Macromolecules

Synthesis of Homopolymers, Diblock Copolymers, and Multiblock Polymers by Organocatalyzed Group Transfer Polymerization of Various Acrylate Monomers

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Supporting Information



ABSTRACT: The group transfer polymerization (GTP) with *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me₃SiNTf₂) and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (*i*Pr-SKA) has been studied using methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA), 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate (*c*HA), dicyclopentanyl acrylate (dcPA), *tert*-butyl acrylate (*t*BA), 2-methoxyethyl acrylate (MEA), 2-(2-ethoxyethoxy)ethyl acrylate (EEA), 2-(dimethylamino)ethyl acrylate (DMAEA), allyl acrylate (AIA), propargyl acrylate (PgA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), and triisopropylsilyl acrylate (TIPSA). Except for *t*BA and DMAEA, the GTPs of all other monomers described above proceeded rapidly in a living manner and produced well-defined homo acrylate polymers. The living nature of the GTPs of such acrylate monomers was further applied to the postpolymerizations of MA, EA, *n*BA, and MEA and also to the sequential GTPs of diverse acrylate monomers for preparing di- and multiblock acrylate polymers. In greater detail, the AB and BA diblock copolymers, (ABC)₄ dodecablock terpolymer, (ABCD)₃ dodecablock quaterpolymer, and ABCDEF hexablock sestopolymer were synthesized by sequential GTP methods using various acrylate monomers.

INTRODUCTION

Block polymers exhibit various properties in the bulk and solution phases depending on the type of polymer segments used and their combinations.^{1–3} For example, AB diblock copolymers with various combinations of A and B polymer segments have been widely designed and synthesized using many controlled/living polymerization methods to study and apply their physical properties as polymeric materials.^{4–7} In addition, the ABA and BAB triblock copolymers and $(AB)_n$ alternate multiblock copolymers have been synthesized for comparison with AB diblock copolymers in terms of the interest in their morphologies.^{8–11} The anionic polymerization by sequentially and preorderly adding designed monomers, i.e., the sequential anionic polymerization, is one of the reliable methods for preparing multiblock polymers with predictable molecular weights and narrow molecular weight distributions. For the ABA and BAB triblock copolymers, Hirao et al. and

Hadjichristidis et al. reported the synthesis of poly(2-vinylpyridine)-*b*-polystyrene-*b*-poly(2-vinylpyridine) (P2VP-*b*-PS-*b*-P2VP), poly(methyl methacrylate)-*b*-P2VP-*b*-poly(methyl methacrylate) (PMMA-*b*-P2VP-*b*-PMMA), and PS-*b*-poly-(dimethylsiloxane)-*b*-PS (PS-*b*-PDMS-*b*-PS).^{9–12} For the (AB)_n alternate multiblock copolymer, the ABABAB hexablock, ABABABAB octablock, and ABABABABABAB dodecablock copolymers were synthesized using the α -chain-end-functionalized AB diblock copolymer of PS-*b*-PMMA.^{9–11} In addition, more complicated multiblock polymer objects, such as those consisting of more than three different polymer segments, have attracted much attention from the viewpoint of the development of advanced nanomaterials. For instance, the ABC

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triblock terpolymers of PS-b-P2VP-b-poly(tert-butyl methacrylate) (PS-b-P2VP-b-PtBMA) was synthesized by Stadler et al. using sequential anionic polymerization.¹³ Recently, the ABCD tetrablock quaterpolymer of PS-b-polyisoprene-b-PDMS-b-P2VP (PS-b-PI-b-PDMS-b-P2VP) and the ABCDE pentablock quintopolymer of PS-b-PI-b-PDMS-b-PtBMA-b-P2VP were synthesized by the combination of the sequential polymer-ization and selective linking methods.^{14,15} However, the anionic polymerization of acrylate monomers hardly controlled the molecular weights and their distributions of the obtained polymers due to the side reactions of the ester carbonyl group and the susceptible α -hydrogen with the anionic initiators and the active chain ends. Therefore, multiblock polymers containing acrylate polymer segments are limited using the sequential anionic polymerization method, meaning that the synthesis of multiblock polymers even though they consist of only acrylate polymer segments, i.e., multiblock acrylate polymers, is a remaining and challenging task. The sequential controlled/living radical polymerization is currently an efficient technique for the synthesis of well-defined acrylate polymers. For instance, Whittaker et al. reported that poly(methyl acrylate)-b-poly(n-butyl acrylate)-b-poly(ethyl acrylate)-b-poly-(2-ethylhexyl acrylate)-b-poly(ethyl acrylate)-b-poly(n-butyl acrylate)-b-poly(n-butyl acrylate)-b-poly(methyl acrylate) (PMA-b-PnBA-b-PEA-b-PEHA-b-PEA-b-PnBA-b-PnBA-b-PMA) and PMA-b-PEA-b-PnBA-b-poly(tert-butyl acrylate)-b-PMA-b-PEA-b-PnBA-b-poly(tert-butyl acrylate)-b-PMA-b-PEA were synthesized as octablock and decablock acrylate polymers, respectively, by the iterative Cu(0)-mediated radical polymerization.16,17

