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Core-First Synthesis of Three-, Four-, and Six-Armed Star-Shaped Poly(methyl methacrylate)s by Group Transfer Polymerization Using Phosphazene Base

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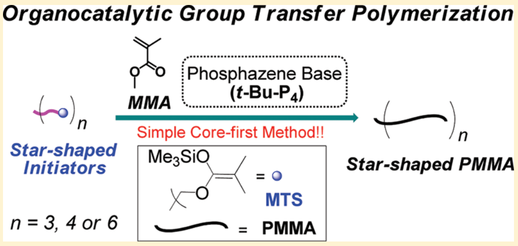
S Supporting Information

ABSTRACT: The core-first synthesis of three-, four-, and six-armed star-shaped poly(methyl methacrylate)s (PMMAs) with predicted molecular weights and narrow molecular weight distributions (M_w/M_ns) was carried out by the *t*-Bu-P_4-catalyzed group transfer polymerization (GTP) of methyl methacrylate (MMA) using the newly designed silyl enolates, such as 1,1,1-tris[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxymethyl]propane (EtC(MTS)$_3$), tetrakis-{[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxy]methyl}methane (C(MTS)$_4$), and bis{2,2,2-tris[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxy]ethyl}ether (O-(C(MTS)$_3$)$_2$), respectively. The absolute molecular weight (M_w(MALS)) of the obtained polymers proportionally increased with the increasing [MMA]$_0$/[initiator]$_0$ ratio, and the highest molecular weight was ca. 132 kg mol^{-1}. Characterizations for the star-shaped PMMAs were conducted by cleavage and intrinsic viscosity [η] experiments. Cleavage experiments of the star-shaped PMMAs provided the evidence for homogeneous growth of the each arm in the *t*-Bu-P_4-catalyzed GTP. The number of arm determined from the shrinking factors (g') of [η] also supported the successful syntheses of the star-shaped polymers by the present core-first method. The versatility of this core-first method toward other methacrylic monomers was confirmed by the *t*-Bu-P_4-catalyzed GTPs of allyl methacrylate (AMA), stearyl methacrylate (SMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) using C(MTS)$_4$ as an initiator leading to well-defined star-shaped polymers.



■ INTRODUCTION

Polymers with branched structures, such as star-shaped, dendritic, and hyperbranched polymers, are well-known to exhibit a low hydrodynamic volume and low viscosity in solution, whose properties significantly differ in comparison with their linear equivalents.[1] It has been extensively accepted that the number and length of the arm are the most important factors, because they significantly influence the properties of the star-shaped polymers. The synthetic methodology of a star-shaped polymer dates back to the 1960s with the arm-first procedure based on the coupling reaction between the living polystyryllithium species and multifunctional linking reagents, such as 1,2,4-tris(chloromethyl)benzene and silicon tetrachloride.[2,3] After these early studies, anionic polymerization using the arm-first method has been employed to prepare star-shaped polybutadiene,[4,5] polyisoprene,[6] and poly(methyl methacrylate) (PMMA).[7−9] For example, Hirao et al. and Hadjichristidis et al. reported the syntheses of star-shaped PMMAs by anionic polymerization using the arm-first method by the strict control of the molecular weight and molecular weight distribution.[10−13] In addition, the arm-first method has been explored by the development of various quantitative reactions in synthetic organic chemistry, such as the copper-catalyzed azide—alkyne cycloaddition and thiol—ene reaction.[14,15] Although the arm-first method provided a useful method for the synthesis of star-shaped polymers, severe reaction conditions and/or complex purification processes have not been avoided because it is difficult to achieve the complete coupling and linking reactions between the propagating polymers and multifunctional linking reagents. In recent years, living radical polymerizations (LRPs), such as atom transfer radical polymerization (ATRP),[16,17] nitroxide-mediated radical polymerization,[18] and reversible addition—fragmentation chain-transfer polymerization,[19] have provided versatile means for the synthesis of star-shaped polymers using a wide range of monomers. In particular, LRPs based on the core-first method have been paid much attention due to their simplicity and easy post processes; for example, the ATRP has been utilized for the core-first synthesis of star-shaped PMMAs though their polydispersity indices generally became as high as ca. 1.20.[20−27] However, the core-first synthesis of star-shaped polymers using LRPs has essentially involved certain difficulties, such as the polymerization should be stopped at an earlier stage to avoid any

