



Copolymers incorporated with β -substituted acrylate synthesized by organo-catalyzed group-transfer polymerization

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Abstract

Various copolymers incorporated with β -substituted acrylates, such as alkyl crotonates (e.g., methyl crotonate (MC), ethyl crotonate (EC), isopropyl crotonate (iPC), and *n*-butyl crotonate (nBC)) and methyl cinnamate (MCin), were synthesized by group-transfer polymerization (GTP) using a silicon-based Lewis acid catalyst. In addition to β -substituted acrylates, α -substituted acrylates (e.g., methyl methacrylate (MMA) and *n*-butyl methacrylate (nBMA)) were examined as comonomers. Proton nuclear magnetic resonance (¹H NMR) spectroscopy and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) characterizations of the obtained copolymers revealed that each monomer component was incorporated sufficiently. The thermal stabilities of the resulting copolymers were investigated by dynamic mechanical analysis (DMA), indicating that the glass-transition temperature (T_g) of the copolymers can be widely varied over a relatively high-temperature range by selecting the optimal comonomer. More specifically, the T_g values of poly(MC-*random*-EC) (MC/EC molar ratio = 50/50), poly(MC-*random*-nBC) (MC/nBC molar ratio = 50/50), poly(MC-*random*-MCin) (MC/MCin molar ratio = 54/46), and poly(nBC-*random*-MCin) (nBC/MCin molar ratio = 56/44) were 173, 130, 216, and 167 °C, respectively.

Introduction

Group-transfer polymerization (GTP) was developed as a controlled living-polymerization method of (meth)acrylates by Webster et al. in the 1980s [1]. The first-generation GTP system used fluoride ions and silyl ketene acetals (SKAs) as the catalyst and the initiator, respectively. Since then, numerous improvements have been made to the GTP system to control the living-polymerization fashion and expand the range of available monomer substrates. Hertler et al.

reported that Lewis acids, such as zinc halides, organo aluminum, and HgI₂, can be applied to the controlled GTP of acrylates [2–6]. In addition, Kakuchi et al. developed a highly efficient organo-catalyzed GTP system using a silicon-based Lewis acid catalyst [7, 8].

Crotonic acid, cinnamic acid, and their derivatives are β -substituted acrylic compounds possessing a methyl or phenyl group at the β -position of the α,β -unsaturated carbonyl compound [9, 10]. The addition polymerization of these compounds is challenging because of the steric hindrance and/or electrical factor of the β -substituent [11–21]. In this context, Chen et al. recently developed a frustrated Lewis pair-catalyzed polymerization system for methyl crotonate (MC) and indenone, which used an *N*-heterocyclic carbene or hydrosilane as a Lewis base and an aluminum or boron compound as a Lewis acid [22–24]. In addition, Ute et al. developed a GTP system for the homopolymerization of various alkyl crotonates using an inorganic Lewis acid (HgI₂ or CdI₂) as the catalyst and iodotrialkylsilane as the cocatalyst [25–28]. Furthermore, our group reported that the organo-catalyzed GTP system using *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Tf₂NSiMe₃) and 1-trimethylsilyloxy-1-methoxy-2-methyl-1-propene (MTS), as described by Kakuchi et al., is applicable to the efficient

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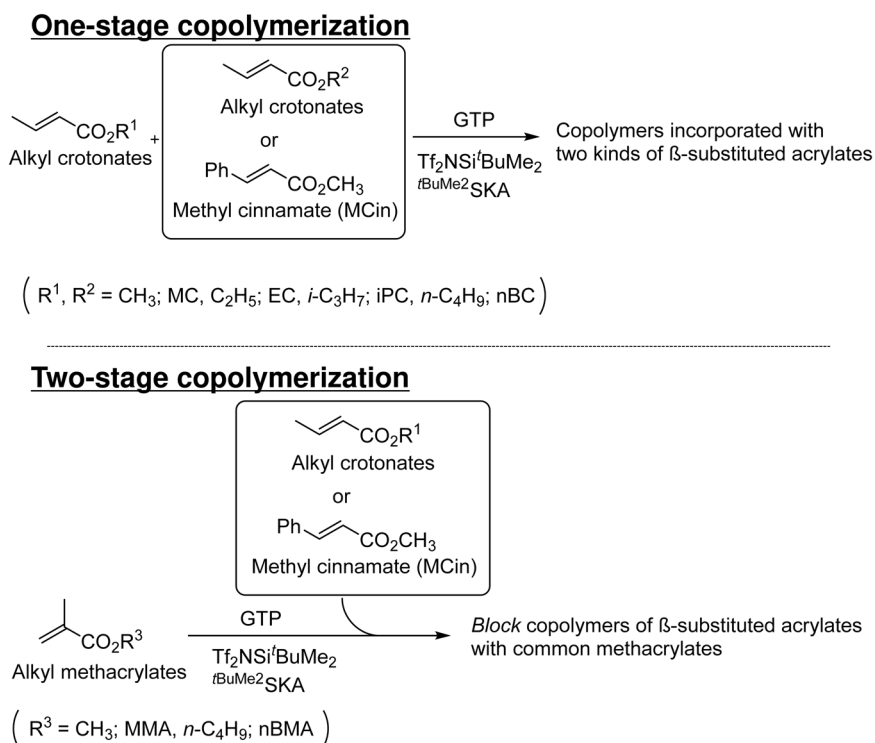
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Scheme 1 Copolymerization strategies toward β -substituted acrylates via GTP using $\text{Tf}_2\text{NSi}^t\text{BuMe}_2$ and ${}^t\text{BuMe}_2\text{SKA}$



homopolymerization of various alkyl crotonates and cinnamates [29, 30]. These studies also demonstrated that the homopolymers synthesized from β -substituted acrylates exhibit relatively high thermal stabilities, likely due to the contribution of the stiff polymer main chain bearing substituents at the α - and β positions.