Group transfer polymerization (GTP), one of the anionic polymerizations, is well-known as the polymerization method for (meth)acrylate monomers using conventional Lewis acids and bases.¹⁸⁻²² Recently, organocatalysts have been found to sufficiently control the GTP, which leads to producing welldefined (meth)acrylate polymers with predicted molecular weights and narrow molecular weight distribution. For instance, Taton et al. and Waymouth et al. reported that N-heterocylic carbenes efficiently catalyzed the GTPs of methyl methacrylate, N,N-dimethylaminoethyl methacrylate, N,N-dimethyacrylamide, tert-butyl acrylate (tBA), and n-butyl acrylate (nBA) to produce the respective well-defined homopolymers as well as their di- and triblock polymers.²³⁻²⁸ In addition, we reported that strong Brønsted acids, such as trifluoromethanesulfonylimide and 1-[bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6pentafluorobenzene, and the Lewis acid of N-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me₃SiNTf₂) performed as promoters and organocatalyst, respectively, for the controlled/ living GTPs of (meth)acrylate and acrylamide monomers.^{29–35} Particularly, the organic-acid-catalyzed GTP using the initiator of 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (iPr-SKA) was the most suitable polymerization method for acrylate monomers, such as methyl acrylate (MA) and nBA, leading to high-molecular-weight acrylate polymers with the molecular weight of up to 10^3 kg mol⁻¹ and those with $\alpha_{,}\omega$ -end-functional groups.33,35 Thus, it is important to elucidate the scope and limit of this GTP system in terms of applicable acrylate monomers and synthesis of multiblock acrylate polymers. Hence, our objective is to establish the Me₃SiNTf₂-catalyzed GTP using iPr-SKA as a versatile method for synthesizing welldefined acrylate polymers, as shown in Scheme 1. This article describes (1) the GTP characteristics of MA, ethyl acrylate (EA), nBA, 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate





R	Acrylate monomer	Acrylate polymer
CH ₃	MA	PMA
C ₂ H ₅	EA	PEA
CH ₂ CH ₂ CH ₂ CH ₃	nBA	P <i>n</i> BA
CH ₂ CH(C ₂ H ₅)C ₄ H ₉	EHA	PEHA
cyclo-C ₆ H ₁₁	cHA	PcHA
C ₁₀ H ₁₅ *	dcPA	PdcPA
C(CH ₃) ₃	tBA	PtBA
CH ₂ CH ₂ OCH ₃	MEA	PMEA
CH ₂ CH ₂ OSi(CH(CH ₃) ₂) ₃	TIPS-HEA	P(TIPS-HEA)
CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃	EEA	PEEA
CH ₂ CH ₂ N(CH ₃) ₂	DMAEA	PDMAEA
CH ₂ CH=CH ₂	AIA	PAIA
CH ₂ C≡CH	PgA	PPgA
Si(CH(CH ₃) ₂) ₃	TIPSA	PTIPSA
* 33		

(cHA), dicyclopentanyl acrylate (dcPA), and tBA as alkyl acrylates and 2-methoxyethyl acrylate (MEA), 2-(2ethoxyethoxy)ethyl acrylate (EEA), allyl acrylate (AIA), propargyl acrylate (PgA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), and triisopropylsilyl acrylate (TIPSA) as functional acrylates, (2) the homopolymer chain extension by the sequential postpolymerizations (nine times) of MA, EA, *n*BA, and MEA, and (3) the synthesis of AB and BA diblock copolymers, (PEHA-*b*-PnBA-*b*-PEA)₄ dodecablock terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PEA-*b*-PMA-*b*-PcHA hexablock sestopolymer.

EXPERIMENTAL SECTION

Materials. Dichloromethane (CH₂Cl₂, >99.5%; water content, <0.001%), toluene (>99.5%; water content, <0.001%), tetrahydrofuran (THF, >99.5%; water content, <0.001%), triethylamine (>99.0%), methanol (>99.5%), and tert-butyl alcohol (>98.0%) were purchased from Kanto Chemicals Co., Inc. Methyl acrylate (MA, >99.8%), ethyl acrylate (EA, >99.0%), n-butyl acrylate (nBA, >99.0%), 2-ethylhexyl acrylate (EHA, 99.0%), cyclohexyl acrylate (cHA, >98.0%), dicyclopentanyl acrylate (dcPA, >95.0%), tert-butyl acrylate (tBA, >98.0%), 2-methoxyethyl acrylate (MEA, >98.0%), 2-(2ethoxyethoxy)ethyl acrylate (EEA, 98.0%), 2-(dimethylamino)ethyl acrylate (DMAEA, >97.0%), allyl acrylate (AlA, >98.0%), 2hydroxyethyl acrylate (>95.0%), acrylic acid (>99.0%), acryloyl chloride (>95.0%), N-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me₃SiNTf₂, >95.0%), and triisopropylsilyl chloride (*i*Pr₃SiCl) were purchased from Tokyo Kasei Kogyo Co., Ltd. MA, EA, nBA, EHA, cHA, dcPA, tBA, MEA, EEA, DMAEA, AlA and CH₂Cl₂ were distilled from CaH₂ and degassed by three freeze-pump-thaw cycles prior to their use. Toluene was distilled from sodium benzophenone ketyl. 1-Methoxy-1-triisopropylsiloxy-2-methyl-1-propene (*i*Pr-SKA) and propargyl acrylate (PgA) were synthesized by previously reported procedures.^{36,37} A spectra/Por 6 membrane (molecular weight cutoff: 1000) was used for the dialysis. All other chemicals were purchased from available suppliers and used without purification.

