

1:3 ABAA Sequence-Regulated Substituted Polymethylenes via Alternating Radical Copolymerization of Methyl Cinnamate and Maleic Anhydride Followed by Post-Polymerization Reactions

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ABSTRACT

Methyl cinnamate (M_1) and maleic anhydride (M_2), which are both non-homopolymerizable 1,2-disubstituted vinyl monomers, were radically copolymerized in toluene to result in 1:1 alternating copolymers. The 1:1 alternating sequence was confirmed by not only the monomer reactivity ratios obtained by using the terminal model fitted by the Kelen-Tüdös method ($r_1 = 0.0035$, $r_2 = 0.069$) but also MALDI-TOF-MS analysis of the copolymers with controlled molecular weights and relatively narrow molecular weight distributions ($M_w/M_n = 1.20$), which were prepared by RAFT copolymerization using 2-cyano-2-propyl ethyl trithiocarbonate (CPETC) as the RAFT agent. The maleic anhydride unit was transformed into two methyl ester groups by hydrolysis followed by methylation. Since the propagation of methyl cinnamate occurred regioselectively via a styrenic radical, the methyl esterified copolymers possessed ABAA sequence-controlled substituted polymethylene structures (A: methyl ester, B: phenyl). The sequence-controlled substituted polymethylene showed good thermal properties ($T_{d5} = 323$ °C, $T_g \geq 192$ °C) due to the rigid main-chain structures, which possessed a phenyl group on every fourth main-chain carbon in the repeating units in addition to three methyl ester groups on the other main-chain carbons. Block copolymers consisting of the rigid substituted polymethylene and soft poly(methyl acrylate) were also synthesized by RAFT polymerization.

Keywords: Cinnamic acid; Maleic anhydride; Radical copolymerization; Alternating

copolymerization; Polymethylene; Monomer sequence

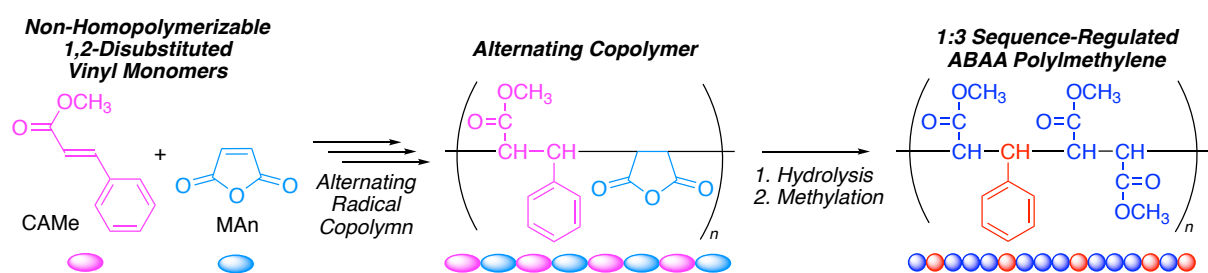
1. Introduction

Substituted polymethylenes with substituents on all their main-chain carbon atoms have been prepared by the polymerization of 1,2-disubstituted vinyl monomers ($\text{CHR}^1=\text{CHR}^2$) [1–9] or so-called C1 monomers ($\text{CHR}=\text{N}_2$) with substituents such as substituted diazoalkanes and diazoacetates [10–15]. These polymers are expected to have unique properties due to their rigid main-chain structures, which are different from those of monosubstituted vinyl ($\text{CH}_2=\text{CHR}$) and 1,1-disubstituted vinylidene ($\text{CH}_2=\text{CR}^1\text{R}^2$) polymers, which have no substituents on the alternate carbon atoms in the main chain. Although many 1,2-disubstituted vinyl compounds, including maleic anhydride (MAN), are difficult to homopolymerize due to steric hindrance, some of them, such as maleimides, fumarates, fumaramides, vinylene carbonate, and acenaphthylene, can be homopolymerized to afford in homosubstituted polymethylene structures [1–9]. In addition, 1,2-disubstituted monomers can be copolymerized to afford copolymers, in which their substituents can be statistically distributed depending on the monomer reactivity ratios [16–21]. For some specific pairs of 1,2-disubstituted comonomers, alternating copolymerizations can afford alternating copolymers. Indeed, there have been a few alternating copolymers obtained from pairs of 1,2-disubstituted comonomers, such as acenaphthylene/MAN [17], *trans*-anethole/MAN [18,19], *trans*-anethole/*N*-ethylmaleimide [18,19], and *trans*-anethole/fumaronitrile [18,19]. Although monomer sequence control in terms of the main-chain methylene units has not been discussed, these copolymers could have sequence-regulated substituted polymethylene structures.