Because copolymerization can greatly enhance the extent of currently attainable polymeric properties, investigations into the copolymerizability and the applicable comonomer range of β -substituted acrylates could expand the potential polymer applications [31–34]. However, our GTP system did not guarantee copolymerization because the living chain end was frequently deactivated via cyclization termination reactions [29, 30, 35, 36]. Recently, we demonstrated that changing the silyl groups of $\text{Tf}_2\text{NSiMe}_3$ and MTS to a bulkier group, such as a *tert*-butyldimethylsilyl moiety, is an effective means for suppressing termination reactions in the GTP system [37]. Thus, we herein report our investigation into the copolymerization of β -substituted acrylates (i.e., crotonates and cinnamate) using an organo-catalyzed GTP system with *N*-(*tert*-butyldimethylsilyl)bis(trifluoromethanesulfonyl)imide ($\text{Tf}_2\text{NSi}^t\text{BuMe}_2$) and 1-methoxy-1-(*tert*-butyldimethylsiloxy)-2-methyl-1-propene (${}^t\text{BuMe}_2\text{SKA}$). Two types of copolymerization strategies are evaluated based on different monomer feed methods. More specifically, a one-stage copolymerization is conducted to obtain a *random* copolymer, where two types of monomers are added simultaneously to the polymerization system. In addition, two-stage polymerization is conducted to obtain a *block* copolymer, where one monomer

is homopolymerized in the first stage, and a second feed of comonomer is subsequently added to the system. The series of copolymers prepared via this one-stage copolymerization approach incorporate two types of β -substituted acrylates selected from MC: ethyl crotonate (EC), isopropyl crotonate (iPC), *n*-butyl crotonate (nBC), and methyl cinnamate (MCin). Moreover, *block* copolymers of β -substituted acrylates with common methacrylates, such as methyl methacrylate (MMA) and *n*-butyl methacrylate (nBMA), are prepared by the two-stage copolymerization approach using the living-polymerization characteristics of the GTP system (Scheme 1). To the best of our knowledge, examples of addition copolymerization strategies incorporating cinnamates into the polymer backbone are limited [38–40]. We also investigated the thermal stabilities of a series of obtained copolymers by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

Experimental

Materials

MC, EC, iPC, nBC, MCin, MMA, nBMA, methyl isobutyrate, *tert*-butyldimethylchlorosilane, *N,N'*-dimethylpropyleneurea, lithium(diisopropylamide) (1.5 M in THF), and bis(trifluoromethanesulfonyl)imide (Tf_2NH) were obtained from Tokyo Chemical Industry Co., Ltd. CH_2Cl_2 and tetrahydrofuran (THF) (Kanto Chemical Co.,

superdehydrated grade) were purified using an SPS 800 system (MBraun). Argon and nitrogen were purified before use by passing through a dry clean column (4 Å molecular sieves) and a gas clean CC-XR column purchased from Nikka Seiko. All monomers, except MCin, were distilled using CaH_2 and stored in a glovebox. MCin was purified using 3 and 4 Å molecular sieves in CH_2Cl_2 and stored in a glovebox.

Synthesis of 1-methoxy-1-(*tert*-butyldimethylsiloxy)-2-methyl-1-propene (^{*t*}BuMe₂SKA)

1-Methoxy-1-(*tert*-butyldimethylsiloxy)-2-methyl-1-propene (^{*t*}BuMe₂SKA) was synthesized by the reaction of methyl isobutyrate and *tert*-butyldimethylchlorosilane, in accord with the literature [41]. More specifically, a solution of methyl isobutyrate (14.0 g, 137 mmol) in THF (200 mL) was charged to a flask filled with dry nitrogen gas, after which a 1.5 M lithium(diisopropylamide) THF solution (100 mL, 150 mmol) was added dropwise with vigorous stirring at -78°C over 30 min. Subsequently, a solution of *N,N'*-dimethylpropyleneurea (200 mmol) and *tert*-butyldimethylchlorosilane (22.6 g, 150 mmol) in THF (50 mL) was added, and stirring continued at -78°C for 60 min. Next, the reaction mixture was warmed to room temperature and stirred for 24 h before concentration. The resulting mixture was taken up in hexane (500 mL), washed with water (3 × 100 mL), saturated aqueous NaHCO_3 (100 mL), and brine (100 mL), and then dried over anhydrous MgSO_4 . After filtration, the organic layer was concentrated. Distillation under vacuum conditions gave the desired ^{*t*}BuMe₂SKA as a clear, colorless liquid (54% yield) with a purity of >99%, as determined by proton nuclear magnetic resonance (¹H NMR) spectroscopy.

Measurements

All molecular weight data for the polymer samples were obtained by gel permeation chromatography (GPC) at 40°C using a Shimadzu GPC system equipped with an RID-10A refractive index detector, a Shodex GPC K-802 column, and a Shodex GPC K-806 M column. CHCl_3 was used as the eluent at a flow rate of 0.8 mL min^{-1} . Polystyrene standards with a low polydispersity were used to obtain a calibration curve.

¹H NMR and ¹³C NMR measurements were performed on a Varian NMR system. The samples were dissolved in CDCl_3 , and 500 MHz ¹H NMR spectra were recorded at room temperature. The 125 MHz ¹³C NMR spectra were recorded at room temperature in a CDCl_3 solution. The data were calibrated against tetramethylsilane (TMS, δ 0.00) and analyzed using Mnova NMR software.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted on an ultrafleXtreme MALDI-TOF spectrometer (Bruker Daltonics, Billerica, MA) operating in linear mode at an accelerating voltage of 20 kV. Samples for MALDI-TOF-MS comprised combinations of the polymer (2 μL), the matrix (1,8-dihydroxy-9(10*H*)-anthracenone (dithranol), 10 mg mL^{-1} , 8 μL), and the ionizing agent (sodium trifluoroacetate, 10 mg mL^{-1} , 2 μL) in THF. Samples were deposited on an MTP 384 ground steel target plate. External calibration was conducted before data acquisition. The detected mass list was extracted using FlexAnalysis software (Bruker Daltonics).

TGA was performed on an SII Nano Technology TG/DTA7200 thermal analyzer from room temperature to 500°C in a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. T_{d5} and T_{d50} were defined as the temperature at which the weight loss reached 5% and 50%, respectively, of the total weight.