Measurements. The ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400II. The polymerization solution was prepared in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O , $O_2 < 1$ ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. Size exclusion chromatography (SEC) measurements of the obtained polymers were performed at 40 °C using a Jasco GPC-900 system equipped with two Shodex KF-804 L columns (linear, 8 mm ×300 mm) using THF at the flow rate of 1.0 mL min⁻¹. SEC measurements for the poly(*n*-butyl acrylate)s were performed at 40 °C using a Shodex GPC-101 gel permeation chromatography (GPC) system (Shodex DU-2130 dual pump, Shodex RI-71 RI detector, and Shodex ERC-3125SN degasser) equipped with two Shodex KF-804 L columns (linear, 8 mm ×300 mm) using THF at the flow rate of 1.0 mL min⁻¹. The numberaverage molecular weight $(M_{n,SEC})$ and dispersity (M_w/M_n) of the polymers were determined by the RI based on PMMA standards with the $M_{\rm w}$ $(M_{\rm w}/M_{\rm n})$ s of 1.25×10^6 g mol⁻¹ (1.07), 6.59×10^5 g mol⁻¹ (1.02), 3.003×10^5 g mol⁻¹ (1.02), 1.385×10^5 g mol⁻¹ (1.05), 6.015× 10^4 g mol⁻¹ (1.03), 3.053 × 10^4 g mol⁻¹ (1.02), and 1.155 × 10^4 g mol⁻¹ (1.04), 4.90 × 10^3 g mol⁻¹ (1.10), 2.87 × 10^3 g mol⁻¹ (1.06), and 1.43 × 10^3 g mol⁻¹ (1.15). The $M_{n,NMR}$ of the polymers were determined by their ¹H NMR spectra in CDCl₃ based on the initiator residue and monomer units. The preparative SEC was performed using CHCl₃ (3.5 mL min⁻¹) at room temperature ($20 \pm 5^{\circ}$ C) using a JAI LC-9201 equipped with a JAI JAIGEL-2H column (20 mm × 600 mm²; exclusion limit, 5×10^3) and a JAI RI-50s refractive index detector.

Synthesis of 2-(Triisopropylsiloxy)ethyl Acrylate (TIPS-HEA). iPr₃SiCl (16.6 g, 86.1 mmol) was dropwise added to a solution of 2hydroxyethyl acrylate (10.0 g, 86.1 mmol) and triethylamine (8.71 g, 86.1 mmol) in CH₂Cl₂ (150 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature and sequentially washed with 1 mol L⁻¹ HCl (100 mL \times 2), conc. aq. NaHCO₃ (100 mL), and distilled water (100 mL). The organic phase was dried over anhydrous MgSO₄. After filtration and evaporation, the residue was purified by distillation under reduced pressure to give TIPS-HEA as a transparent liquid. Yield: 12.51 g (53.3%). Bp: 67 °C/0.02 mmHg. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.40 (dd, J = 17.4, 1.4 Hz, 1H, -CH= $C^{E}H^{Z}H$), 6.12 (dd, J = 17.4, 10.6 Hz, 1H, $-CH = C^{E}H^{Z}H$), 5.81 (dd, J= 10.4, 2.0 Hz, $-CH = C^{E}H^{Z}H$, 4.26 (t, J = 5.2 Hz, 2H, $-COCH_2CH_2OSi$ -), 3.93 (t, J = 5.2 Hz, 2H, $-COCH_2CH_2OSi$ -), 1.01–1.13 (m, 21H, $-OSi[CH(CH_3)_2]_3$). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.2, 130.8, 128.4, 65.9, 61.5, 17.9, 11.9. Anal. Calcd for C14H28O3Si (272.46): C, 61.72; H, 10.36. Found: C, 61.40; H, 10.30.

Synthesis of Triisopropylsilyl Acrylate (TIPSA). *i*Pr₃SiCl (30.1 g, 156 mmol) was dropwise added to a solution of acrylic acid (11.3 g, 156 mmol) and triethylamine (15.8 g, 156 mmol) in CH₂Cl₂ (150 mL) at 0 °C. The following procedure was similar to that for synthesizing TIPS-HEA, which gave TIPSA as a transparent liquid. Yield: 19.5 g (54.6%). Bp: 87 °C/6.0 mmHg. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.37 (dd, J = 17.4, 1.4 Hz, 1H, $-CH=C^EH^ZH$), 6.12 (dd, J = 17.2, 10.4 Hz, 1H, $-CH=C^EH^ZH$), 5.84 (dd, J = 10.2, 1.4 Hz, $-CH=C^EH^ZH$), 1.01–1.13 (m, 21H, $-OSi[CH(CH_3)_2]_3$). ¹³C NMR (100 MHz, CDCl₃), δ (ppm) 165.8, 130.8, 130.3, 17.8, 12.0. Anal. Calcd for C₁₂H₂₄O₂Si (288.40): C, 63.10; H, 10.59. Found: C, 63.02; H, 10.57.

Me₃SiNTf₂-Catalyzed GTP of Acrylates Initiated by *i*Pr-SKA. A typical procedure is as follows. A stock solution of Me₃SiNTf₂ (10 μ L, 1.0 μ mol, 0.10 mol L⁻¹ in toluene) was added to a solution of MA (430 mg, 0.449 mL, 5.0 mmol) and *i*Pr-SKA (14.4 μ L, 12.9 mg, 50.0 μ mol) in toluene (4.48 mL) under an argon atmosphere at room temperature (23 ± 5 °C). After stirring for 1 h, the polymerization was quenched by adding a small amount of methanol. The crude product was purified by reprecipitation in *n*-hexane, dialysis, and preparative size exclusion chromatography (SEC) in CHCl₃ to give the poly(methyl acrylate) (PMA) as a white solid. Yield: 425 mg (99%). $M_{n,NMR} = 8600 \text{ g mol}^{-1}; M_{n,SEC} = 9700 \text{ g mol}^{-1}; M_w/M_n = 1.03$. The

GTP of the acrylates (5.0 mmol) produced PEA (yield, 491 mg, 98%), PnBA (yield, 612 mg, 96%), PEHA (yield, 892 mg, 97%), PcHA (yield, 748 mg, 97%), PdcPA (yield, 490 mg, 95%; monomer, 2.5 mmol), PtBA (yield, n.d., no polymerization), PMEA (yield, 638 mg, 98%), PEEA (yield, 885 mg, 94%), PDMAEA (yield, 638 mg, 98%), PEEA (yield, 885 mg, 94%), PDMAEA (yield, n.d., no polymerization), PAIA (yield, 522 mg, 93%), PPgA (yield, 518 mg, 94%), P(TIPS-HEA) (yield, 1.31 g, 96%), and PTIPSA (yield, 1.09 g, 95%) in a controlled manner.