Cinnamic acids are abundant, naturally occurring phenylpropanoids, and they possess unsymmetrical 1,2-disubstituted vinyl groups bearing phenyl and carboxylic acid groups [22–24]. They can thus be regarded as conjugated vinyl monomers and can, in principle, generate both styrenic and acrylic radicals depending on the regioselectivity of the two vinyl carbons. Although cinnamic acid derivatives cannot be radically homopolymerized due to the steric hindrance around the vinyl groups, they can be copolymerized with vinyl monomers such as acrylates and styrenes [25–27]. We have recently clarified that the propagation of cinnamic acid methyl ester or methyl cinnamate (CAME) occurs regioselectively via the styrenic radical by analyzing the products of atom transfer radical additions as model reactions of the radical copolymerizations [27]. These results suggest the possible incorporation of the AB disubstituted methylene sequence (A: methyl ester, B: phenyl) in an ordered manner in the resulting copolymers. Furthermore, if regioselective propagation also

occurs in the 1:1 alternating copolymerization with other 1,2-disubstituted monomers, sequence-regulated substituted polymethylene structures can be constructed. Although there have been a few reports on the radical copolymerizations of cinnamic acid esters with MAn, the resulting copolymers were not alternating copolymers possessing sequence-regulated substituted polymethylene structures [16,20].

This study thus focuses on the alternating radical copolymerization of CAME and MAn followed by post-polymerization reactions of the anhydride unit to construct a sequence-regulated substituted polymethylene structure (Scheme 1). MAn is one of the most electron-deficient and non-homopolymerizable 1,2-disubstituted vinyl monomers, and it can be efficiently copolymerized with styrene in an alternating fashion, suggesting that the styryl radical generated from CAME should have high reactivity with MAn. In addition, the MAn unit in the resulting copolymers can be converted into adjacent ester units via post-polymerization reactions consisting of hydrolysis and alkylation [17,28–30]. We assumed that if CAME efficiently copolymerizes with MAn in an alternating fashion via the styryl radical, the formed alternating repeating unit of CAME and MAn can be transformed into a 1:3 ABAA (A: CO₂Me, B: Ph) sequence-regulated substituted polymethylene units via hydrolysis of the anhydride followed by methylation. In this paper, we report the alternating radical and RAFT copolymerizations of CAME and MAn, the transformation of the resulting regioregular alternating copolymers into the 1:3 sequence-regulated substituted polymethylene, and the thermal properties of the resulting polymers.



Scheme 1. 1:3 Sequence-regulated ABAA polymethylene via alternating radical copolymerization of methyl cinnamate (CAME) and maleic anhydride (MAn) followed by post-polymerization reactions

2. Materials and methods

2.1. Materials

Methyl cinnamate (CAME) (TCI, >99%), methyl acrylate (MA) (TCI, >99%), 1,4-dioxane (DO) (Kanto Chemical, >99.5%; H₂O <10 ppm), and PhC(CF₃)₂OH (FUJIFILIM Wako Chemical, >99%) were distilled over calcium hydride under reduced pressure before

use. Maleic anhydride (MAN) (TCI, >99%) and *N*-cyclohexylmaleimide (CyMI) (Sigma-Aldrich, 97%) were purified by recrystallization from acetone and toluene, respectively. Toluene (Kanto Chemical, >99.5%; H₂O <10 ppm) was dried and deoxygenized by passage through columns from Glass Contour Solvent Systems before use. α,α -Azobisisobutyronitrile (AIBN) (Kishida Chemical, >99%) was purified by recrystallization from methanol. 2-Cyano-2-propyl ethyl trithiocarbonate (CPETC) was synthesized according to the literature [31]. Trimethylsilyl diazomethane (2.0 M solution in hexanes) (Sigma-Aldrich) was used as received.

