-PhCHO, >97%), and *p*-*tert*-butoxybenzaldehyde (*p*-*t*BuO-PhCHO, >98%) were purchased from Tokyo Chemical Industries Co., Ltd., (TCI) and used after distillation over CaH_2 under reduced pressure. D-Lactide (DLA) was also purchased from TCI and purified by recrystallization from dry toluene (twice). 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4, 1.0 mol L^{-1} in *n*-hexane) was purchased from Sigma-Aldrich Chemicals Co., and used as received. Trifluoromethanesulfonimide ($HNTf_2$, 1.0 mol L^{-1} in CH_2Cl_2), 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TiBP), and 2,3,4,5,6-pentafluorophenylbis(trifluoromethanesulfonyl)methane ($C_6F_5CHTf_2$, 1.0 mol L^{-1} in CH_2Cl_2) were purchased from Wako

Scheme 1. Synthesis of AB block and A_2B_2 and A_3B_3 miktoarm star-shaped copolymers consisting of PMMA and PDLA by combining GTP of MMA, ω-end-functionalization of PMMA using benzaldehyde as terminator, and ROP of DLA.



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Pure Chemical Industries, Ltd., and used as received. 4-Diethylaminobenzaldehyde (*p*-Et_2N-PhCHO, >98%) and terepthalaldehyde ($Ph(CHO)_2$, >98%) were purchased from TCI and used after recrystallization from methanol. Benzene-1, 3, 5-tricarbaldehyde ($Ph(CHO)_3$, >98%) was purchased from the Sigma-Aldrich Chemicals Co. and used after recrystallization from methanol. 4-(3-(Trimethylsilyl)prop-2-ynyloxy)benzaldehyde (*p*-$Me_3SiC{\equiv}CCH_2O$-PhCHO) was prepared according to a reported procedure (see Supplementary Information).[38-41] 1-Ethoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA_{Et}) was synthesized according to a previously reported procedure(see Supplementary Information).[36-37] Dry toluene (> 99.5%; water content, < 0.001%) was purchased from Kanto Chemical Co., Inc., and passed through the dry solvent system, MBRAUN MB SPS, prior to use. Tetrahydrofuran (THF > 99.5%; water content, < 0.001%) purchased from Kanto Chemical Co., Inc., was distilled from sodium benzophenone prior to use. All other reagents unless otherwise stated were used as received without further purification.

Measurements. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by a JEOL JNM-ECS400. 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 polydispersity (M_w/M_n) of the resulting PMMAs were determined by 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). 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-2H column (20 mm × 600 mm; exclusion limit, 5 × 10^3), a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7 × 104) 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-ns pulse width). Two hundred shots were accumulated for the spectra at a 20-kV acceleration voltage in the reflector mode and calibrated using polystyrene as the internal standard. Samples for MALDI-TOF MS measurements were prepared by mixing the polymer (10 g L^{-1}, 100 µL, in THF), a matrix (dithranol, 20 g L^{-1}, 20 µL, in THF), and a cationizing agent (sodium trifluoroacetate, 10 g L^{-1}, 20 µL, in THF).

Synthesis of ω-end-functionalized PMMA with a hydroxyl group using benzaldehyde as the terminator. A typical procedure for the synthesis of ω-end-functionalized PMMA with a hydroxyl group (PMMA-OH) is described as follows: SKA_{Et} (160 µL, 80 µmol; 0.50 mol L^{-1} in toluene), a *t*-Bu-P_4 stock solution (16 µL, 0.80 µmol; 0.05 mol L^{-1} in THF), and THF (0.50 mL) were added to a test tube at room temperature under an argon atmosphere, followed by the dropwise addition of MMA (213 µL, 2.0 mmol) in THF (2.0 mL). The polymerization was terminated by adding benzaldehyde (82 µL, 0.80 mmol) to the polymerization solution immediately afterwards and the ω-end-functionalization reaction was allowed to proceed for 6 h. Aliquots were taken out from the reaction mixture before termination to determine the conversion of MMA by ^1H NMR measurements. The polymer product was purified by precipitation in *n*-hexane after quenching the reaction with methanol to give a white solid powder. Yield, 172 mg (86%); $M_{n,SEC}$ = 2.9 kg mol^{-1}, M_w/M_n = 1.15; $M_{n,NMR}$ = 2.7 kg mol^{-1}. A deprotection reaction was then carried out to remove the trimethylsilyl group by reacting the polymer with 1N HCl in MeOH/THF for 30 minutes to quantitatively obtain PMMA-OH. The synthesis of PMMA-OHs with other functional groups was carried out using a similar procedure with functional terminators.

Arm-first synthesis of two-arm PMMA functionalized with two hydroxyl groups and three-arm PMMA with three hydroxyl groups using terepthalaldehyde and benzene-1,3,5-carbaldehyde respectively. The synthetic method for PMMA-OH was applied to MMA (2.0 mmol), SKA_{Et} (160 µL, 80 µmol; 0.50 mol L^{-1} in toluene), a *t*-Bu-P_4 stock solution (16 µL, 0.80 µmol; 0.05 mol L^{-1} in THF), THF (0.50 mL), and terephthalaldehyde (4.3 mg, 32 µmol). The resulting polymer was then purified by preparative SEC using $CHCl_3$ as an eluent to afford $PMMA_2$-OH_2 as a white solid. Yield, 135 mg (67.5%); $M_{n,SEC}$ = 6.0 kg mol^{-1}, M_w/M_n = 1.08. The synthesis of $PMMA_3$-OH_3 using benzene-1,3,5-carbaldehyde was carried out by a similar procedure.