Chain Extension by Postpolymerization. A typical procedure is as follows. The polymerization of MA (86 mg, 1.0 mmol) with iPr-SKA (14.4 μ L, 50 μ mol) and Me₃SiNTf₂ (10 μ L, 1.0 μ mol, 0.10 mol L^{-1} in toluene) in toluene (0.89 mL) at room temperature was carried out under the condition of $[MA]_0/[iPr-SKA]_0/[Me_3SiNTf_2]_0 = 20/1/$ 0.02 and $[MA]_0 = 1.0 \text{ mol } L^{-1}$ for 5 min as the first polymerization $((PMA)_1)$. The second polymerization was subsequently started by adding 20 equiv of MA (86.1 mg, 1.0 mmol) in toluene (0.89 mL) to the polymerization mixture after an aliquot was removed from the reaction mixture to determine the monomer conversion and the molecular weight and dispersity of the resulting polymer $((PMA)_2)$. The continuous postpolymerizations for the synthesis of $(PMA)_{3-10}$ were carried out by the same procedure after the complete consumption of MA was confirmed. After all the postpolymerizations, a small amount of methanol was added to the reaction mixture to terminate the polymerization. The obtained polymers were purified by dialysis and preparative SEC to give the (PMA)₁₀ as a clear solid (yield, 851 mg; 99%). The syntheses of (PEA)₁₀, (PnBA)₁₀, and (PMEA)₁₀ were carried out using the same procedure with 1.0 mmol, for each polymerization, of acrylates to give the respective acrylate polymers in quantitative yields ((PEA)₁₀, yield, 970 mg, 97%; (PnBA)₁₀, yield, 1.22 g, 95%; (PMEA)₁₀, yield, 1.24 g; 95%).

Synthesis of Di- and Multiblock Acrylate Polymers. The diblock copolymerizations were carried out using *n*BA (160 mg, 1.25 mmol) with MEA (162 mg, 1.25 mmol), AlA (140 mg, 1.25 mmol), and PgA (137 mg, 1.25 mmol). The multiblock polymerizations of MA (86 mg, 1.0 mmol), EA (100 mg, 1.0 mmol), *n*BA (128 mg, 1.0 mmol), EHA (184 mg, 1.0 mmol), *c*HA (154 mg, 1.0 mmol), *dc*PA (206 mg, 1.0 mmol), and MEA (130 mg, 1.0 mmol) were carried out using *i*Pr-SKA (28.8 μ L, 100 μ mol) and Me₃SiNTf₂ (20 μ L, 2.0 μ mol, 0.1 mol L⁻¹ in toluene) to produce (PHEA-*b*-PnBA-*b*-PEA)₄ (1.57 g, 95%), (PnBA-*b*-PEA-*b*-PMEA-*b*-PMA)₃ (1.28 g, 96%), and PdcPA-*b*-PnBA-*b*-PEHA-*b*-PEA-*b*-PMA-(842 mg, 98%).

RESULTS AND DISCUSSION

Me₃SiNTf₂-Catalyzed GTP of Alkyl Acrylates. The group transfer polymerization (GTP) of the acrylate monomers was carried out using N-(trimethylsilyl)bis-(trifluoromethanesulfonyl)imide (Me₃SiNTf₂) and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (*i*Pr-SKA) as the organocatalyst and initiator, respectively. We initially determined the GTP characteristics of the alkyl acrylates, such as methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (nBA), 2ethylhexyl acrylate (EHA), cyclohexyl acrylate (cHA), dicyclopentanyl acrylate (dcPA), and tert-butyl acrylate (tBA). In order to compare their polymerization rates, the polymerizations of MA, EA, nBA, EHA, cHA, and dcPA were carried out under the conditions of the fixed monomer (M)-to-initiator molar ratio $([M]_0/[iPr-SKA]_0)$ of 200 in toluene at room temperature. The kinetic experiments exhibited a distinct firstorder relationship between the reaction time and monomer conversion, as shown in Figure 1. There was no significant difference in the polymerization rates among MA, EA, and *n*BA, whose rates were higher than that of EHA. Although the loading amount of the catalyst was greater than that used for the polymerizations of MA, EA, nBA, and EHA, no polymerization proceeded for cHA and dcPA within the polymerization time of 30 min. There was an obvious difference in the



Figure 1. Kinetic plots for the Me₃SiNTf₂-catalyzed GTP of MA, EA, *n*BA, EHA, *c*HA, and dcPA using *i*Pr-SKA in toluene ($[M]_0/[iPr-SKA]_0/[Me_3SiNTf_2]_0$, 200/1/0.02; $[M]_0$, 1.0 mol L⁻¹; temperature, 27 °C).

polymerization ability between the primary and secondary alkyl acrylates for the Me₃SiNTf₂-catalyzed GTP using *i*Pr-SKA.

In order to ensure the synthesis of the targeted molecular weight polymers, which is one of the important characteristics for the living polymerization system, the polymerizations of MA, EA, nBA, EHA, and cHA were carried out under the conditions with the $[M]_0/[iPr-SKA]_0$ s of 100, 400, and 1000 in toluene at room temperature. All the polymerization results are listed in Table S1. The loading amount of the catalyst, i.e., the $[Me_3SiNTf_2]_0/[iPr-SKA]_0$, was 0.02 for the $[M]_0/[iPr-SKA]_0$ s of 100 and 400, whereas a higher amount of catalyst was required for the [Me₃SiNTf₂]₀/[*i*Pr-SKA]₀ of 0.05 and the $[M]_0/[iPr-SKA]_0$ of 1000. The polymerization time increased with the increasing $[M]_0/[iPr-SKA]_0$, and all of the monomers were consumed except for cHA. The number-average molecular weights of the obtained polymers estimated using SEC measurements $(M_{nSEC}s)$ linearly increased with the increasing $[M]_0/[iPr-SKA]_0$ (Figure 2), and the molecular weight distributions $(M_w/M_n s)$ of the obtained polymers were as low as 1.02–1.06, as shown in Figure S1. For the $[M]_0/[iPr-SKA]_0$ of 1000, the $M_{n,SEC}s$ ($M_w/M_n s$) were 97 500 g mol⁻¹ (1.04) for PMA, 108 400 g mol⁻¹ (1.04) for PEA, 141 900 g mol⁻¹ (1.05) for PnBA, and 220 000 g mol⁻¹ (1.06) for PEHA, which agreed