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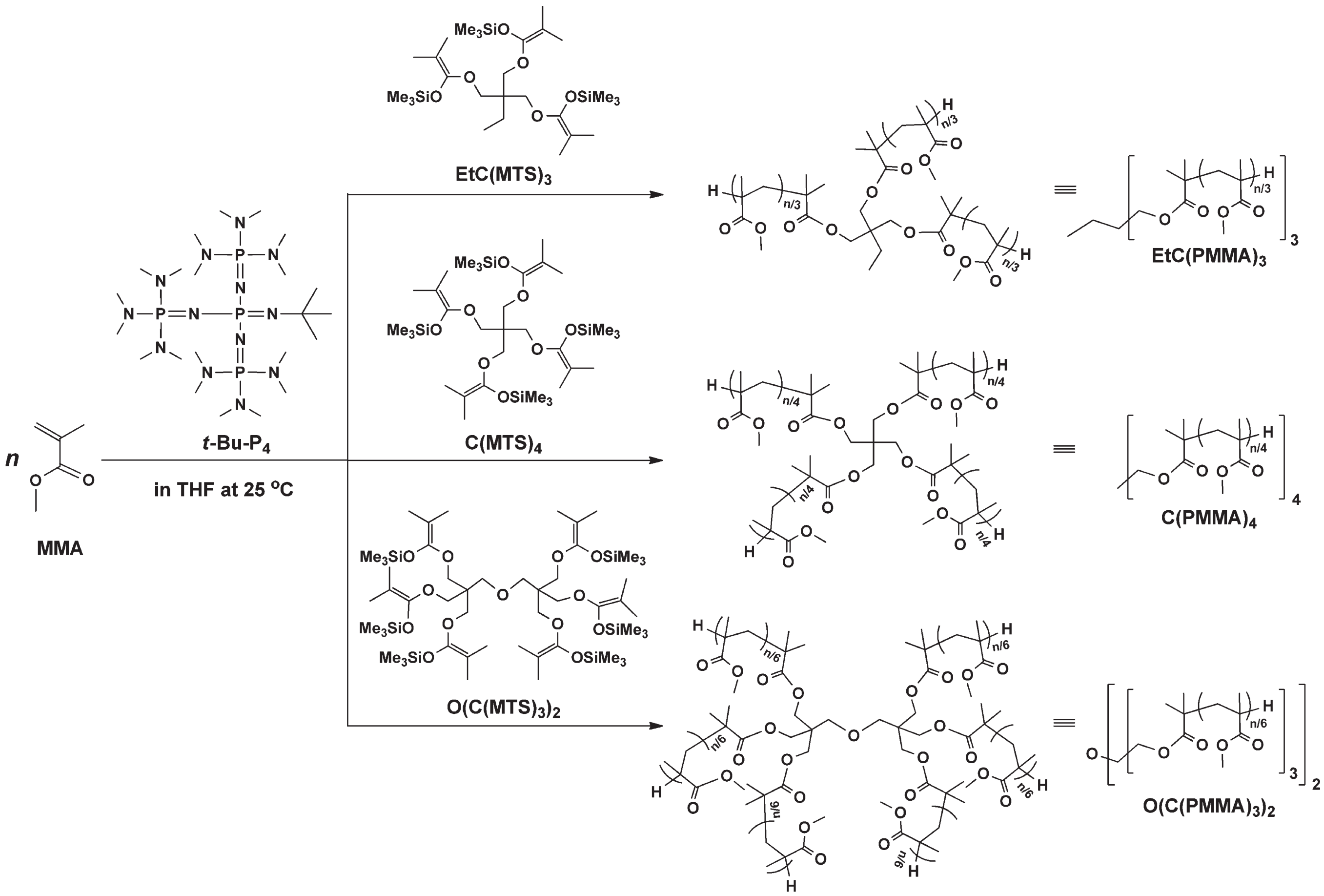
Scheme 1. Synthesis of Three-, Four- and Six-Armed Star-Shaped PMMAs, $EtC(PMMA)_3$, $C(PMMA)_4$, and $O(C(PMMA)_3)_2$, by the *t*-Bu-P_4-Catalyzed GTP of MMA Using $EtC(MTS)_3$, $C(MTS)_4$, and $O(C(MTS)_3)_2$ as Initiators

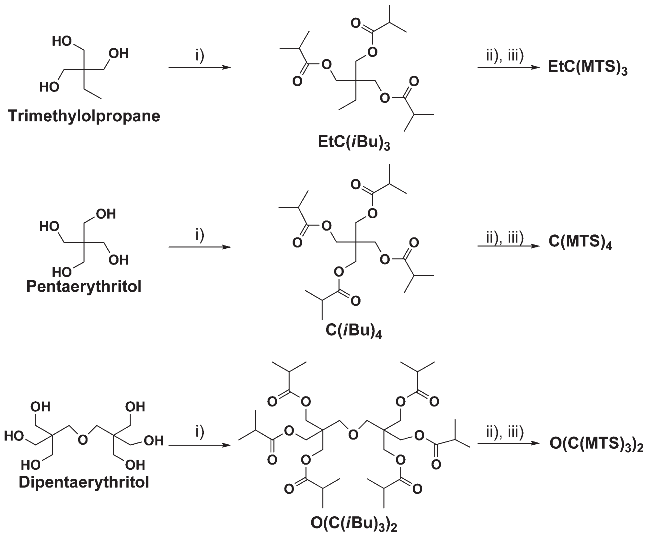


radical recombination among propagating ends, which causes a low monomer conversion. Besides, living catalytic coordination polymerization technique has also been developed recently for star polymer synthesis through both core-first and arm-first strategies.[28−30]

Group transfer polymerization (GTP), one of the important living polymerization methods, is recognized as the procedure involving a mechanism of the numerous iterations of the Mukaiyama−Michael reaction, featuring the fact that a silyl enolate with a propagating polymer chain end is stable and neutral, causing recombination-free polymerization.[31−34] The living nature of GTP was used to prepare complicated macromolecular architectures, such as block copolymers,[32−44] a hyperbranched polymer,[45] and a star-shaped polymer, using a Lewis acid or base as a catalyst. For star-shaped polymers, Webster and Sogah first reported the core-first synthesis of three- and four-armed star-shaped poly(ethyl acrylate)s,[32] Wnek et al. reported the core-first synthesis of the four-armed star-shaped PMMA,[46] and Patrickios et al. reported the arm-first synthesis of various star-shaped poly(methacrylate)s using a bifunctional monomer as a linking agent.[47−54] However, these star-shaped poly(methacrylate)s were insufficient for controlling the molecular weights and their distributions. Thus, the precise synthesis of star-shaped PMMAs still remains as a challenging task from the viewpoint of polymer science.