Synthesis of miktoarm star-shaped copolymers using PMMAs functionalized with hydroxyl groups. A typical procedure for the synthesis of A_2B_2 miktoarm star-shaped copolymers using $PMMA_2$-OH_2 for the ROP of DLA[42] under the conditions of $[DLA]_0/[PMMA_2\text{-}OH_2]_0/[DBU]_0$ = 150/1/2 is described as follows: $PMMA_2$-OH_2 (66 mg, 6.6 kg mol^{-1}, 10 µmol), DLA (216 mg, 1.5 mmol) and CH_2Cl_2 (1.5 mL) were added to a test tube followed by the addition of DBU (20 µL, 20 µmol; 1.0 mol L^{-1} in CH_2Cl_2) under an argon atmosphere. The polymerization was allowed to proceed at room temperature for 20 min. after which it was quenched by the addition of excess benzoic acid. The mixture was then purified by reprecipitation from CH_2Cl_2 into cold MeOH to give $PMMA_2$-$PDLA_2$ as a white solid. The product was further purified by preparative SEC using $CHCl_3$ as the eluent. Yield, 140 mg (65%); $M_{n\,SEC}$ = 27.6 kg mol^{-1}, M_w/M_n = 1.17. The synthesis of the AB block and A_3B_3 miktoarm copolymers was carried out by a similar procedure using PMMA-OH and $PMMA_3$-OH_3, respectively as macroinitiators.

Results and Discussion

Synthesis of ω-end-functionalized PMMA with a hydroxyl group by *t*-Bu-P_4-catalyzed GTP using benzaldehydes. In this study, the newly prepared 1-ethoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA_{Et}) was used as the initiator instead of the

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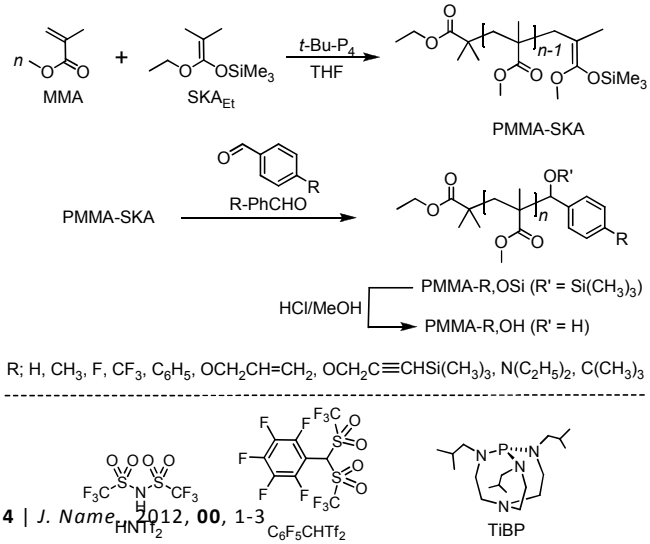
common silyl ketene acetal (SKA) of 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA_{Me}) to provide an indicative α-end for the estimation of the ω-end-functionalization efficiency (%*F*), which is described later. For the synthesis of the ω-end-functionalized PMMA with a hydroxyl group (PMMA-OH) by the *t*-Bu-P_4-catalyzed group transfer polymerization (GTP), benzaldehyde (PhCHO) and various *p*-substituted benzaldehydes (*p*-R-PhCHO) were used as terminators due to their ability to promote the Mukaiyama aldol reaction with the reactive SKA group at the ω-end of PMMA, as shown in Scheme 2. In order to achieve this objective, the synthesis of a living PMMA carrying a reactive SKA group at its ω-end, PMMA-SKA, was first prepared by the *t*-Bu-P_4-catalyzed GTP of MMA in the absence of any terminating agents. The resulting living polymer chain end was then reacted with an excess amount of a benzaldehyde terminator. Importantly, the ω-end-functionalization reaction was required to be implemented immediately after the monomer consumption to suppress any side reactions, such as the back-biting reaction, which results in the cyclization of the ω-terminal trimer, to the barest minimum. The polymerization of MMA with $[MMA]_0/[SKA_{Et}]_0/[t\text{-Bu-}P_4]_0 = 25/1/0.01$ and the termination reaction with PhCHO were initially carried out in toluene at room temperature under an argon atmosphere, as listed in Table S1 (runs S1-3 and 1). These polymerizations produced PMMA products with polydispersities of ca. 1.20 and molar masses in the range of 3.6-4.1 kg mol^{-1} by size exclusion chromatography (SEC) measurements and in the range of 3.2-3.6 kg mol^{-1} by ^{1}H NMR measurements, either of which were ca. 20 ~ 50% higher than the calculated molar mass ($M_{n,cald.}$) of 2.7 kg mol^{-1}. This could be attributed to the fact that the low polarity of toluene led to a relatively lower initiation efficiency. It was found that the initial molar ratio of terminator to initiator ($[T]_0/[I]_0$) significantly affected the %*F* of the resulting polymers. A relatively high $[PhCHO]_0/[SKA_{Et}]_0$ ratio was preferred for synthesizing the PMMA-OH with a high %*F*. The %*F* increased with the increasing $[PhCHO]_0/[SKA_{Et}]_0$ ratio and a quantitative %*F* was eventually achieved at the $[PhCHO]_0/[SKA_{Et}]_0$ ratio of 10 (run 1). This ratio was thus applied to all the subsequent termination reactions when benzaldehyde derivatives were used as terminators.