Figure 2. Plots for the molecular weights $(M_{n,SEC})$ of the obtained polymers vs the initial molar ratios of the monomer and initiators $([M]_0/[iPr-SKA]_0)$ MA, EA, *n*BA, EHA, and *c*HA along with the value of molecular weight and molecular weight distribution.

with the predicted values $(M_{\rm n,calcd.}s)$ of 86 100, 100 200, 128 300, and 184 400 g mol⁻¹, respectively. For the polymerization of cHA, the monomer conversion was 90.5% even after 24 h. Although the $M_{n,SEC}$ of 166 700 g mol⁻¹ approximately agreed with the $M_{n,calcd}$ of 139 700 g mol⁻¹, the molecular weight distribution slightly increased for the M_w/M_p of 1.15. Though the polymerization of dcPA needs long polymerization time as 24 h, it proceeded to produce well-defined PdcPA with $M_{\rm n,NMR}~(M_{\rm w}/M_{\rm n})$ of 10670 (1.08). On the other hand, the polymerization of tBA did not proceed at all even though given a polymerization time of 20 h, which was caused by the ester cleavage of the monomer in the presence of the strong Lewis acid of Me₃SiNTf₂. These results indicated that the polymerization ability of the primary alkyl acrylate was much higher than that of the secondary alkyl acrylate, and the tertiary alkyl acrylate possessed no polymerization ability for the Me₃SiNTf₂catalyzed GTP using the iPr-SKA initiator.

Me₃SiNTf₂-Catalyzed GTP of Functional Acrylates. In order to elucidate the scope and limit of the applicable monomers, we examined the polymerization of functional acrylates, such as 2-methoxyethyl acrylate (MEA), 2-(2ethoxyethoxy)ethyl acrylate (EEA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), 2-(dimethylamino)ethyl acrylate (DMAEA), allyl acrylate (AlA), propargyl acrylate (PgA), and triisopropylsilyl acrylate (TIPSA) using the iPr-SKA initiator. Table 1 summarizes the polymerization results. The polymerizations of MEA with the $[MEA]_0/[iPr-SKA]_0$ s of 100, 400, and 1000 produced the targeted molecular weight PMEAs, such as the $M_{n,SEC}$ s of 14400, 58800, and 140300 g mol⁻¹ respectively, which well agreed with the $M_{n,calcd}$ s of 13 100, 52 200, and 130 200 g mol⁻¹, respectively (runs 1–3). In addition, the molecular weight distributions of the PMEAs were as narrow as $M_{\rm w}/M_{\rm n}$ of 1.03–1.05. In order to more hydrophilic acrylate polymers relative to PMEA, the GTPs of EEA and TIPS-HEA were examined. For the polymerization condition of $[M]_0/[iPr-SKA]_0/[Me_3SiNTf_2]_0 = 100/1/0.02$, the $M_{n,SEC}$ of poly(2-(2-ethoxyethoxy)ethyl acrylate) (PEEA) was 18 900 g mol⁻¹ and the $M_{n,NMR}$ of poly(2-(triisopropylsiloxy)ethyl acrylate) (P(TIPS-HEA)) was 26700 g mol⁻¹, which agreed with the $M_{n,calcd.}$ s of 18 900 and 27 300 g mol⁻¹, respectively (runs 4 and 5). The M_w/M_n of PEEA was 1.06 even though a small peak was observed in the high molecular weight region, and that of P(TIPS-HEA) was 1.02. On the other hand, the polymerization of DMAEA did not proceed after 20 h, which should have been caused by the incentive that the dimethyamino group in the monomer deactivating the catalytic performance of Me₃SiNTf₂ (run 6). The deprotection of the triisopropylsilyl group in the P(TIPS-HEA) using tetra-*n*-butylammonium fluoride smoothly proceeded to produce the well-defined poly(2-hydoxyethyl acrylate). The Me₃SiNTf₂-catalyzed GTPs of AlA and PgA under the condition of $[M]_0/[iPr-SKA]_0 = 100/1$ produced gelfree polymers with the $M_{n,NMR}$ s of 11 800 and 11 000 g mol⁻¹, respectively, which agreed with the predicted values by the initial monomer-to-initiator ratio (runs 7 and 8). The characteristic proton signals of the allyl and ethynyl groups were observed at 5.91, 5.30-5.15, and 2.55 ppm respectively, together with those of the acrylate polymer main-chain at 2.60-2.40 ppm, in the ¹H NMR spectra, indicating that the polymerization of AlA and PgA proceeded through a controlled/living GTP mechanism in even in the presence of the reactive allyl and ethynyl groups (Figures S10 and S12). In addition, the GTP of TIPSA proceeded without cleavage of the