Metal-free catalysts, so-called organocatalysts, have been extensively developed in organic chemistry and recently applied for use as polymerization catalysts in polymer synthesis. For the organocatalytic GTP, Taton et al. and Hedrick et al. independently reported that the *N*-heterocyclic carbene was an efficient catalyst for the GTPs of (meth)acrylates, acrylamides, and methacrylonitrile using 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS) as the initiator to produce well-defined homo- and block copolymer.[39,40] Previously, we also reported that trifluoromethanesulfonimide, a very strong Brønsted acid, could catalyze the GTPs of methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide to afford the well-defined corresponding polymers.[55,56] In addition, we recently reported that 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4), a very strong base, could activate a silyl enolate to allow the living polymerization of MMA using MTS, which was capable of producing PMMA with a molecular weight of up to 100 kg mol^{-1} and a narrow molecular weight distribution.[57] Therefore, the exploitation of the *t*-Bu-P_4-catalyzed GTP is expected to be a promising approach to realize the core-first synthesis of star-shaped PMMAs, and we recently reported a preliminary result for the core-first synthesis of a three-armed star-shaped polymer by the *t*-Bu-P_4-catalyzed GTP of 4-(diphenylamino)benzyl methacrylate.[58] This study has ensured that the *t*-Bu-P_4-catalyzed GTP is applicable for the core-first synthesis of star-shaped poly(methacrylate)s. In this study, we aim to precisely synthesize star-shaped PMMAs with different arm numbers by the GTP based on the core-first method and study their properties in a diluted solution. This article describes (1) the evaluation of the synthesis of the three-, four-, and six-armed star-shaped PMMAs (EtC(PMMA)$_3$, C(PMMA)$_4$, and O(C(PMMA)$_3$)$_2$, respectively) by the *t*-Bu-P$_4$-catalyzed GTP using the silyl enolate initiators, 1,1,1-tris[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxymethyl]propane (EtC(MTS)$_3$), tetrakis{[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxy]methyl}-methane (C(MTS)$_4$), and bis{2,2,2-tris[2-methyl-1-(trimethylsilyloxy)prop-1-enyloxy]ethyl}ether (O(C(MTS)$_3$)$_2$), respectively, as shown in Scheme 1, (2) the structural characterization of the synthesized star-shaped PMMAs by their cleavage into linear arm PMMAs, (3) the synthesis of four-armed star-shaped polymers consisting of allyl methacrylate (AMA), stearyl methacrylate (SMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA), and (4) the systematic insight into the solution behavior of the star-shaped PMMAs in tetrahydrofuran (THF).

Scheme 2. Synthetic Diagrams of EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$



i) (CH$_3$)$_2$CHCOCl, Et$_3$N in dry THF, ii) *n*-BuLi / ^{i}Pr$_2$NH in dry THF, iii) (CH$_3$)$_3$SiCl

EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA), allyl methacrylate (AMA), stearyl methacrylate (SMA), (2-dimethylamino)ethyl methacrylate (DMAEMA), and diisopropylamine were purchased from Tokyo Kasei Kogyo Co., Ltd., (TCI) and used after distillation over CaH$_2$ as the drying agent under reduced pressure. Trimethylolpropane (>98%), dipentaerythritol (>85%), and isobutyryl chloride (>98%) were purchased from TCI and used as received. Chlorotrimethylsilane (>98%) was available from TCI and distilled (without drying agent) under argon atmosphere before use. Pentaerythritol (≥99%) and 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) were available from Sigma-Aldrich Chemicals Co. and used as received. *n*-Butyllithium was purchased from Kanto Chemical Co., Inc. (1.62 mol L^{-1} in *n*-hexane) and Sigma-Aldrich Chemicals Co. (2.50 mol L^{-1} in *n*-hexane) and used as received. Trimethylsilyldiazomethane (TMSCH$_2$N$_2$, 2.0 mol L^{-1} in THF) was available from Sigma-Aldrich Chemicals Co. and used as received. Tetrahydrofuran (THF, > 99.5%, dehydrated stabilizer free) and *n*-hexane (>95.0%) were purchased from Kanto Chemical Co., Inc. and distilled over Na/benzophenone under an argon atmosphere prior to use. All other reagents were used as received without further purification.

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-A400II and JEOL-ECP-400 instruments. The polymerization solution was prepared in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) and a dry argon atmosphere (H$_2$O, 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 absolute molecular weight (M_w(MALS)) and intrinsic viscosity ([η]) were estimated by size exclusion chromatograph (SEC) in THF (1.0 mL min^{-1}) at 40 °C using an Agilent 1100 series instrument equipped with two Shodex KF-804 L columns (linear, 8.0 mm ×300 mm; exclusion limit, 4 × 10^5; bead size, 7 μm), a DAWN 8 multiangle laser light scattering (MALS) detector (Wyatt Technology, Santa Barbara, CA), a Viscostar viscosity detector (Wyatt Technology), and an Optilab rEX refractive index detector (Wyatt Technology). The molecular weight distributions (M_w/M_ns) of the polymers were determined by another SEC at 40 °C in THF (1.0 mL min^{-1}) equipped with a Jasco GPC-900 system along with a set of Waters Ultrastyragel 7 mm columns (linear, 7.8 mm × 300 mm), two Shodex KF-804 L columns (linear, 8 mm ×300 mm) and a refractive index (RI) detector, and calculated on the basis of a poly(methyl methacrylate) calibration.