Scheme 2. Synthesis of ω-end-functionalized PMMA with a hydroxyl group by organocatalyzed GTP of MMA using benzaldehydes.



In order to obtain a better molar mass control, polymerization in THF (run 2, Table 1) was examined. The fine tuning of the molar mass of the resulting polymer suggested that THF was the preferred solvent for the *t*-Bu-P_4-catalyzed GTP of MMA compared to polymerization in toluene, *i.e.*, the polymerization in THF affording a PMMA with an $M_{n,NMR}$ of 2.7 kg mol^{-1} and an M_w/M_n of 1.15, obviously allowed a much better polymerization control than that in toluene, which produced a PMMA (run 1, Table 1) with an $M_{n,NMR}$ of 3.5 kg mol^{-1} and an M_w/M_n of 1.23. Accordingly, THF was used as the polymerization solvent for all the *t*-Bu-P_4-catalyzed GTPs of MMA in the following sections.

In the ^{1}H NMR spectrum of the PMMA terminated using PhCHO (PMMA-$OSiMe_3$, Figure 1a), the characteristic proton signals due to both the α- and ω-ends simultaneously appeared, *i.e.*, the methylene protons at 4.03 ppm (peak a) due to the SKA_{Et} residue and the aromatic protons at 7.18-7.42 ppm (peak c) due to the benzaldehyde residue were clearly observed. In addition, the signals at 0.2 and −0.4 ppm (peak d) due to the trimethylsilyl group were also clearly observed even after the eventual termination by methanol. The *O-Si* bond was actually stable enough in methanol so that the trimethylsilyl group was still bonded as a protection moiety. Based on the fact that a polymer chain must possess an initiator residue at its α-end during the GTP process, the %*F* of the resulting PMMA was readily calculated by comparing the integral areas of peaks a and c, which was the reason that SKA_{Et} was used instead of SKA_{Me}. The incorporation of a benzaldehyde moiety into the ω-end of the polymer chain was directly verified by matrix assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) analysis. As a typical example, the MALDI-TOF MS spectrum of PMMA-$OSiMe_3$ (run 2, Figure 2a) showed only one population of molecular ion peaks. The distance between any two neighbouring molecular ion peaks was extremely close to 100.05, which corresponded to the exact mass of 100.12 (MMA unit). In addition, the *m*/*z* values of the observed molecular ion peaks were very consistent with the calculated molar masses of the PMMAs having an SKA_{Et} residue as the α-end group and a terminator residue as the ω-end group; for example, the observed value of 2318.89 Da agreed well with the calculated value of 2318.20 for the sodium-cationized 20-mer of PMMA-$OSiMe_3$ [EtO_2CMe_2C-MMA_{20}-$CH(OSiMe_3)Ph + Na]^+$. This result strongly suggested that the termination reaction using benzaldehyde smoothly proceeded to produce structurally defect-free PMMA-$OSiMe_3$ without any side reactions after the *t*-Bu-P_4-catalyzed GTP of MMA. To obtain the hydroxyl functionality at the ω-end of PMMA, a deprotection reaction was further carried out to remove the trimethylsilyl group. This deprotection was implemented by treating PMMA-$OSiMe_3$ with 1N *aq*. HCl in methanol to produce PMMA-OH. The completion of deprotection was confirmed by ^{1}H NMR and MALDI-TOF MS measurements; the proton signals of trimethylsilyl group completely disappeared after processing the polymer with 1N *aq*. HCl, as shown in Figure 1b. In the MALDI-TOF MS spectrum of the deprotected product (PMMA-OH), as shown in Figure 2b, the *m*/*z* values of the observed molecular ion peaks were in good agreement with the calculated molar masses of PMMA-OHs; for example, the observed ion peak value of 2318.89

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Da of the 20-mer of PMMA-$OSiMe_3$ showed an obvious shift to 2246.73 corresponding to its deprotected 20-meric product of PMMA-OH, which has a sodium-cationized structure of $[EtO_2CMe_2C\text{-}MMA_{20}\text{-}CH(OH)Ph + Na]^+$, clearly indicating that the deprotection was very successful and the targeted structurally defect-free PMMA-OH was eventually obtained.