Table 1. Me ₃ SiNTf ₂ -Catalyzed (Group Transfer !	Polymerization o	of MEA, EEA,	TIPS-HEA,	DMAEA, AIA,	PgA, and	TIPSA	Using
the <i>i</i> Pr-SKA Initiator ^a								

run	monomer (M)	$[M]_0/[iPr\text{-}SKA]_0/[Me_3SiNTf_2]_0$	time/h	conv/% ^b	$M_{\rm n, calcd.}/{ m g}~{ m mol}^{-1}{}^c$	$M_{n,SEC} ({M_{n,NMR}}^b)/g \text{ mol}^{-1} d$	$M_{\rm w}/{M_{\rm n}}^d$
1	MEA	100/1/0.02	1	>99	13 100	14 400 (13 700)	1.03
2	MEA	400/1/0.02	3	>99	52 200	58 800	1.03
3	MEA	1000/1/0.05	18	>99	130 200	140 300	1.05
4	EEA	100/1/0.02	1	>99	18 900	18 900	1.06
5	TIPS-HEA	100/1/0.02	3	>99	27 300	21 200 (26 700)	1.02
6	DMAEA	100/1/0.02	20	<1	-	-	-
7	AlA	100/1/0.02	1	>99	11 300	11 000 (11 800)	1.04
8	PgA	100/1/0.05	3	>99	11 100	18 600 (11 000)	1.10
9	TIPSA	100/1/0.02	21	91.5	21 000	10 700 (23 520)	1.15

^{*a*}Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L⁻¹; temperature, room temperature. ^{*b*}Determined by ¹H NMR in CDCl₃. ^{*c*}Calculated from $([M]_0/([iPr-SKA]_0) \times (conv) \times (MW of monomer; MEA, 130.14; EEA, 188.22; TIPS-HEA, 272.46; DMAEA, 143.19; AIA, 112.13; PgA, 110.11; TIPSA, 228.40) + (MW of initiator residue, 102.13). ^{$ *d*}Determined by SEC in THF using poly(methyl methacrylate) standard.

silyl ester linkage to produce the poly(triisopropylsilyl acrylate) (PTIPSA) with the $M_{n,NMR}$ of 23 520 g mol⁻¹ though the polydispersity slightly increased for the M_w/M_n of 1.15 (run 9). PTIPSA was also deprotected using tetra-*n*-butylammonium fluoride to produce poly(acrylic acid), which could be used as the hydrophilic polymer segment in amphiphilic materials.⁸

For the GTP of the functional acrylates, the GTP characteristics of MEA were similar to those of the primary alkyl acrylate. The GTPs of EEA, TIPS-HEA, AlA, PgA, and TIPSA could be controlled at any initial monomer-to-initiator ratio not more than 100. The amino group containing the acrylate of DMAEA possessed no GTP reactivity. Importantly, AIA, PgA, and TIPSA are new functional monomers applicable for the anionic polymerization method, and their polymers should be expected to serve as precursors for producing various macromolecular architectures.

Synthesis of Di- and Multiblock Acrylate Polymers. The Me₃SiNTf₂-catalyzed GTP using the initiator of *i*Pr-SKA was an efficient controlled/living system for producing welldefined acrylate homopolymers, which should be applicable to the synthesis of acrylate block polymers. Thus, we first investigated the stability of the propagating chain end of the acrylate polymer by a chain extension experiment. For the postpolymerizations of MA, EA, nBA, and MEA, the first GTP was carried out under the conditions for the $[M]_{first}/[iPr-SKA]_0$ of 20 and the $[M]_0$ of 1.0 mol L^{-1} in toluene at room temperature, after all the first monomer was consumed, the second GTP was sequentially started by adding the second monomer with $[M]_{second}/[iPr-SKA]_0$, and the same procedure was repeated for another eight times. The postpolymerization results for MA, EA, nBA, and MEA are listed in Tables S2, S3, S4, and S5, respectively. The molecular weight $(M_{n,NMR})$ of the obtained polymers linearly increased with the increasing number of GTPs, as shown in Figure 3; from the $M_{n,NMR}$ of 1920 g mol⁻¹ for (PMA)₁ to the $M_{n,NMR}$ of 17 380 g mol⁻¹ for $(PMA)_{10}$, from 2100 g mol⁻¹ for $(PEA)_1$ to 20 230 g mol⁻¹ for $(PEA)_{10}$, from 2800 g mol⁻¹ for $(PnBA)_1$ to 26 100 g mol⁻¹ for $(PnBA)_{10}$, and from 2770 g mol⁻¹ for $(PMEA)_1$ to 26760 g mol^{-1} for (PMEA)₁₀. All the $M_{n,NMR}$ s of the obtained acrylate polymers well agreed with the $M_{n,calcd}$ s. In addition, Figure 4 shows the monomodal SEC traces of $(PMA)_{n}$, $(PEA)_{n}$ $(PnBA)_{n}$ and $(PMEA)_{n}$ and the molecular weight distributions were as narrow as the M_w/M_n s of 1.02–1.10 for (PMA)_n, 1.02– 1.09 for $(PEA)_n$ 1.03–1.11 for $(PnBA)_n$ and 1.02–1.11 for $(PMEA)_n$. These results strongly indicated that the propagating chain end should retain the structure of *i*Pr-SKA even though



Figure 3. Chain extensions of MA, EA, *n*BA, and MEA produced by the sequential GTPs (PMA (\bullet), PEA (red \blacksquare), P*n*BA (violet \blacktriangle), and PMEA (green \blacktriangledown)).

the postpolymerizations were carried out nine times, which promises the synthesis of various block acrylate polymers.