The T_g of each polymer sample was measured by DMA (Perkin Elmer DMA800) under a nitrogen atmosphere by cooling the sample to -50°C at a rate of $10^\circ\text{C min}^{-1}$ and then recording the DMA scan from -50 to $+250^\circ\text{C}$ at a heating rate of 5°C min^{-1} and a frequency of 1 Hz.

Group-transfer polymerization

All manipulations were performed in a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or a glovebox. A typical procedure for the one-stage polymerization process (entry 3, Table 1) was as follows: MC (501 mg, 5 mmol), nBC (711 mg, 5 mmol), ^{*t*}BuMe₂SKA (10.8 mg, 0.050 mmol), and CH_2Cl_2 (6.0 mL) were charged to a Schlenk tube in a glovebox. A CH_2Cl_2 solution (2.7 mL) of Tf_2NH (7.0 mg, 0.025 mmol) was added to initiate the polymerization reaction at 0°C . After 48 h, methanol (10 mL) was added to the reaction mixture, after which the solvents were removed by evaporation under reduced pressure. The residue was then dissolved in CHCl_3 , and the solution was poured into a large volume of hexane. The precipitated polymer was collected as the hexane-insoluble component by filtration, washed several times with hexane, and dried under vacuum for 24 h. For the two-stage polymerization process (entry 8, Table 1), the procedure was as follows: MC (501 mg, 5 mmol), ^{*t*}BuMe₂SKA (10.8 mg, 0.050 mmol), and CH_2Cl_2 (4.0 mL) were charged to a Schlenk tube in a glovebox. A CH_2Cl_2 solution (2.7 mL) of Tf_2NH (7.0 mg, 0.025 mmol) was added to initiate the polymerization reaction at 0°C . After 24 h, a CH_2Cl_2 solution (2.0 mL) of nBC (711 mg, 5 mmol) was added dropwise, and the polymerization reaction was allowed to continue for an additional 24 h. The second

Table 1 Summarized data for the copolymerization of two types of β -substituted acrylates^a

Entry	M^1	M^2	Initiator mmol	Catalyst mmol	Solvent mL	$[M^1]_0$ mol L ⁻¹	$[M^2]_0$ mol L ⁻¹	Time h	x^1 ^c %	x^2 ^c %	yield ^d %	M_n ^e g mol ⁻¹	\mathcal{D} ^e M_w/M_n	f^f %
1	MC	EC	0.025	0.025	8.9	0.50	0.50	48	100	100	100	84,500	1.18	51
2	MC	iPC	0.025	0.025	8.8	0.50	0.50	96	61	87	59	76,600	1.14	45
3	MC	nBC	0.025	0.025	8.7	0.50	0.50	48	100	100	100	107,600	1.18	45
4	MC	MCin	0.10	0.10	6.5	0.64	0.64	168	100	84	95	24,900	1.26	48
5	EC	MCin	0.10	0.10	6.4	0.64	0.64	168	100	85	94	25,200	1.25	50
6	iPC	MCin	0.10	0.10	6.3	0.64	0.64	168	100	41	62	16,300	1.23	60
7	nBC	MCin	0.10	0.10	6.3	0.64	0.64	168	100	79	83	27,800	1.19	49
8 ^b	MC	nBC	0.025	0.025	8.7	0.69	–	24 + 24	100	20	44	53,100	1.10	48
9 ^b	nBC	MC	0.025	0.025	8.7	0.69	–	24 + 24	100	10	59	63,900	1.09	48

^aPerformed on an aluminum block at 0 °C in an argon atmosphere. The polymerization conditions were as follows: M^1 feed and M^2 feed = 5.0 mmol, initiator = ^tBuMe₂SKA, catalyst = Tf₂NSi^tBuMe₂ (generated via the in situ reaction between ^tBuMe₂SKA and Tf₂NH (Scheme S1, Supporting Information)), solvent = CH₂Cl₂. M^1 and M^2 were fed simultaneously into the polymerization system (one-stage polymerization)

^bTwo-stage polymerization was conducted. M^1 was homopolymerized for 24 h in the first stage, and then a second feed of M^2 was added to the system. The second stage of polymerization was conducted for an additional 24 h

^cMonomer conversions ($x^1 = M^1$ conv., and $x^2 = M^2$ conv.) were calculated directly using ¹H NMR measurements (500 MHz, rt, CDCl₃) of the reaction mixture

^dThe polymer yield was calculated based on the total weight of the feed monomers

^eThe number-averaged molecular weight (M_n) and dispersity (\mathcal{D}) were determined using conventional GPC against PSt standards in CHCl₃

^fInitiator efficiency: $f = [\text{molecular weight of polymer calculated by a feed ratio}] / [\text{number-average molecular weight of polymers determined by GPC}]$

monomer feed was introduced without sampling from the first step because this manipulation may deactivate the living polymers by introducing trace amounts of water. Finally, the reaction was worked up using the same process that was employed for the one-stage polymerization.

Results and discussion

Copolymerization using two types of β -substituted acrylates

Initially, the preparation of a series of copolymers incorporating two types of β -substituted acrylates (M^1 and M^2) selected from the MC, EC, iPC, nBC, and MCin groups was attempted by GTP using Tf₂NSi^tBuMe₂ (generated via the in situ reaction between ^tBuMe₂SKA and Tf₂NH (Scheme S1, Supporting Information)) as the catalyst and ^tBuMe₂SKA as the initiator in CH₂Cl₂ at 0 °C at a molar feed ratio of M^1 : M^2 = 1:1. Table 1 summarizes the conversions of M^1 and M^2 (x^1 and x^2 , respectively), the polymer yields, the number-average molecular weights (M_n), and the dispersities (\mathcal{D}) of the obtained polymers. Figure 1 shows the GPC curves for the synthesized polymers.