These results demonstrate that *t*-Bu-P_4 is an effective catalyst for the GTP of MMA along with the ω-end-functionalization of the propagating PMMA end with benzaldehydes. We thereby investigated the catalyst effect on the %*F* of PMMAs. Apart from *t*-Bu-P_4, other organocatalysts, such as 2,8,9-triisobutyl- 2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TiBP), trifluoromethanesulfonimide ($HNTf_2$), and 2,3,4,5,6-pentafluorophenylbis(trifluoromethanesulfonyl)methane ($C_6F_5CHTf_2$), which have been previous proven to be effective for the GTP of MMA,[29-35] were used, as shown in Scheme 2. Table 1 lists the polymerization results (runs 3-5). For quantitative monomer conversion, the catalysts of TiBP, $HNTf_2$, and $C_6F_5CHTf_2$ needed 2 - 24 h even though only 3 min was sufficient for *t*-Bu-P_4. In addition, the molar mass control using these catalysts was less effective with the molar masses much higher than their respective calculated values in comparison to *t*-Bu-P_4. It is very clear that all the termination reactions using these catalysts did not achieve quantitative ω-end-functionalization, *i.e.*, TiBP, $HNTf_2$, and $C_6F_5CHTf_2$ achieved %*F*s of 65.5, 47.3 and 15.2%, respectively. These results obviously indicated that the organic base catalysts are more suitable than organic acid catalysts for the termination reaction. The ω-end-functionalization by benzaldehyde is assumed to be significantly dependent on the polymerization mechanism because the base catalysts should promote the SKA ends of the polymer to produce extremely reactive enolate anions while the SKA structures are maintained for the acid catalysts. These results demonstrated again that *t*-Bu-P_4 is the most effective catalyst for the synthesis of the ω-end-functionalized polymers with a hydroxyl group using the GTP method. Also unlike previous conventional catalysts used to synthesize hydroxyl end-functionalized PMMA, [10] *t*-Bu-P_4 could suppress back-biting side reactions.

We next estimated the effect of the molar mass of PMMA on the %*F* (Runs 2, 6-7). The molar mass of the synthesized polymers increased with the increasing monomer-to-initiator ratio ($[MMA]_0/[SKA_{Et}]_0$) and maintaining the terminator ratio constant at 10 while monitoring the effect that had on the %*F*. The polymerization results showed that the living nature of the GTP afforded excellent control of the molar mass and narrow polydispersity. The $M_{n,SEC}$s well agreed with their $M_{n,cald.}$s in that sense, and the polydispersities were also narrow for the polymerizations of all the $[M]_0/[I]_0$ ratios investigated. For the %*F*, the results showed that an increase in the molar mass made the end-functionalization reaction more difficult due to increased steric hindrance for the longer polymer chains. Therefore, an increased amount of the catalyst was required to achieve quantitative functionalization. The %*F* results showed that the quantitative ω-end-functionalization of PMMA by *t*-BuP_4-catalyzed GTP using benzaldehyde could be effectively achieved at even high molar masses ($M_{n,NMR}$) of 5.2 (run 6) and 11.4 kg mol^{-1} (run 7), which were directly confirmed by ^1H NMR measurements by comparing the proton signals at the α and ω-ends, as already described. In addition, the quantitative ω-end-functionalization of run 6 was further verified by MALDI-TOF MS measurements (see Figure S1). The same confirmation by MALDI-TOF MS measurements for run 7 was also tried, but failed due to its high molar mass.

Electron-withdrawing and electron-donating substituents play significant role in organic reactions, and their introduction to a reactant generally affects the reaction rate and yield. In this study, we also investigated the effect of the *para*-substituent of the benzaldehydes on the %*F* of PMMAs by using benzaldehydes with electron-withdrawing groups, such as *p*-phenylbenzaldehyde, *p*-fluorobenzaldehyde, and *p*-trifluoromethylbenzaldehyde, and that with an electron-donating group, such as *p*-anisaldehyde. The termination results for runs S4-7 firmly indicated that the *para*-substituents had little or no significant effect on the %*F* because the %*F* values using the *para*-substituted benzaldehydes were almost the same as that using benzaldehyde (run 2) under the same conditions. Nevertheless, the kinetic studies, as shown in Figure 3, proceeded at different rates and implied that *para*-substituents affected the rate of the reaction with the end-functionalization reaction proceeding faster when terminators carried an electron-

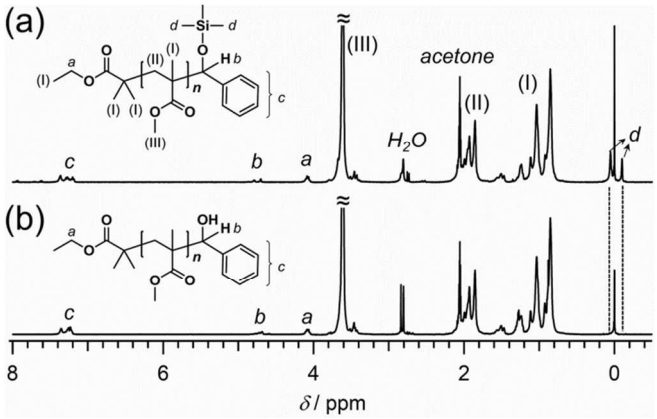

Figure 1. ^1H NMR spectra of (a) PMMA-$OSiMe_3$ obtained from run 2 and (b) PMMA-OH obtained from run 2 in acetone-d_6.