Polymerization of MMA. A typical procedure for the polymerization of MMA carried out under the condition of [MMA]$_0$/[EtC(MTS)$_3$]$_0$/[*t*-Bu-P4]$_0$ = 300/1/0.03 as follows: a stock solution (100 μL) of EtC(MTS)$_3$ (20.0 μmol, 0.20 mol L^{-1}) in THF and a stock solution (60 μL) of *t*-Bu-P$_4$ (0.60 μmol, 0.01 mol L^{-1}) in THF in a test tube were stirred for a few minutes, and then a stock solution (3.0 mL) of MMA (6.0 mmol, 2.0 mol L^{-1}) in THF was added within about 5 min. The polymerization was quenched after 1 h by adding a small amount of benzoic acid. A portion of the polymerization mixture was used for the determination of the MMA conversion, which was directly estimated from the ^{1}H NMR measurement of the polymerization mixture. The polymer was purified by reprecipitation from CH$_2$Cl$_2$ in methanol. Conversion > 99%. SEC(RI): M_n = 28.0 kg mol^{-1}; M_w/M_n = 1.12. SEC(MALS): M_w = 34.5 kg mol^{-1}. Yield: 562 mg (93.6%).

Polymerization of AMA, SMA and DMAEMA. The synthesis of four-armed poly(allyl methacrylate) (C(PAMA)$_4$), poly(stearyl mecthacrylate) (C(PSMA)$_4$), and poly((2-dimethylamino)ethyl methacrylate) (C(PDMAEMA)$_4$) were carried out by the similar polymerization procedure as that of the polymerization of MMA. The purification of C(PAMA)$_4$s, C(PSMA)$_4$s, and C(PDMAEMA)$_4$s were performed by passing the polymerization mixture through an Al$_2$O$_3$ gel using dichloromethane as an eluent solvent, followed by filteration and evaporation; the C(PDMAEMA)$_4$s were further dried by lyophilizing.

Cleavage of Star-Shaped PMMA. A typical procedure for the hydrolysis of the star-shaped PMMA is as follows: EtC(PMMA)$_3$ (run 4, 200 mg, 2.00 mmol of MMA units) in THF (10 mL) was added to a mixture of KOH (5.6 g, 0.10 mol) in methanol (22.4 g) in a 100 mL PTFE bottle. After the addition of distilled water, the mixture was refluxed at 70 °C for 48 h. The mixture was then neutralized using concentrated hydrochloric acid and dialyzed against distilled water for 3 days. After the water was evaporated, the residue was lyophilized for 2 days to give a partly hydrolyzed linear PMMA as a white powder. The white powder was dissolved in diethyl ether and then methylated for 3 h by adding an excess amount of TMSCH$_2$N$_2$ (2.0 mL, 4.0 mmol, 2.0 mol L^{-1} in THF). After the residual TMSCH$_2$N$_2$ was removed by adding an excess amount of acetic acid, the residue was finally reprecipitated in a

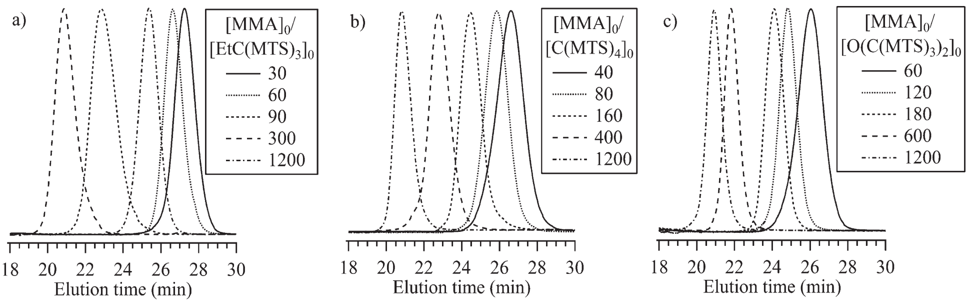


Figure 1. SEC traces of (a) three-armed star-shaped PMMAs (EtC(PMMA)$_3$), (b) four-armed star-shaped PMMAs (C(PMMA)$_4$), and (c) six-armed star-shaped PMMAs (O(C(PMMA)$_3$)$_2$) measured with an RI detector in THF.

large amount of methanol to give a linear PMMA. Yield: 182.4 mg (91.2%).

RESULTS AND DISCUSSION

Synthesis of Star-Shaped PMMA. For the core-first synthesis of the star-shaped PMMAs by group transfer polymerization (GTP), we newly designed and synthesized initiators possessing multiple numbers of silyl enolate groups, such as EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$ for the synthesis of the three-, four-, and six-armed star-shaped PMMAs (EtC(PMMA)$_3$, C(PMMA)$_4$, and O(C(PMMA)$_3$)$_2$, respectively), as shown in Scheme 2. Trimethylolpropane, pentaerythritol, and dipentaerythritol were reacted with isobutyryl chloride to give their tri-, tetra-, and hexaisobutyrates, i.e., EtC(*i*Bu)$_3$, C(*i*Bu)$_4$, and O(C(*i*Bu)$_3$)$_2$, respectively. These esters were treated with lithium diisopropylamide (LDA), followed by chlorotrimethylsilane ($(CH_3)_3SiCl$) to afford EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$ in moderate to high yields (66−88%). EtC(MTS)$_3$ and C(MTS)$_4$ were used after distillation, while O(C(MTS)$_3$)$_2$ was used after removing the *n*-hexane-insoluble impurities. The purities of the synthesized initiators were confirmed by the ^{1}H and ^{13}C NMR spectra, as shown in Figures S1, S2, and S3 (see Supporting Information). We have successfully established a method of synthesizing polyvalent initiators for GTP from precursors with multiple ester groups.