When the polymerization reaction was conducted using a simultaneous feed of M^1 and M^2 (one-stage polymerization) (entries 1–7, Table 1), the consumption of both monomers was observed. In the cases of entries 1–3, the use of MC as M^1 and an alkyl crotonate (EC, iPC, or nBC) as M^2 , where the molar feed ratio of the sum of M^1 and M^2 versus the

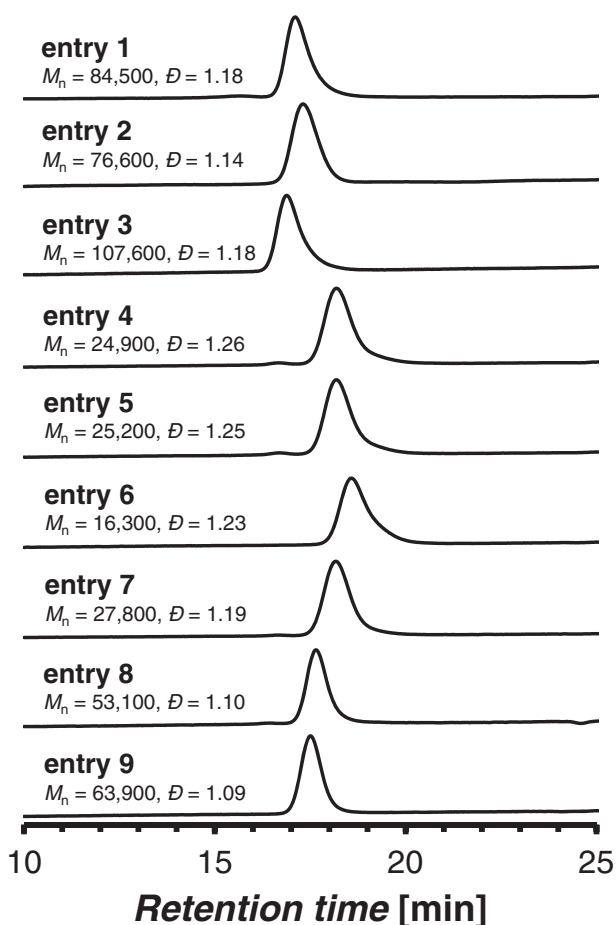


Fig. 1 GPC curves of the obtained polymers for the reaction presented in entries 1–9 (Table 1)

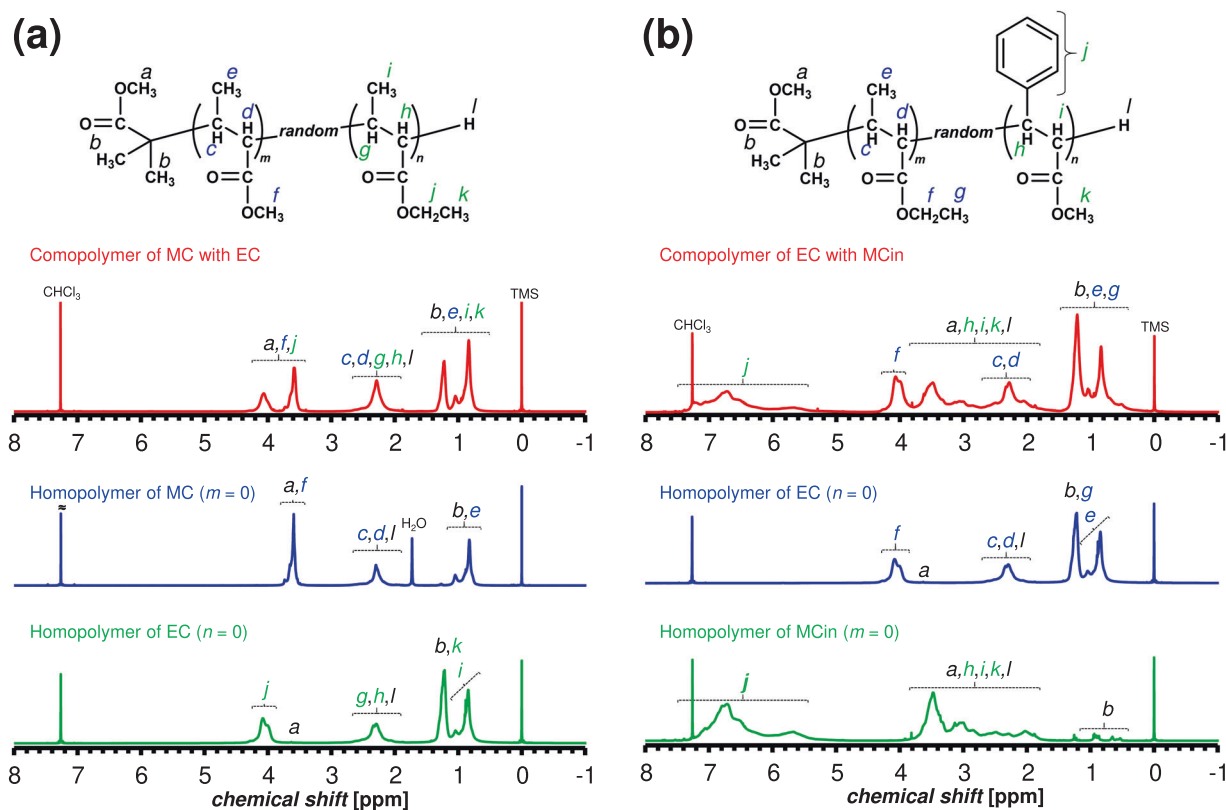


Fig. 2 ^1H NMR spectra (red lines) of the polymers synthesized from **a** MC as M^1 and EC as M^2 (entry 1, Table 1) and **b** EC as M^1 and MCin as M^2 (entry 5, Table 1), measured at 500 MHz in CDCl_3 at room

temperature. The blue and green lines represent the ^1H NMR spectra of the homopolymers synthesized from M^1 and M^2 , respectively

initiator was 400, polymers possessing a high molecular weight ($M_n > 76 \text{ kg mol}^{-1}$) and a relatively narrow dispersity ($D < 1.2$) were obtained. In particular, the polymer obtained by the reaction outlined in entry 3 (i.e., from MC and nBC) exhibited a high molecular weight of $>107 \text{ kg mol}^{-1}$. In terms of entries 4–7, the use of alkyl crotonates (MC, EC, iPC, or nBC) as M^1 and MCin as M^2 , where the molar feed ratio of the sum of M^1 and M^2 versus the initiator was 100, gave polymers possessing a relatively high molecular weight ($M_n > 24 \text{ kg mol}^{-1}$) and a relatively narrow dispersity ($D < 1.3$). The exception to this rule was entry 6, where the reactivity of iPC was low, which was likely due to the steric hindrance of the ester group.