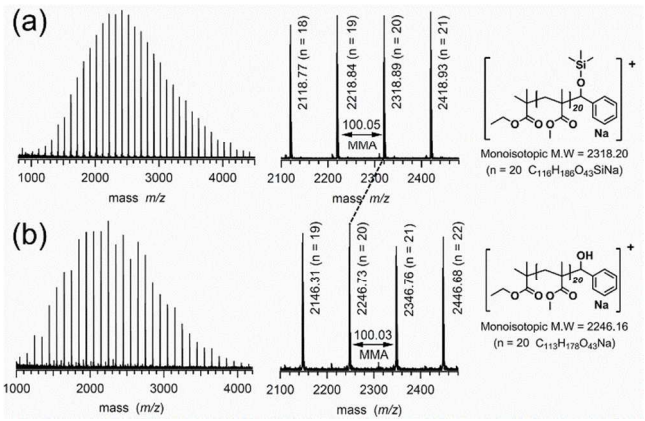

Figure 2. MALDI-TOF MS spectra in reflector mode of of (a) PMMA-$OSiMe_3$ obtained from run 2 and (b) PMMA-OH obtained from run 2.

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Table 1. Synthesis of hydroxyl ω-end-functionalized PMMAs by organocatalyzed GTP using benzaldehyde (PhCHO) as terminator [a]

run	Catalyst	Solvent	$[MMA]_0/[SKA_{Et}]_0$	$M_{n,calcd}$ [b] (kg mol^{-1})	$M_{n,SEC}$ [c] (kg mol^{-1})	$M_{n,NMR}$ [d] (kg mol^{-1})	M_w/M_n [c]	%F [d]
1	*t*-Bu-P_4	Toluene	25	2.7	4.1	3.5	1.23	>99
2	*t*-Bu-P_4	THF	25	2.7	2.9	2.7	1.15	>99
3 [e]	TiBP	THF	25	2.7	4.9	4.5	1.41	65.5
4 [f]	$HNTf_2$	CH_2Cl_2	25	2.7	4.5	4.1	1.07	47.3
5 [g]	$C_6F_5CHTf_2$	CH_2Cl_2	25	2.6	4.0	3.7	1.08	15.2
6 [h]	*t*-Bu-P_4	THF	50	5.2	5.9	5.2	1.17	>99
7 [i]	*t*-Bu-P_4	THF	100	10.2	11.1	11.4	1.14	>99

[a] Ar atmosphere; room temperature; $[t\text{-Bu-P}_4]_0/[SKA_{Et}]_0$, 0.01; Polymerization time, 3 min; $[PhCHO]_0/[SKA_{Et}]_0$, 10; Termination time, 12 h; MMA conversion > 99%. [b] Calculated from $([MMA]_0/[SKA_{Et}]_0) \times$ (MMA conversion) × (M.W. of MMA) + (M.W. of initiator residue) + (M.W. of terminator residue) × %F. [c] Determined by SEC in THF using PMMA standards. [d] Estimated by ^{1}H NMR measurements in acetone-d_6. [e] $[TiBP]_0/[SKA_{Et}]_0$, 0.02; Polymerization time, 2 h; Termination time, 24 h. [f] $[HNTf_2]_0/[SKA_{Et}]_0$, 0.05; Solvent, CH_2Cl_2; Polymerization time, 24 h; Termination time, 24 h. [g] $[C_6F_5CHTf_2]_0/[SKA_{Et}]_0$, 0.05; Polymerization time, 24 h; Termination time, 24 h. [h] $[t\text{-Bu-P}_4]_0/[SKA_{Et}]_0$, 0.02. [i] $[t\text{-Bu-P}_4]_0/[SKA_{Et}]_0$, 0.02; 0.64 equiv. of *t*-Bu-P_4 was further added to the polymerization mixture followed by the addition of PhCHO.

withdrawing substituent like –F, whereas those carrying an electron-donating *para*-substituents like $–OCH_3$ were relatively slower compared to benzaldehyde with no substituents.

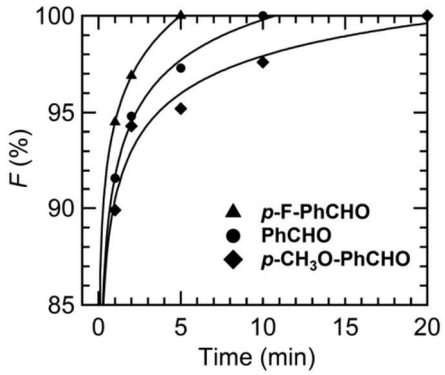

Figure 3. Dependence of %F on the reaction time of termination using benzaldehydes of (▲) *p*-F-PhCHO, (●) PhCHO, and (◆) *p*-CH_3O-PhCHO.

The effectiveness of the ω-end-functionalization by *t*-Bu-P_4-catalyzed GTP was also used to synthesize ω-end-bifunctionalized PMMAs (runs S8-11) using functional benzaldehydes as terminators. Similar to the case using *para*-substituted benzaldehydes, functional benzaldehyde terminations also provided quantitative %F values. The quantitative ω-end-bifunctionalization using functional benzaldehyde terminators was also verified by MALDI-TOF MS measurements. After the end-functionalization reaction, a deprotection reaction was further carried out to remove the trimethylsilyl groups with 1N *aq.* HCl, affording the hydroxyl and alkynyl, hydroxyl and butoxy, hydroxyl and allyloxy, and hydroxyl and amino ω-end-bifunctionalized PMMAs.