For the synthesis of block acrylate polymers, we synthesized the AB and BA diblock copolymers using the alkyl acrylate of nBA and the functional acrylates of MEA, AlA, and PgA. Table S6 summarizes the results of the block copolymerization under the condition of the $([M_{\text{first}} + M_{\text{second}}]_0/[i\text{Pr-SKA}]_0/$ $[Me_3SiNTf_2]_{0}$, of 25 + 25/1/0.02 and the $[M]_0$ of 1.0 mol L^{-1} in toluene at room temperature. In the case of *n*BA with MEA. MEA was added as the second monomer to the reaction mixture after the first GTP of *n*BA was completed. The product of the first GTP showed a monomodal molecular weight distribution in the SEC trace, which shifted to a higher molecular weight region in the SEC trace of the product of the second GTP, while keeping a narrow polydispersity, as shown in Figure 5a. The $M_{n,NMR}$ increased from 3360 to 6640 g mol⁻¹ and the M_w/M_n s decreased from 1.09 to 1.04 after the block copolymerization. The structure of PnBA-b-PMEA was confirmed by a ¹H NMR measurement (Figure S7). Alternatively, MEA was first polymerized to form the PMEA with the $M_{n,NMR}$ of 3480 g mol⁻¹, and *n*BA was then subsequently polymerized to produce the PMEA-b-PnBA with the $M_{n,NMR}$ of 6860 g mol⁻¹ and the M_w/M_n of 1.05. For the block copolymerization of nBA with AlA, the PnBA-b-PAlA and PAIA-b-PnBA diblock copolymers had the well-controlled $M_{\rm n,NMR}$ s of 6240 and 6580 g mol⁻¹, respectively. The $M_{\rm w}/M_{\rm n}$ of PnBA-b-PAIA was as low as 1.07, while that of PAIA-b-PnBA was relatively high at 1.13 due to a small peak observed in the low molecular weight region of the SEC trace (Figure 5b). This small peak was attributed to the unreacted PAIA, meaning that the second GTP of nBA initiated by the propagating PAIA



Figure 4. SEC traces of (a) $(PMA)_n$, (b) $(PEA)_n$, (c) $(PnBA)_n$, and (d) $(PMEA)_n$ obtained from the sequential GTPs of MA, EA, *n*BA, and MEA (eluent, THF; flow rate, 1.0 mL min⁻¹).



Figure 5. SEC traces of the diblock copolymers of (a) *n*BA and MEA, (b) *n*BA and AlA, and (c) *n*BA and PgA ($[M_{first} + M_{second}]_0/[iPr-SKA]_0/[Me_3SiNTf_2]_0$, 25 + 25/1/0.02; $[M]_0$, 1.0 mol L⁻¹) (dashed line, first polymer; solid line, block copolymer; eluent, THF; flow rate, 1.0 mL min⁻¹).

chain end was slightly insufficient. The block copolymerization of *n*BA and PgA produced the structurally defect-free P*n*BA-*b*-PPgA with the $M_{n,NMR}$ and M_w/M_n of 6320 g mol⁻¹ and 1.07, and the PPgA-*b*-P*n*BA with values of 6120 and 1.05, respectively. These results indicated that amphiphilic and reactive di- and multiblock acrylate copolymers can be synthesized using the Me₃SiNTf₂-catalyzed GTP by the appropriate combinations of acrylate monomers.

Finally, multiblock acrylate polymers were synthesized by the sequential Me₃SiNTf₂-catalyzed GTP using various acrylate monomers, as shown in Scheme 2. The synthetic result of the (PEHA-*b*-P*n*BA-*b*-PEA)₄ dodecablock terpolymer is listed in Table S7. Each GTP was carried out under the condition of the $[M]_0/[iPr-SKA]_0$ of 10 and the $[Me_3SiNTf_2]_0/[iPr-SKA]_0$ of 0.02. The first series of the sequential GTPs of EHA, *n*BA, and EA produced the PEHA with the $M_{n,NMR}$ of 1980 g mol⁻¹, the PEHA-*b*-P*n*BA diblock copolymer with 3350 g mol⁻¹, and the

PEHA-*b*-P*n*BA-*b*-PEA triblock terpolymer with 4390 g mol⁻¹, which agreed with the $M_{n,calcd.}$ s of 1940, 3220, and 4220 g mol⁻¹, respectively. The SEC traces of the homo, diblock, and triblock polymers were monomodal and the polydispersity (M_w/M_n) decreased from 1.11 to 1.07, as shown in Figure 6a. This procedure was repeated three more times. The SCE traces of the multiblock polymers shifted to a higher molecular weight region with the increasing number of sequential GTPs. Similarly, the $(PnBA-b-PEA-b-PMEA-b-PMA)_3$ dodecablock quaterpolymer was synthesized by the sequential Me₃SiNTf₂catalyzed GTP of nBA, EA, ME, and MA. Table S6 summarizes the results of the sequential GTPs. With the increasing number of sequential GTPs, the $M_{n,NMR}$ of the multiblock polymers theoretically increased and their SCE traces shifted to the higher molecular weight region while maintaining a monomodal and narrow polydispersity (Figure 6b). For the synthesis of the PdcPA-b-PnBA-b-PEHA-b-PEA-b-PMA-b-PcHA hexablock sestopolymer, the sequential Me₃SiNTf₂-catalyzed GTP of dcPA, nBA, EHA, EA, MA, and cHA produced the homo-, co-, ter-, quarter-, quinto-, and sestopolymers with predictable $M_{\rm n NMR}$ s and narrow $M_{\rm w}/M_{\rm n}$ s (Table S9). Figure 7 shows the ¹H NMR spectra of the homo-, co-, ter-, quarter-, quinto-, and sestopolymers in the polymerization mixtures after all the monomers were consumed. The characteristic signal *a* observed at 4.55 ppm was attributed to the methyne proton of the dcPA unit and that at 3.63 ppm to the methoxy proton b of the initiator residue (Figure 7a), that at 4.04 ppm to the methylene proton c of the *n*BA unit (Figure 7b), that at 3.96 ppm to the methylene proton d of the EHA unit (Figure 7c), that at 4.09 ppm to the methylene proton *e* of the EA unit (Figure 7d), that at 3.64 ppm to the methoxy proton f of the MA unit (Figure 7e), and that at 4.73 ppm to the methyne proton g of the cHA unit (Figure 7f). Similarly, the syntheses of (PEHA-b-PnBA-b- $PEA)_4$ and $(PnBA-b-PEA-b-PMEA-b-PMA)_3$ were also confirmed by the same method (Figures S13 and S14), and the structures of the multiblock polymers were assigned as the final products by the ¹H NMR spectra (Figures S15-S17). Finally, we obtained the (PEHA-b-PnBA-b-PEA)₄ dodecablock terpolymer with the $M_{n,NMR}$ of 16 890 g mol⁻¹ and the M_w/M_n of 1.03, the (PnBA-b-PEA-b-PMEA-b-PMA)₃ dodecablock quaterpolymer with the $M_{\rm n,NMR}$ of 13 520 g mol⁻¹ and the $M_{\rm w}/M_{\rm n}$ of 1.02, and the PdcPA-b-PnBA-b-PEHA-b-PEA-b-PMA-b-PcHA hexablock sestopolymer with the $M_{n,NMR}$ of 9240 g mol^{-1} and the $M_{\mathrm{w}}/M_{\mathrm{n}}$ of 1.05 (Table 2). These results clearly indicated that the sequential GTP was an efficient method for the syntheses of the well-defined multiblock acrylate polymers.