In the case of the two-stage polymerization process (entries 8 and 9, Table 1), where M^1 was homopolymerized for 24 h in the first stage, followed by a second feed of M^2 and polymerization for an additional 24 h, the consumption of M^2 was barely observed. The molecular weights of the obtained polymers ($M_n = 53 \text{ 100 g mol}^{-1}$ in entry 8 and $63 \text{ 900 g mol}^{-1}$ in entry 9) were clearly smaller than that obtained for the reaction of entry 3 ($M_n = 107 \text{ 600 g mol}^{-1}$), where the polymerization process was conducted under conditions identical to those for entries 8 and 9, with the exception of the monomer feeding method. This result

suggests that in the two-stage polymerization of β -substituted acrylates, the amount of living polymer derived from M^1 was low during the additional M^2 feed. This deactivation of a living polymer is thought to be caused by a side reaction, such as an intramolecular termination reaction (e.g., terminal cyclization of the propagating chain-end groups), as proposed for the GTP system [35, 36].

Structural analyses of the obtained polymers

To confirm the structures of the obtained polymers, ^1H NMR analyses were conducted. Figure 2a shows the ^1H NMR spectrum of the polymer synthesized using MC as M^1 and EC as M^2 (entry 1, Table 1), in addition to those of poly(MC) and poly(EC), which were synthesized via a similar GTP route for comparison (Table S3, Supporting Information). Furthermore, Fig. 2b shows the ^1H NMR spectrum of the polymer synthesized using EC as M^1 and MCin as M^2 (entry 5, Table 1), in addition to those of the prepared poly(EC) and poly(MCin) (Table S3, Supporting Information). As shown in Fig. 2a, the ^1H NMR spectrum of entry 1 agrees well with the overlap of the spectra of poly(MC) and poly(EC). Similarly, as shown in Fig. 2b, the ^1H NMR spectrum of entry 5 is comparable to the superposition of

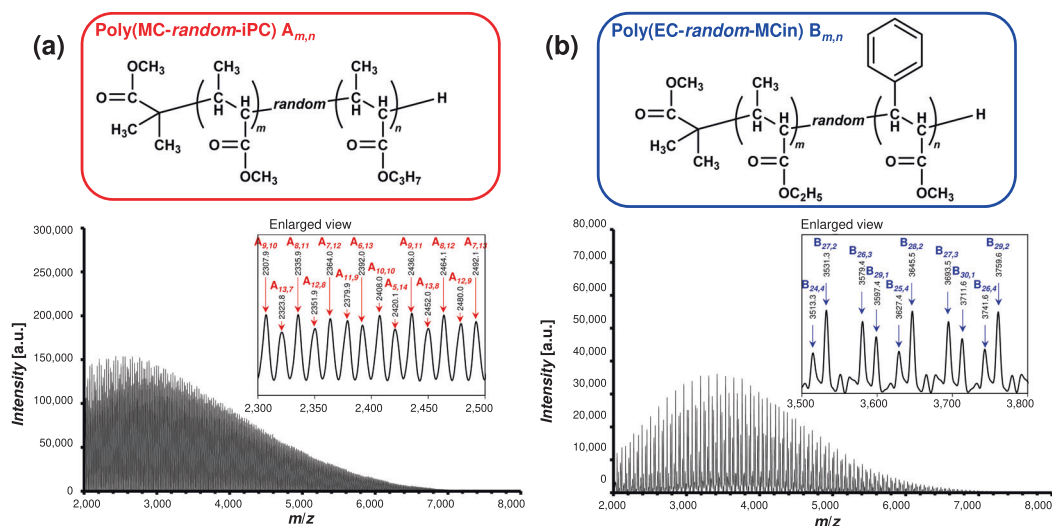


Fig. 3 MALDI-TOF-MS spectra of the polymers synthesized from **a** MC as M^1 and iPC as M^2 (entry 2, Table 1) and **b** EC as M^1 and MCin as M^2 (entry 5, Table 1), measured using dithranol as a matrix and CF_3COONa as an ionizing agent

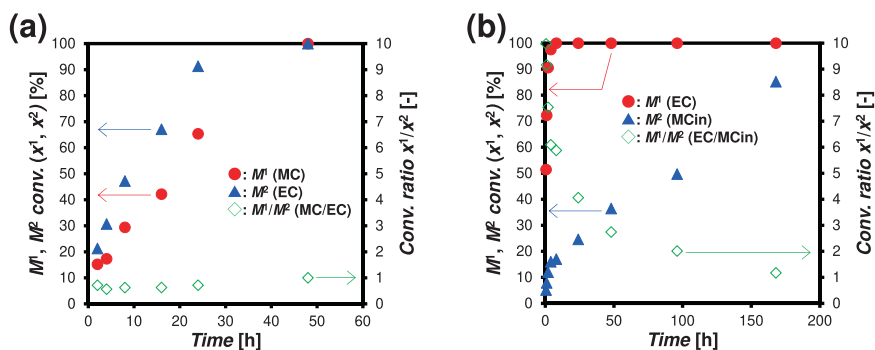


Fig. 4 Time-conversion curves for the copolymerization of **a** MC with EC and **b** EC with MCin. Copolymerization was conducted using $t\text{BuMe}_2\text{SKA}$ as the initiator and $\text{Ti}_2\text{NSi}^t\text{BuMe}_2$ (generated via the in situ reaction between $t\text{BuMe}_2\text{SKA}$ and Ti_2NH (Scheme S1, Supporting

Information)) as the catalyst in CH_2Cl_2 at 0°C . The polymerization conditions were as follows: **a** $[\text{MC}]_0 = [\text{EC}]_0 = 0.50\text{ M}$, $[t\text{BuMe}_2\text{SKA}]_0 = 0.0025\text{ M}$, and $[\text{Ti}_2\text{NSi}^t\text{BuMe}_2]_0 = 0.0025\text{ M}$, **b** $[\text{EC}]_0 = [\text{MCin}]_0 = 0.64\text{ M}$, $[t\text{BuMe}_2\text{SKA}]_0 = 0.013\text{ M}$, and $[\text{Ti}_2\text{NSi}^t\text{BuMe}_2]_0 = 0.013\text{ M}$

the spectra of poly(EC) and poly(MCin). These results suggest that the consumed monomers (M^1 and M^2) were successfully introduced into the polymer backbone.