Synthesis of two- and three-arm PMMAs functionalized with hydroxyl groups. The propagating end of polymers in GTP is stable and electronically neutral, which is advantageous for the synthesis of star-shaped polymers in comparison to other controlled/living polymerization systems. Unlike in living radical polymerization systems, GTP is not prone to intermolecular termination reactions that normally involve two propagating polymers species. Although there are several reports for the core-first synthesis of star-shaped polymers by GTP using multi-functionalized initiators,[29,41] there is no report for the arm-first synthesis of star-shaped polymers by GTP using terminators to the best of our knowledge.

Thus, two- and three-arm PMMAs functionalized with hydroxyl groups were synthesized by *t*-Bu-P_4-catalyzed GTP using terminators with two and three aldehyde groups, such as terepthalaldehyde and benzene-1,3,5-tricarbaldehyde, respectively, as shown in Scheme 3. Table 2 summarizes the polymerization results. For this arm-first method, we first synthesized a linear living PMMA as the arm by *t*-Bu-P_4-catalyzed GTP and then the terminators with multiple aldehyde groups were added as the core to the prior synthesized arms. When carrying out the termination reaction, the initiator ratios in double and triple excess to that of the appropriate terminators were required to synthesize the two- and three-arm polymers, respectively. The results obtained from the SEC(RI) measurements showed that the SEC trace in Figure S2 shifted to the high molar mass region after the termination using the terepthalaldehyde and benzene-1,3,5-tricarbaldehyde and the molar masses of the acquired polymers were exactly two and three times those of the pre-synthesized linear PMMA arms to produce the two- and three-arm PMMAs, respectively, which were also directly confirmed by the ^{1}H NMR calculations of the molar masses, as listed in Table 2 (runs 8b and 9b). These results indicated that all the obtained polymers consisted of a core unit derived from the terminators and the PMMA arms; *i.e.*, two- and three-arm PMMAs.

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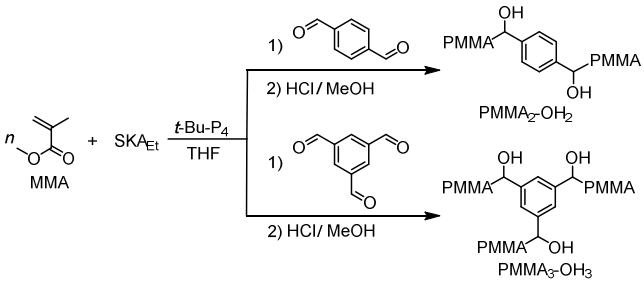
Table 2. Synthesis of hydroxyl functionalized two- and three-arm PMMAs by *t*-Bu-P_4-catalyzed GTP using multifunctional benzaldehydes as terminators [a]

run	$[M]_0/[I]_0$	Terminator (T)	$[T]_0/[I]_0$	$M_{n,calcd}$ [b] (kg mol^{-1})	$M_{n,SEC}$ [c] (kg mol^{-1})	$M_{n,NMR}$ [d] (kg mol^{-1})	M_w/M_n [c]
8a	25	--	--	2.6	2.9	3.2	1.18
8b	--	$Ph(CHO)_2$	0.45	5.8	6.0	6.4	1.08
9a	25	--	--	2.6	3.2	2.9	1.12
9b	--	$Ph(CHO)_3$	0.30	9.6	11.6	10.8	1.05

[a] Ar atmosphere; room temperature; I, SKA_{Et} ; M, MMA; [*t*-Bu-P_4]/$[I]_0$, 0.01; Polymerization time, 3 min; Termination time, 12 h; MMA conversion >99%. [b] Calculated from ($[M]_0/[I]_0$) × (MMA conversion) × (M.W. of MMA) + (M.W. of initiator residue) + (M.W. of terminator residue) × %*F*. [c] Determined by SEC in THF using PMMA standards. [d] Calculated by ^{1}H NMR measurements in acetone-d_6.

Scheme 3. Synthesis of two- and three-arm PMMAs functionalized with two and three hydroxyl groups by organocatalyzed GTP of MMA using terepthalaldehyde and benzene-1,3,5-tricarbaldehyde, respectively as terminators.