Article

Scheme 2. Synthesis of (PEHA-*b*-P*n*BA-*b*-PEA)₄ Dodecablock Terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)₃ Dodecablock Quaterpolymer, and PdcPA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-PcHA Hexablock Sestopolymer, as (ABC)₄, (ABCD)₃, and ABCDEF Block Polymers by Sequential Group Transfer Polymerization



Figure 6. SEC traces for the synthesis of (a) (PEHA-*b*-P*n*BA-*b*-PEA)₄ dodecablock terpolymer, (b) (P*n*BA-*b*-PEA-*b*-PMA)₃ dodecablock quaterpolymer, and (c) PdcPA-*b*-PnBA-*b*-PEHA-*b*-PMA-*b*-PCHA hexablock sestopolymer (eluent, THF; flow rate, 1.0 mL min⁻¹).

CONCLUSION

The organocatalyzed group transfer polymerization (GTP) of acrylate monomers was studied in order to clarify its scope and limits. The primary alkyl acrylate possessed a high GTP ability compared to the secondary alkyl acrylate, and the tertiary alkyl acrylate exhibited no polymerization ability. The GTPs of the allyl acrylate and propargyl acrylate proceeded without gelation and that of the triisopropylsilyl acrylate without cleavage of the silyl ester linkage, correspondingly producing their well-defined acrylate polymers. These GTP characteristics were caused by the living nature that the triisopropylsilyl ketene acetal of the initiator and the propagating chain-end efficiently reacted with the acrylate monomer activated by the strong organic Lewis acid, which was proved by the sequential GTP leading to the polymer chain extension. In addition, the (PEHA-*b*-P*n*BA-*b*-PEA)₄ dodecablock terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)₃ dodecablock quaterpolymer, and PdcPA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer were



Figure 7. ¹H NMR spectra of the hexablock sestopolymer obtained by sequential Me₃SiNTf₂-catalyzed GTP; (a) PdcPA, (b) PdcPA-b-PnBA, (c) PdcPA-b-PnBA-b-PEHA, (d) PdcPA-b-PnBA-b-PEHA-b-PEA, (e) PdcPA-b-PnBA-b-PEHA-b-PEA-b-

Table 2. Synthesis of $(PEHA-b-PnBA-b-PEA)_4$ Dodecablock Terpolymer, $(PnBA-b-PEA-b-PMEA-b-PMA)_3$ Dodecablock Quaterpolymer, and PdcPA-b-PnBA-b-PEHA-b-PEA-b-PMA-b-PcHA Hexablock Sestopolymer by Sequential Me₃SiNTf₂-Catalyzed Group Transfer Polymerization of EHA, *n*BA, EA, MEA, MA, dcPA, and cHA^a

block polymer	$M_{\rm n, calcd.}/{ m g}~{ m mol}^{-1}$ c	$M_{ m n,NMR}/ m g\ mol^{-1}$ b	$M_{ m w}/M_{ m n}^{\ d}$
(PEHA-b-PnBA-b-PEA) ₄	16 580	16 890	1.03
$(PnBA-b-PEA-b-PMEA-b-PMA)_3$	13 420	13 520	1.02
PdcPA-b-PnBA-b-PEHA-b-PEA-b-PMA-b-PcHA	8 680	9 240	1.05

^{*a*}Argon atmosphere; solvent, toluene; initiator, *i*Pr-SKA; $[M]_0$, 1.0 mol L⁻¹; $[M]_0/[i$ Pr-SKA]_0, 10; $[Me_3SiNTf_2]_0/[i$ Pr-SKA]_0, 0.02; temperature, room temperature; polymerization time, 5 min; monomer conversion, > 99%. ^{*b*}Determined by ¹H NMR in CDCl₃. ^{*c*}Calculated from ($[M]_0/([i$ Pr-SKA]_0) × (conv) × (MW of monomer); dcPA, 206.29; *n*BA, 128.17;EHA, 184.28; EA, 100.12; MA, 86.09; cHA, 154.21; MEA, 130.14) + (MW of the initiator residue, 102.13). ^{*d*}Determined by SEC in THF using poly(methyl methacrylate) standards.

synthesized by the sequential GTP method. To the best of our knowledge, the synthesis of the multiblock acrylates polymers was the first reliable demonstration of the precisely designed acrylate polymers using the living anionic polymerization, i.e., the organocatalyzed GTP.

ASSOCIATED CONTENT

S Supporting Information

Additional data for the polymerizations of MA, EA, EHA, *n*BA, *c*HA, *dc*PA, and *t*BA (tables and SEC traces), postpolymerizations of MA, EA, *n*BA, and MEA (tables and ¹H NMR spectra), diblock copolymerizations (tables and ¹H NMR spectra), and multiblock polymerizations (tables and ¹H NMR spectra). This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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