The molecular structures of the obtained polymers were investigated in greater detail by MALDI-TOF-MS analysis. Figure 3a shows the mass spectrum of the polymer synthesized using MC as M^1 and iPC as M^2 (entry 2, Table 1), while Fig. 3b shows the mass spectrum of the polymer synthesized using EC as M^1 and MCin as M^2 (entry 5 in Table 1).

From the detailed analysis, it was confirmed that the observed peaks correspond to the sum of the masses of the copolymers containing M^1 and M^2 generated by GTP using $t\text{BuMe}_2\text{SKA}$ and Na^+ (derived from CF_3COONa added as an ionizing agent in the MALDI-TOF-MS measurements). The polymer shown in Fig. 3a was therefore determined to have the structural formula $(\text{CH}_3)_2[\text{CH}_3\text{OC}(=\text{O})]\text{C}-(\text{MC})_m(\text{iPC})_n-\text{H}$, where the $(\text{CH}_3)_2[\text{CH}_3\text{OC}(=\text{O})]\text{C}$ moiety at the initiation chain-end was derived from $t\text{BuMe}_2\text{SKA}$, and the

methylene group at the termination chain-end was generated by acid treatment of the terminal silyl ether group in the living polymer (Scheme S2, Supporting Information). Similarly, the polymer shown in Fig. 3b was determined to have the structural formula $(\text{CH}_3)_2[\text{CH}_3\text{OC}(=\text{O})]\text{C}-(\text{EC})_m(\text{MCin})_n-\text{H}$. Therefore, MALDI-TOF-MS structural analyses of the obtained polymers afforded clear evidence that copolymerization using a simultaneous feed of two types of β -substituted acrylates proceeded smoothly.

Time-conversion curve

Subsequently, we attained the time-conversion curve data to obtain information regarding the monomer unit arrangement in the copolymer backbone. Figure 4a shows the time-conversion curve for the copolymerization reaction using MC as M^1 and EC as M^2 (entry 1, Table 1), while Fig. 4b shows the time-conversion curve for the

Table 2 Summarized data for the copolymerization reactions of α -substituted acrylates with β -substituted acrylates^a

Entry	M^1	M^2	Initiator mmol	Catalyst mmol	Solvent mL	$[M^1]_0$ mol L ⁻¹	$[M^2]_0$ mol L ⁻¹	Time h	x^1 ^d %	x^2 ^d %	Yield ^e %	M_n ^f g mol ⁻¹	\bar{D} ^f M_w/M_n	f ^g %
10	MMA	MC	0.025	0.025	8.9	1.0	–	24 + 24	78	81	72	58,300 ^h	1.27 ^h	55
11	MMA	nBC	0.025	0.025	8.7	1.0	–	24 + 24	79	97	81	77,000 ^h	1.25 ^h	56
12	nBMA	MC	0.025	0.025	8.7	1.0	–	24 + 24	73	70	56	57,600 ^h	1.24 ^h	60
13	nBMA	nBC	0.025	0.025	8.4	1.0	–	24 + 24	78	100	84	68,200 ^h	1.23 ^h	75
14	nBMA	MC	0.025	0.025	8.7	1.0	–	12 + 24	51	92	59	56,300	1.21	59
15	nBMA	MCin	0.100	0.100	6.3	1.0	–	6 + 162	100	38	67	16,800	1.17	61
16 ^b	MC	nBMA	0.025	0.025	8.7	1.0	–	24 + 24	100	4	40	49,300	1.11	43
17 ^c	nBMA	MC	0.025	0.025	8.7	0.50	0.50	48	6	90	35	46,700	1.16	42

^aPerformed on an aluminum block at 0 °C under an argon atmosphere. The polymerization conditions were as follows: M^1 feed and M^2 feed = 5.0 mmol, initiator = ^tBuMe₂SKA, catalyst = Tf₂NSi^tBuMe₂ (generated via the in situ reaction between ^tBuMe₂SKA and Tf₂NH (Scheme S1, Supporting Information)), solvent = CH₂Cl₂. Two-stage polymerization was conducted. M^1 was homopolymerized in the first stage, and then a second feed of M^2 was added to the polymerization system

^bMC was used as M^1 , and nBMA was used as M^2

^c M^1 and M^2 were fed simultaneously into the polymerization system

^dMonomer conversions ($x^1 = M^1$ conv., $x^2 = M^2$ conv.) were calculated directly using ¹H NMR measurements (500 MHz, rt, CDCl₃) of the reaction mixture

^eThe polymer yield was calculated based on the total weight of the feed monomers (M^1 and M^2)

^fThe number-averaged molecular weight (M_n) and dispersity (\bar{D}) were determined using conventional GPC against PSt standards in CHCl₃

^gInitiator efficiency: $f = [\text{molecular weight of polymer calculated by a feed ratio}] / [\text{number-average molecular weight of polymers determined by GPC}]$

^hBimodal in GPC as for entries 10–13

copolymerization reaction using EC as M^1 and MCin as M^2 (entry 5, Table 1).

As shown in Fig. 4a, the conversion ratio of M^1 (MC) versus M^2 (EC) was within the range of 0.5–1 from the initial term to the end term of the copolymerization process, suggesting that the polymerization rate of EC was only slightly faster than that of MC. This result indicates that in the case of the copolymer obtained for the reaction outlined in entry 1 (Table 1), the MC and EC monomer units were incorporated throughout the polymer backbone.

In contrast, as shown in Fig. 4(b), the conversion of M^1 (EC) was approximately tenfold greater than that of M^2 (MCin) in the initial stage of copolymerization. This result indicates that in the case of entry 5 (Table 1), EC monomer units were primarily incorporated at the head part of the polymer backbone, while MCin monomer units were mainly incorporated at the tail end. Thus, copolymerization using two types of β -substituted acrylates with greatly different polymerizabilities leads to the generation of a *gradient-like random* copolymer.