Synthesis of diblock and miktoarm star-shaped copolymers. Having demonstrated the effectiveness of GTP for the synthesis of linear and two- and three-arm PMMAs functionalized with hydroxyl groups by the termination reactions with bezaldehydes, we proceeded to demonstrate the applicability of the hydroxyl functionalities by employing the hydroxyl end-functional groups to initiate the ring-opening polymerization (ROP) of D-lactide (DLA), as shown in Scheme 4. The polymerization results are listed in Table 3. The hydroxyl ω-end-functionalized PMMA (PMMA-OH; $M_{n,SEC}$ = 3.2 kg mol^{-1}, M_w/M_n = 1.20) and hydroxyl functionalized two- ($PMMA_2$-OH_2; $M_{n,SEC}$ = 6.6 kg mol^{-1}, M_w/M_n = 1.17) and three-arm ($PMMA_3$-OH_3; $M_{n,SEC}$ = 11.6 kg mol^{-1}, M_w/M_n = 1.05) PMMAs were used to initiate the ROP of DLA in CH_2Cl_2 to produce the expected AB-type diblock copolymer, A_2B_2-type four-arm and A_3B_3-type six-arm miktoarm star-shaped copolymers, respectively. The molar ratio of DLA to the hydroxyl group was fixed at a value of 75 in order to keep each AB arm having a total degree of polymerization (DP) of 100. The DBU catalyst was used because a previous report [42] had shown it to be a best catalyst for the ROP of hydroxyl initiated lactide monomers. The quantity of catalyst was appropriately tuned in light of the macroinitiator used. All the ROPs of DLA (runs 10-12) afforded high DLA conversions (90 – 94%). After purification by preparative SEC, the $M_{n,SEC}$ (kg mol^{-1}) (M_w/M_n)s of the final polymer products of PMMA-*b*-PDLA (run 10), $PMMA_2$-$PDLA_2$ (run 11), and $PMMA_3$-$PDLA_3$ (run 12) were 18.9 (1.08), 27.6 (1.17), and 40.5 (1.21), respectively.

Scheme 4. Synthesis of PMMA-*b*-PDLA diblock copolymer and $PMMA_2$-$PDLA_2$ and $PMMA_3$-$PDLA_3$ miktoarm star-shaped copolymers via DBU-catalyzed ROP of DLA using PMMA-OH, $PMMA_2$-OH_2, and $PMMA_3$-OH_3, respectively.

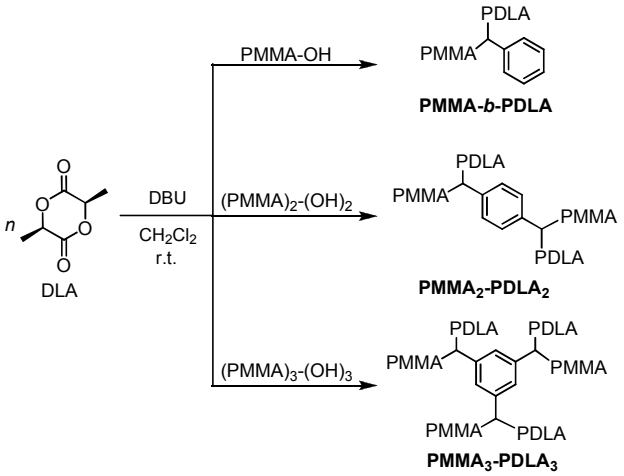


Table 3. Synthesis of AB diblock and A_2B_2 and A_3B_3 miktoarm star-shaped copolymers by DBU-catalyzed ROP of DLA using PMMAs functionalized with hydroxyl groups as macroinitiators.

run	Polymers	Macroinitiator (MI) ($M_{n,SEC}$ (kg mol^{-1}), M_w/M_n)	$[DLA]_0/[MI]_0/[DBU]_0$	Conv. [b] (%)	$M_{n,theo.}$ [c] (kg mol^{-1})	$M_{n,SEC}$ [d] (kg mol^{-1})	M_w/M_n [d]
10	PMMA-*b*-PDLA	PMMA-OH (3.2, 1.20)	75/1/0.5	94	13.8	18.9	1.08
11	$PMMA_2$-$PDLA_2$	$PMMA_2$-OH_2 (6.6, 1.17)	150/1/2	90	26.0	27.6	1.17
12	$PMMA_3$-$PDLA_3$	$PMMA_3$-OH_3 (11.6, 1.05)	225/1/3	93	38.3	40.5	1.21

[a] Ar atmosphere; solvent, CH_2Cl_2; temperature; r.t.; $[DLA]_0$ = 1.0 mol L^{-1}; polymerization time; 20 min. [b] Estimated by ^{1}H NMR measurements. [c] Calculated from ($[DLA]_0/[I]_0$) × (DLA Conv.) × (M.W. of DLA) + (M.W. of MI). [d] Estimated by SEC in THF using PMMA standards.

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The results obtained from the SEC(RI) measurements showed that the SEC trace in Figure 4 clearly shifted to the high molar mass region from the pre-terminated PMMA to the hydroxyl-functionalized macroinitiator to its respective corresponding diblock copolymer or miktoarm star-shaped copolymer, respectively. In addition, a typical ^{1}H NMR measurement of PMMA-*b*-PDLA in Figure 5 simultaneously showed the proton signals from the PMMA main chain (peaks B and C) and PDLA main chain (peaks a and b). The same results were also obtained for $PMMA_2$-$PDLA_2$ and $PMMA_3$-$PDLA_3$. These results strongly indicated that all the obtained polymers consisted of a core unit derived from the benzaldehyde terminators and two types of chemically different polymer arms.