t-Bu-P$_4$ was used as the catalyst for the GTP using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$ to synthesize the star-shaped PMMAs with well-defined structures and high molecular weights because *t*-Bu-P$_4$ is one of the powerful organocatalysts, which are capable of synthesizing linear PMMAs with a molecular weight greater than 100 kg mol^{-1}. All the *t*-Bu-P$_4$-catalyzed GTPs of MMA were carried out in THF at 25 °C for 1 h under an argon atmosphere. The ratio of [*t*-Bu-P$_4$]$_0$ and [initiator]$_0$ ([I]$_0$) significantly affected the polymerization rate and molecular weight distribution (M_w/M_n) of the resulting polymers. In order to synthesize the star-shaped PMMAs with high molecular weights, a relatively high [*t*-Bu-P$_4$]$_0$/[I]$_0$ ratio was suitable. EtC(PMMA)$_3$s, C(PMMA)$_4$s, and O(C(PMMA)$_3$)$_2$s with different molecular weights were synthesized by changing the [MMA]$_0$/[I]$_0$ ratio. Correspondingly, the appropriate [*t*-Bu-P$_4$]$_0$/[I]$_0$ ratio was chosen in the range of 0.005−0.05 according to the [MMA]$_0$/[I]$_0$ ratio. The synthesis of the three-armed star-shaped PMMA (EtC(PMMA)$_3$) was carried out under the conditions of [MMA]$_0$/[EtC(MTS)$_3$]$_0$ = 30, 60, 90, 300, and 1200 (runs 1−5). The number-average molecular weights (M_n(SEC)s) of the obtained EtC(PMMA)$_3$, estimated by size exclusion chromatography with an refractive index (RI) detector using a linear PMMA calibration, were 3.6, 5.3, 10.3, 28.0, and 111.3 kg mol^{-1}, which showed a slight deviation from their theoretical number-average molecular weights (M_n(theor.)s) calculated by M_n(theor.) = ([MMA]$_0$/[I]$_0$) × (MW of MMA) × (conversion of MMA) + (MW of initiator residue). The deviation could be attributed to the different hydrodynamic volume between the star-shaped PMMAs and the linear PMMA used as a calibration. The absolute weight-average molecular weights (M_w(MALS)) of the obtained PMMAs using EtC(MTS)$_3$ were estimated by size exclusion chromatography (SEC) using a multiangle laser light scattering instrument (MALS). The measured M_w(MALS)s were 3.9, 7.8, 11.8, 34.5, and 132.0 kg mol^{-1}, which fairly agreed with their theoretical molecular weights (M_w(theor.)) calculated by the following equation: M_w(theor.) = [([MMA]$_0$/[I]$_0$) × (conversion of MMA) × (MW of MMA) + (MW of initiator residue)] × M_w/M_n(SEC). For the synthesis of the four- and six-armed star-shaped PMMAs (C(PMMA)$_4$ and O(C(PMMA)$_3$)$_2$, respectively), the polymerizations were performed with [MMA]$_0$/[C(MTS)$_4$]$_0$ = 40, 80, 160, 400, and 1200 (runs 6−10) and [MMA]$_0$/[O(C(MTS)$_3$)$_2$]$_0$ = 60, 120, 180, 600, and 1200 (runs 11−15). The M_w(MALS)s of the obtained PMMAs using C(MTS)$_4$ were 5.5, 12.7, 18.0, 45.0, and 130.3 kg mol^{-1} and those using O(C(MTS)$_3$)$_2$ were 7.5, 14.2, 20.0, 69.5, and 131.6 kg mol^{-1}, which fairly agreed with the M_w(theor.)s of 5.3−132.7 kg mol^{-1} and 7.7−130.5 kg mol^{-1}, respectively.

Parts a−c of Figure 1 show the SEC traces for the PMMAs obtained using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$, respectively. All the SEC traces exhibited a narrow and unimodal molecular weight distribution, and the SEC trace shifted to the higher molecular weight region with the increasing [MMA]$_0$/[I]$_0$ ratio. In addition, the M_w/M_ns were in the range of 1.07−1.14, 1.07−1.17, and 1.06−1.15 for the PMMAs obtained using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$, respectively. In addition, the structures of the PMMAs obtained using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$ (runs 3, 7, and 12, respectively) were further verified by their ^{1}H NMR spectra, as shown in Figure S4 (see Supporting Information). Every spectrum showed typical resonances due to the methyl group and methylene group on the main chain of PMMA. In addition, the resonances due to the methylene group of the core unit linking to the PMMA arms are clearly observed in the range of 3.85−4.00 ppm (Figure S4a, peak a), 3.95−4.15 ppm (Figure S4b, peak b, Supporting Information), and 3.87−4.12 ppm (Figure S4c, peak c, Supporting Information) for the PMMAs obtained using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$, respectively.