Copolymer of α -substituted acrylate and β -substituted acrylate

Subsequently, the preparation of a series of copolymers from an α -substituted acrylate (M^1 , MMA or nBMA) and a β -substituted acrylate (M^2 , MC, nBC, or MCin) was

attempted using the GTP protocol with Tf₂NSi^tBuMe₂ as the catalyst and ^tBuMe₂SKA as the initiator in CH₂Cl₂ at 0 °C, using a molar feed ratio of $M^1:M^2 = 1:1$. Table 2 summarizes the conversions of M^1 and M^2 (x^1 and x^2 , respectively), the polymer yields, and the M_n and \bar{D} values of the obtained polymers, while Fig. 5 shows their GPC curves.

In the case of the two-stage polymerization reactions, where the α -substituted acrylate was homopolymerized in the first stage, followed by a second feed of the β -substituted acrylate and an additional polymerization phase (entries 10–15, Table 2), sufficient consumption of both monomers was observed. When MMA or nBMA was employed as M^1 and an alkyl crotonate (MC or nBC) was used as M^2 , where the molar feed ratio of the sum of M^1 and M^2 versus the initiator was 400 (entries 10–14, Table 2), polymers possessing a relatively high molecular weight ($M_n > 56$ kg mol⁻¹) were obtained. In contrast, (entry 15, Table 2), when nBMA was used as M^1 and MCin was employed as M^2 , where the molar feed ratio of the sum of M^1 and M^2 versus the initiator was 100, a polymer possessing a relatively low molecular weight of 16,800 g mol⁻¹ was obtained.

On the other hand, in the case of entry 16 (Table 2), where the first feed monomer was a β -substituted acrylate (MC) and the second feed monomer was an α -substituted acrylate (nBMA), the conversion of nBMA was particularly low ($x^2 < 10\%$). In addition, in the case of entry 17, where

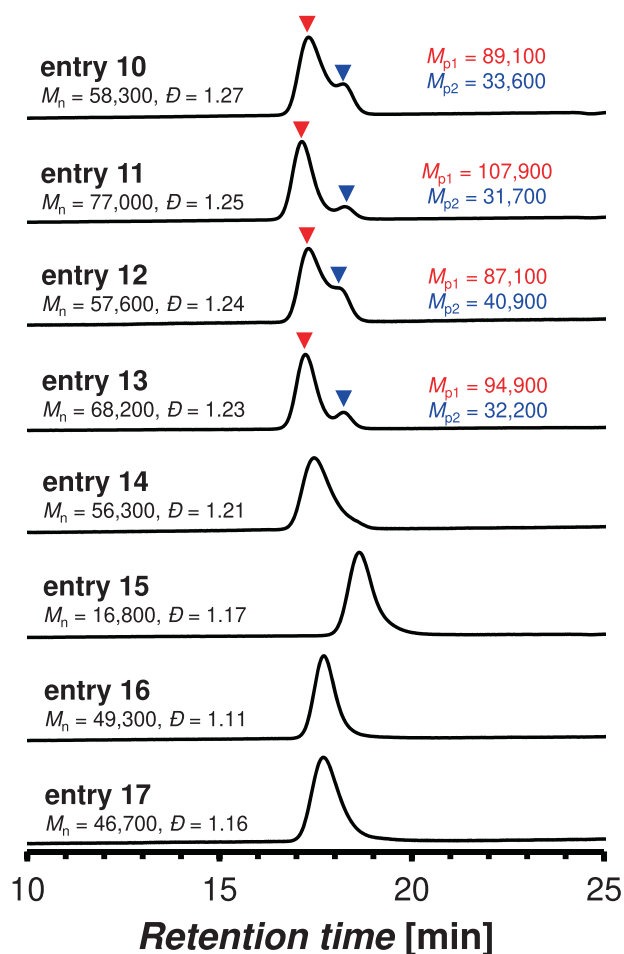


Fig. 5 GPC curves of the polymers obtained from the reactions outlined in entries 10–17 (Table 2). The blue and red inverted triangles represent lower- and higher-molecular-weight polymers, respectively

one-stage copolymerization was conducted, the conversion of the α -substituted acrylate (nBMA) was low (<10%). The molecular weights of the obtained polymers ($M_n = 49\,300\text{ g mol}^{-1}$ for entry 16, $M_n = 46\,700\text{ g mol}^{-1}$ for entry 17) were smaller than that of entry 12 ($M_n = 57\,600\text{ g mol}^{-1}$), despite the polymerization process being conducted under conditions identical to those used for entries 16 and 17 (with the exception of the monomer feeding method). These results suggest that the living chain end derived from the β -substituted acrylate exhibits poor reactivity toward the α -substituted acrylate monomer. In addition, it was suggested that the living chain end derived from a β -substituted acrylate is more susceptible to a termination reaction, such as a cyclization reaction, than that derived from an α -substituted acrylate [29, 35, 36] (Table S1 and Fig. S35, Supporting Information).

As shown in Fig. 5, the polymers obtained from the reactions outlined in entries 10–13 (Table 2) exhibit bimodal peaks in their GPC curves that correspond to lower- and higher molecular weight polymers. The peaks corresponding

to a lower molecular weight were attributed to the homopolymers of the α -substituted acrylate generated by a termination reaction (e.g., cyclization reaction) of the living chain end in the first stage. On the other hand, the peaks corresponding to a higher-molecular weight were attributed to the *block* copolymers of M^1 and M^2 , which propagated from the living homopolymers of the α -substituted acrylate that were alive during the second feed of the β -substituted acrylate monomer (Table S2, Supporting Information).

The polymer corresponding to entry 14 was obtained by shortening the time of the first-stage polymerization of nBMA with respect to entry 12 (12 h for entry 14 c.f. 24 h for entry 12). As shown in Fig. 5, the polymer obtained by the reaction presented in entry 14 gave an almost unimodal peak by GPC. This result confirms the hypothesis that the observed bimodal peaks for entry 12 were caused by the terminated homopolymers of nBMA. In addition, this result indicates that the *block* copolymer content can be enhanced by optimizing the polymerization time in the first stage.