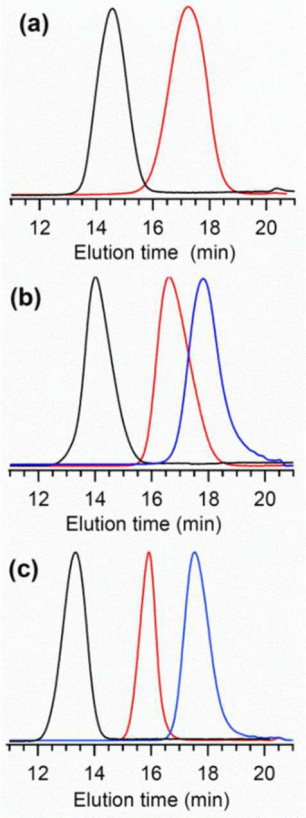

Figure 4. SEC traces of (a) PMMA-*b*-PDLA (black line) and its precursor of PMMA-OH (red line), (b) $PMMA_2$-$PDLA_2$ (black line) and its precursors of $PMMA_2$-OH_2 and a PMMA arm (red and blue lines, respectively), and (c) $PMMA_3$-$PDLA_3$ and its precursors of $PMMA_3$-OH_3 and a PMMA arm (red and blue lines, respectively).

Conclusion

In this report, we described the precise synthesis of PMMAs functionalized with a hydroxyl group by *t*-Bu-P_4-catalyzed GTP using aromatic aldehydes as terminators. The termination reaction between a living PMMA and benzaldehyde was proved to be an efficient system for synthesizing the ω-end-functionalized PMMAs with the hydroxyl groups with controlled molar masses, relatively narrow polydispersities, and quantitative ω-end

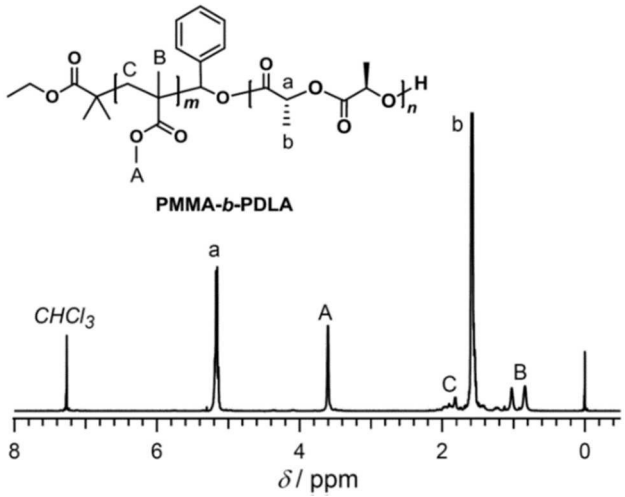

Figure 5. A typical ^{1}H NMR spectrum of PMMA-*b*-PDLA in $CDCl_3$.

functionalization efficiencies. In addition, the ω-end-bifunctionalized PMMAs with a hydroxyl group along with an alkynyl, a butoxy, an allyloxy, and an amino group were successfully synthesized using functional benzaldehydes according to the aforementioned method. In this study, we also established the arm-first method for the synthesis of two- and three-arm PMMAs with hydroxyl groups existing in the core, which is the first report about this kind of synthesis in GTP chemistry to the best of our knowledge. Finally, the preparation of the miktoarm star-shaped polymers was achieved using the multi-arm PMMAs functionalized with hydroxyl groups as macroinitiators.

Acknowledgment

This work was financially supported by the MEXT (Japan) program "Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions" of Hokkaido University and the MEXT Grant-in-Aid for Scientific Research on Innovative Areas "Advanced Molecular Transformation by Organocatalysts". K. Takada was funded by the JSPS Fellowship for young Scientists.

Notes and references

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† Electronic Supplementary Information (ESI) available: The synthetic details of 1-ethoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA_{Et}) and 4-(3-(trimethylsilyl)prop-2-ynyloxy)benzaldehyde, ^{1}H NMR and MALDI-TOF MS data of ω end-functionalized PMMAs as well as the SEC traces of the two and three arm hydroxyl functionalized PMMAs are available. See DOI: 10.1039/b000000x/

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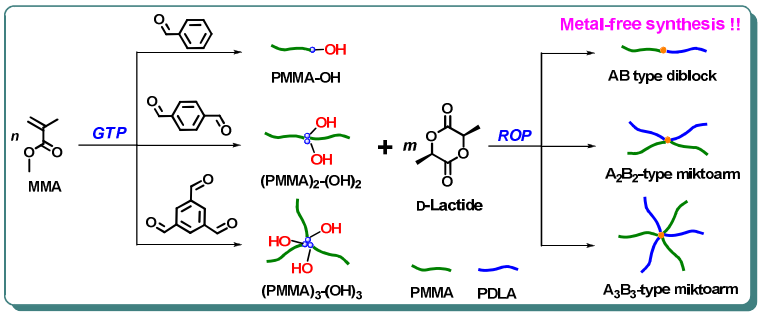
Synthesis of AB Block and A_2B_2 and A_3B_3 Miktoarm Star-shaped Copolymers Using ω-End-functionalized Poly(methyl methacrylate) with A Hydroxyl Group Prepared by Organocatalyzed Group Transfer Polymerization

Ofosu-Twum Eric,[†] Yougen Chen,[§] Kenji Takada,[†] Shin-ichiro Sato,[†‡] Toshifumi Satoh,[†‡] and Toyoji Kakuchi[§†‡]*

Metal-free synthesis of AB block copolymer, A_2B_2 and A_3B_3 type miktoarm star-shaped copolymers consisting of PMMA and PDLA arms were achieved by combining organocatalyzed GTP and ROP.



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