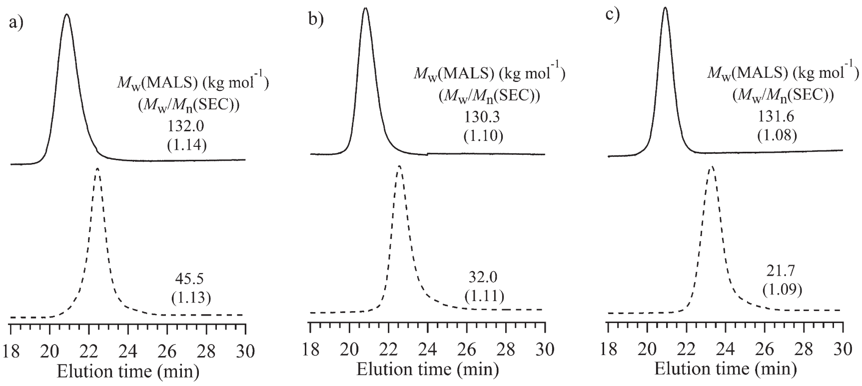


Figure 2. SEC traces of the parent star-shaped PMMAs (upper, solid line) and the cleaved linear PMMAs (lower, dashed line) obtained from (a) run 5, (b) run 10, and (c) run 15 measured by an RI detector in THF.

Table 1. Synthesis of Three-, Four-, and Six-Armed Star-Shaped PMMAs by the *t*-Bu-P$_4$-Catalyzed GTP of MMA Using EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$ [a]

			star-shaped PMMA						cleaved PMMA arm			
			M_n (kg mol^{-1})[b]		M_w (kg mol^{-1})[d]				M_w (kg mol^{-1})[d]			
run	initiator (I)	[MMA]$_0$/[I]$_0$/[*t*-Bu-P$_4$]$_0$	theor.[c]	SEC	theor.	MALS	M_w/M_n[b]	$[\eta]$[d] (mL g^{-1})	theor.[e]	MALS	M_w/M_n[b]	arm number[f]
1	EtC(MTS)$_3$	30/1/0.01	3.4	3.6	3.8	3.9	1.13	4.1				
2		60/1/0.01	6.4	5.3	7.3	7.8	1.14	6.7				
3		90/1/0.02	9.4	10.3	10.1	11.8	1.07	7.8				
4		300/1/0.03	30.4	28.0	34.0	34.5	1.12	14.4	10.9	11.3	1.09	3.05
5		1200/1/0.05	120.5	111.3	137.4	132.0	1.14	32.2	45.2	45.5	1.13	2.90
6	C(MTS)$_4$	40/1/0.005	4.5	4.7	5.3	5.5	1.17	4.8				
7		80/1/0.005	8.5	7.9	9.4	12.7	1.10	7.9				
8		160/1/0.005	16.5	15.0	17.7	18.0	1.07	9.5				
9		400/1/0.03	40.5	37.6	45.0	45.0	1.11	17.8	11.5	11.1	1.15	4.05
10		1200/1/0.05	120.6	117.1	132.7	130.3	1.10	31.3	33.3	32.0	1.11	4.07
11	O(C(MTS)$_3$)$_2$	60/1/0.005	6.7	7.3	7.7	7.5	1.15	5.9				
12		120/1/0.005	12.7	13.7	13.5	14.2	1.06	7.6				
13		180/1/0.005	18.7	17.6	19.8	20.0	1.06	9.1				
14		600/1/0.03	60.7	57.8	65.0	69.5	1.07	20.5	10.5	11.7	1.05	5.94
15		1200/1/0.05	120.8	118.0	130.5	131.6	1.08	31.4	21.8	21.7	1.09	6.06

[a] Argon atmosphere; temperature, 25 °C; [MMA]$_0$, 2.0 mol L^{-1}; time, 1 h. Conversion of MMA in all the runs was determined as greater than 99% by ^{1}H NMR measurements in CDCl$_3$. [b] Determined by SEC equipped with an RI detector in THF. [c] Calculated as follows: M_n(theor.) = ([MMA]$_0$/[I]$_0$) × (MW of MMA) + (MW of initiator residue). [d] Determined by SEC equipped with MALS and viscosity detectors in THF. [e] Calculated as follows: M_w(theor.) = M_n(theor.) × M_w/M_n (SEC). [f] The number of arms = (M_w(MALS) of star-shaped PMMA)/(M_w(MALS) of cleaved linear PMMA).

These results indicated that all the obtained polymers consisted of a core unit derived from the initiator and the PMMA arms; i.e., the obtained polymers were star-shaped PMMAs.

In order to offer more information about the structure of the star-shaped PMMAs, cleavage of the linkage between the core unit and the PMMA arms was further carried out. During the cleavage experiment, the star-shaped PMMA was hydrolyzed using KOH in methanol/THF and esterified using trimethylsilyldiazomethane (TMSCH$_2$N$_2$), leading to the cleaved PMMA arms. Figure S5 (Supporting Information) displays the ^{1}H NMR spectra of the star-shaped PMMAs and their cleaved PMMAs. The signal of the methylene protons due to the core unit linking to the PMMA arms completely disappeared, indicating that the hydrolysis of the star-shaped PMMAs perfectly proceeded to afford the cleaved PMMAs. Figure 2 shows the SEC traces of EtC(PMMA)$_3$ (run 5), C(PMMA)$_4$ (run 10), and O(C(PMMA)$_3$)$_2$ (run 15) and their cleaved PMMAs. The SEC traces shifted to the lower molecular weight region after the cleavage, while the SEC traces retained the unimodal and narrow molecular weight distributions; the M_w/M_n(SEC)s changed from 1.14 to 1.13 for run 5, from 1.10 to 1.11 for run 10, and from 1.08 to 1.09 for run 15 before and after the cleavage experiment. The M_w(MALS) values of the obtained linear PMMAs were around 1/3, 1/4 and 1/6 of those of the parent star-shaped PMMAs, i.e., 45.5 kg mol^{-1} for run 5, 32.0 kg mol^{-1} for run 10, and 21.7 kg mol^{-1} for run 15. Similar results were obtained from the cleavage experiment for the PMMAs obtained from runs 4, 9, and 14, as shown in Figure S6, Supporting Information. The number of