Thermal properties of the copolymers

We then investigated the thermal properties (i.e., T_g , T_{d5} , and T_{d50}) of the obtained copolymers by DMA and TGA, as summarized in Table 3. In this study, T_g was defined as the temperature corresponding to the maximum $\tan \delta$ value in the DMA measurements because differential scanning calorimetry did not afford a clear T_g .

Table 3 shows that the T_g values of the copolymers obtained in the reactions outlined in entries 1–7 and prepared from two types of β -substituted acrylates were $>130\text{ }^\circ\text{C}$, indicating a relatively high heat stability. This high T_g can be rationalized via the stiffness of the polymer main chain containing substituents at the α -position (ester group) and the β -position (methyl or phenyl group). A high T_g was also confirmed for the homopolymers of β -substituted acrylates synthesized by GTP using $\text{Tf}_2\text{NSi}^t\text{BuMe}_2$ and $^t\text{BuMe}_2\text{SKA}$ (Table S3, Supporting Information). Comparing entry 4 (copolymer of MC with MCin) with entries 1–3 (copolymer of MC as M^1 with EC, iPC, or nBC, respectively, as M^2) shows that the copolymer obtained using the conditions outlined in entry 4 exhibited the highest T_g . This result suggests that cinnamate is a better comonomer than crotonate for enhancing the T_g of the resulting copolymers. Among entries 1–3, greater numbers of carbon atoms on the ester group of M^2 resulted in lower T_g values for the resulting copolymers. Similarly, among entries 4–7 (copolymers synthesized using MC, EC, iPC, or nBC, respectively, as M^1 , and MCin as M^2), the ester group of crotonate (as M^1) significantly influenced the T_g value of the resulting copolymers. These results indicate that the T_g of the copolymers described herein can be varied over a relatively high-temperature range by selecting the optimal comonomer.

Table 3 Thermal properties of the obtained copolymers

Entry	M^1, M^2	Molar ratio in copolymer ^a M^1/M^2	M_n ^b g mol ⁻¹	\mathcal{D} ^b M_w/M_n	T_g ^c °C	T_{d5} ^d °C	T_{d50} ^d °C
1	MC, EC	50/50	84,500	1.18	173	357	397
2	MC, iPC	41/59	76,600	1.14	153	326	376
3	MC, nBC	50/50	107,600	1.18	130	341	394
4	MC, MCin	54/46	24,900	1.26	216	343	378
5	EC, MCin	54/46	25,200	1.25	189	348	382
6	iPC, MCin	71/29	16,300	1.23	172	310	383
7	nBC, MCin	56/44	27,800	1.19	167	331	377
10	MMA, MC	49/51	58,300 ^e	1.27 ^e	132	348	393
11	MMA, nBC	45/55	77,000 ^e	1.25 ^e	116	333	383
12	nBMA, MC	51/49	57,600 ^e	1.24 ^e	51	325	389
13	nBMA, nBC	44/56	68,200 ^e	1.23 ^e	53	327	377
15	nBMA, MCin	73/27	16,800	1.17	58	285	318

^aCalculated from the monomer conversions^bThe number-averaged molecular weight (M_n) and dispersity (\mathcal{D}) were determined using conventional GPC against PSt standards in CHCl₃^c T_g was defined as the temperature corresponding to the maximum $\tan \delta$ value in the DMA measurement^d T_{d5} and T_{d50} were defined as the temperatures at which the weight loss reached 5 and 50%, respectively, of the total weight in a nitrogen atmosphere^eBimodal in GPC as for entries 10–13

In terms of the *block* copolymers prepared from an α -substituted acrylate (MMA or nBMA) and a β -substituted acrylate (MC, nBC, or MCin), the T_g corresponding to the poly(MMA) block was detected at approximately 116–32 °C (entries 10 and 11), while the T_g corresponding to the poly(nBMA) block was detected at approximately 51–58 °C (entries 12, 13, and 15). It has been previously reported that the T_g of poly(MMA) ranges from 51–122 °C, while that of poly(nBMA) ranges from 15–50 °C [42]. In contrast, the value of T_g derived from the poly(β -substituted acrylate) block was confirmed only as an indistinguishable or a small region. Thus, the T_g values of the *block* copolymers in this DMA study strongly reflected the characteristics of the poly(α -substituted acrylate).

Finally, in the context of their thermal decomposition, the copolymers obtained herein were found to exhibit relatively high heat resistance, with $T_{d5} > 325$ °C and $T_{d50} > 376$ °C. The exceptions to this rule were the copolymers obtained under the conditions presented in entries 6 (Table 1) and 15 (Table 2), which had relatively low molecular weights of < 20 kg mol⁻¹.

Conclusion

We herein reported the preparation of various copolymers incorporated with β -substituted acrylates, such as alkyl crotonates (MC, EC, iPC, and nBC), and MCin, via the

GTP process using a silicon-based Lewis acid catalyst and SKAs possessing a relatively bulky silyl moiety, such as the *tert*-butyldimethylsilyl group. Our results indicated that using this organo-catalyzed GTP system, the copolymerization of β -substituted acrylates could be achieved by selecting a suitable comonomer. When multiple β -substituted acrylates were used, a simultaneous monomer feed system was necessary to ensure smooth copolymerization. In addition, when an α -substituted acrylate was used as the comonomer, a multistage copolymerization method (where the α -substituted acrylate is homopolymerized in the first stage followed by a second feed of the β -substituted acrylate) resulted in the formation of a *block* copolymer incorporated with each component. This monomer feed method must consider the susceptibility of termination reactions and/or the copolymerizability of the living chain end derived from the monomers used. ¹H NMR spectroscopy and MALDI-TOF-MS were used to confirm the successful copolymerization reactions, and the thermal stabilities of the resulting copolymers were investigated by DMA and TGA. These results indicated that the T_g values of the prepared copolymers can be varied by changing the comonomer. Future studies should focus on the use of additional comonomers, such as acrylamides and acrylonitriles, which are known to be suitable for application in GTP systems, to gain a better understanding of the comonomer scope and to develop high-performance polymeric materials.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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