Table 2. Synthesis of Four-Armed Poly(methacrylate)s by the *t*-Bu-P$_4$-Catalyzed GTPs of Allyl Methacrylate (AMA), Stearyl Methacrylate (SMA), and 2-(Dimethylamino)ethyl Methacrylate (DMAEMA) Using C(MTS)$_4$ in THF [a]

				M_n (kg mol^{-1})[b]		M_w (kg mol^{-1})[d]		
run	monomer (M)	$[M]_0$ (mol L^{-1})	$[M]_0/[C(MTS)_4]_0/[t\text{-Bu-P}_4]_0$	theor.[c]	SEC	theor.[e]	MALS	M_w/M_n[b]
16	AMA	2.0	80/1/0.005	10.6	8.7	11.8	13.6	1.11
17	AMA	2.0	160/1/0.01	20.6	19.1	23.9	21.2	1.16
18	SMA	1.0	80/1/0.005	32.5	20.5	34.5	34.5	1.06
19	SMA	1.0	160/1/0.01	64.4	35.8	69.6	65.2	1.08
20	DMAEMA	2.0	80/1/0.005	13.0	7.8	15.1	15.5[f]	1.16
21	DMAEMA	2.0	160/1/0.01	25.4	12.3	27.9	23.3[f]	1.10

[a] Argon atmosphere; temp., 25 °C; time, 1 h; monomer conv. (determined by ^{1}H NMR in CDCl$_3$), > 99%. [b] Determined by SEC equipped with an RI detector in THF. [c] Calculated as follows: $M_n(\text{theor.}) = ([M]_0/[C(MTS)_4]_0) \times (\text{MW of monomer}) + (\text{MW of initiator residue})$. [d] Determined by SEC equipped with MALS and viscosity detectors in THF. [e] Calculated as follows: $M_w(\text{theor.}) = M_n(\text{theor.}) \times M_w/M_n$ (SEC). [f] Determined by SEC equipped with MALS detector in DMF containing 0.01 mol L^{-1} of LiBr.

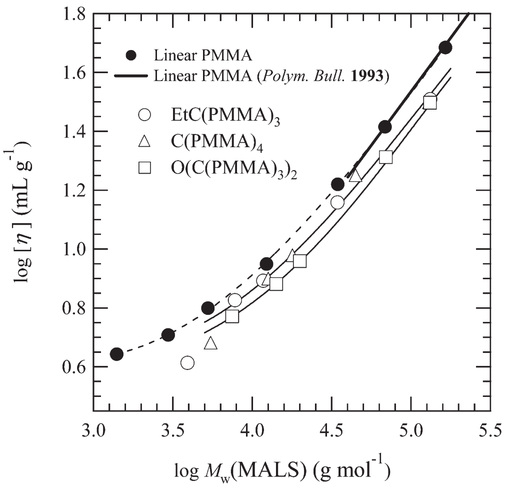


Figure 3. Double−logarithmic plots of $[\eta]$ versus M_w(MALS) for three-armed star-shaped PMMAs (○), four-armed star-shaped PMMAs (△), and six-armed star-shaped PMMAs (□) in a good solvent such as THF. The data for linear PMMA standards (●) are presented for comparison. The thick solid line is the reference value in THF at 30 °C.[59]

PMMA arms, which was calculated by dividing the M_w(MALS)s of the parent star-shaped PMMAs by those of the cleaved linear PMMAs, were 3.05 and 2.90 for EtC(PMMA)$_3$, 4.05 and 4.07 for C(PMMA)$_4$, and 5.94 and 6.06 for O(C(PMMA)$_3$)$_2$. These results provided evidence for homogeneous growth of each PMMA arm during the polymerization, which strongly led to the conclusion that the precise synthesis of the three-, four-, and six-armed PMMAs with well-defined star-shaped structures were achieved by the *t*-Bu-P$_4$-catalyzed GTP based on the core-first method. Importantly, the three-, four-, and six-armed star-shaped PMMAs with up to 132 kg mol^{-1} high molecular weights and 1.06 to 1.17 low polydispersities were obtained with easy procedures under moderate conditions, which significantly differed from the core-first synthesis of the star-shaped PMMAs using ATRP and anionic polymerization.

Synthesis of Star-Shaped Poly(methacrylate)s. The *t*-Bu-P$_4$-catalyzed GTPs of the allyl methacrylate (AMA), stearyl methacrylate (SMA), and (2-dimethylamino)ethyl methacrylate (DMAEMA) using C(MTS)$_4$ were also tried in order to check the generality for other methacrylic monomers. Table 2 summarizes these polymerization results. AMA, SMA, and DMAEMA were quantitatively consumed within 1 h, affording the four-armed poly(allyl methacrylate) (C(PAMA)$_4$), poly(stearyl mectharylate) (C(PSMA)$_4$), and poly((2-dimethylamino)ethyl methacrylate) (C(PDMAEMA)$_4$) with defined molecular weights and narrow molecular weight distributions. For example, under the condition of [AMA, SMA, or DMAEMA]/[C(MTS)$_4$] = 160/1, the M_w(MALS) values were 21.2, 65.2, and 23.3 kg mol^{-1}, respectively, which agreed with the M_w(theor.) values of 23.9, 69.6, and 27.9, for the C(PAMA)$_4$, C(PSMA)$_4$, and C(PDMAEMA)$_4$, respectively. These results indicated that the *t*-Bu-P$_4$-catalyzed GTP is one of the useful methods for the core-first synthesis of the star-shaped poly(methacrylate)s.

Viscometrical Properties of Star-shaped PMMA. In order to provide further insights into the properties of the prepared star-shaped PMMAs, their intrinsic viscosities ($[\eta]$) were measured in THF at 40 °C and compared to those for linear PMMA standards. As shown in Table 1, the values of $[\eta]$ were estimated in the range of 4.1−32.2 mL g^{-1} for the three-armed star-shaped PMMA, 4.8−31.3 mL g^{-1} for the four-armed star-shaped PMMA, and 5.9−31.4 mL g^{-1} for the six-armed star-shaped PMMA. Double logarithmic plots of $[\eta]$ of the star-shaped PMMA against M_w are presented in Figure 3. The experimental data for linear PMMA standards with the $M_w(M_w/M_n)$s of 1.40 kg mol^{-1}-(1.15), 2.96 kg mol^{-1}(1.06), 5.26 kg mol^{-1}(1.10), 12.3 kg mol^{-1}-(1.04), 34.5 kg mol^{-1}(1.02), and 68.2 kg mol^{-1}(1.03), and 165 kg mol^{-1}(1.05) were also shown for comparison. The thick solid line in this figure is one calculated from the Mark−Houwink−Sakurada (MHS) equation for a series of linear PMMAs with M_w higher than 40.0 kg mol^{-1} in THF at 30 °C, which is given by the equation,[59]

$$[\eta](\text{mL g}^{-1}) = 7.56 \times 10^{-3} M_w^{0.731} \quad (1)$$

The experimental data for linear PMMAs with M_w higher than 40.0 kg mol^{-1} were consistent with the eq 1 within the experimental error. In contrast, the noticeable upward deviation of the $[\eta]$ values from the MHS equation is observed for the linear PMMAs below M_w = 40.0 kg mol^{-1}. This is most likely due to the thickness effects in the low molecular weight components.

The $[\eta]$ values of the three-, four-, or six-armed star-shaped PMMAs prepared in the present study were lower than those of the linear PMMAs with the corresponding M_w, implying the existence of the branching architecture. The slope in the plots for the star polymers gradually increases with an increase of M_w and reaches the same slope as linear PMMA in the region of M_w higher than 100 kg mol^{-1}. This is well-known behavior for the intrinsic viscosity of star-shaped polymers.[5] The shrinking factor or contraction factor for the intrinsic viscosity of branched polymers, g' may be defined as[60]

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{2}$$

where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosity for the branched and linear polymers with the same M_w.

Whereas the theoretical work on g' still remains not fully understood, a useful empirical equation for regular star polymers in a good solvent has been proposed.[61] The equation is written as

$$g' = \left(\frac{3f-2}{f^2}\right)^{0.58} \frac{0.724 - 0.015(f-1)}{0.724} \tag{3}$$

where f is the number of arm. One applied eq 3 to the present experimental data of the star-shaped polymers having M_w higher than 100 kg mol^{-1} (runs 5, 10, and 15), because eq 3 was one derived originally for a long Gaussian coil. The g' values were 0.77 and 0.75 and the f value was estimated to be 3.4 and 3.6 for the three- and four-armed star-shaped PMMAs, respectively. This strongly supported the successful syntheses of the three- and four-armed star-shaped polymers by the present core-first method. On the other hand, for the six-armed star-shaped PMMA, the g' value was 0.75 and the f value was 3.6, which was considerably smaller value than expected. Whereas the disagreement in the six-armed star-shaped polymer has been insufficiently understood, a feasible explanation was based on the fact that molecular weight of an arm polymer was low (21.7 kg mol^{-1}) and eq 3 was not fully applicable.

■ CONCLUSION

The three-, four- and six-armed star-shaped PMMAs with different designed molecular weights were obtained by the core-first GTP catalyzed by *t*-Bu-P$_4$ using initiators possessing three, four, and six trimethylsilyl ketene acetal groups, respectively. The cleavage experiment for the star-shaped PMMA determined that the star-shaped PMMA consisted of the predicted number of linear PMMA arms with a narrow molecular weight distribution. In addition, these results indicated that the *t*-Bu-P$_4$-catalyzed GTP is one of the useful methods for the core-first synthesis of the star-shaped poly(methacrylate)s. This study provided a useful core-first methodology for the synthesis of star-shaped poly(methacrylate)s and provided a much deeper insight into the GTP method.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures with full characterizations for the syntheses of EtC(*i*Bu)$_3$, C(*i*Bu)$_4$, O(C(*i*Bu)$_3$)$_2$, EtC(MTS)$_3$, C(MTS)$_4$, and O(C(MTS)$_3$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org/.

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