2.2. Free radical copolymerization

The free radical copolymerizations were carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example of the copolymerization of CAME and MAN with AIBN in toluene is given below. After MAN (0.49 g, 5.0 mmol) was placed in a baked 25-mL graduated Schlenk flask, a three-way stopcock was attached. After degassing and filling the flask with dry nitrogen, CAME (0.78 mL, 5.0 mmol), a 100 mM solution of AIBN (0.50 mL in toluene, 0.05 mmol), and toluene were added at room temperature to a total volume of 5.0 mL ($[CAME]_0/[MAN]_0/[AIBN]_0 = 1000/1000/10$ mM). Immediately after mixing, aliquots (0.6 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C. At predetermined intervals, the polymerizations were terminated by cooling the reaction mixture to -78 °C. The monomer conversion was determined from the concentration of residual monomer as measured by ¹H NMR spectroscopy with toluene as an internal standard (310 h, 69% for CAME and 67% for MAN). The quenched reaction mixtures were concentrated to dryness to give the product copolymer ($M_n = 16,100$, $M_w/M_n = 1.82$).

2.3. Hydrolysis of poly(CAME-*alt*-MAN) and methylation

Poly(CAME-*alt*-MAN) ($M_n = 16,100$, $M_w/M_n = 1.82$, 500 mg), methanol (40 mL), and concentrated HCl (1.0 mL) were placed in a 50-mL round-bottom flask equipped with a Dimroth condenser at room temperature. The flask was put into an oil bath and heated at 80 °C with stirring for 12 h. After evaporation of the solvents, the obtained solid was washed twice with diethyl ether. The product was dried under vacuum overnight to afford a white solid (311 mg).

A portion of the obtained solid (183 mg), toluene (8.0 mL), and methanol (2.0 mL) were placed in a 50-mL round-bottom flask equipped with a three-way stopcock. A 2.0 M

solution of trimethylsilyl diazomethane (1.0 mL in hexanes) was added. After stirring the mixture at room temperature for 12 h, acetic acid (1.0 mL) was added. The reaction mixture was diluted with toluene and washed twice with water twice. After evaporation of the solvents and drying under vacuum overnight, the 1:3 sequence-controlled substituted polymethylene ($M_n = 16,700$, $M_w/M_n = 1.46$) was obtained as a transparent film (75 mg).

2.4. RAFT copolymerization

The RAFT copolymerization of CAME and MAn with CPETC in the presence of AIBN was carried out by the syringe technique under dry nitrogen in sealed glass tubes. After MAn (0.49 g, 5.0 mmol) was placed in a baked 25-mL graduated Schlenk flask, a three-way stopcock was attached. After degassing and filling the flask with dry nitrogen, CAME (0.78 mL, 5.0 mmol), a 1028 mM solution of CPETC (0.097 mL, 0.10 mmol), a 100 mM solution of AIBN (0.50 mL in toluene, 0.05 mmol), and toluene were added at room temperature to a total volume of 5.0 mL ($[CAME]_0/[MAn]_0/[CPETC]_0/[AIBN]_0 = 1000/1000/20/10$ mM). Immediately after mixing, aliquots (0.6 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C. At predetermined intervals, the polymerizations were terminated by cooling the reaction mixtures to -78 °C. The monomer conversions were determined from the concentration of residual monomer as measured by 1H NMR spectroscopy with toluene as the internal standard (150 h, 53% for CAME and 53% for MAn). The quenched reaction solutions were concentrated to dryness to give the product copolymer.

2.5. RAFT block copolymerization

The RAFT polymerization of MA with CPETC in the presence of AIBN was first carried out by the syringe technique under dry nitrogen in sealed glass tubes. To a baked 50-mL round-bottomed flask were added toluene (4.7 mL), MA (4.3 mL, 48 mmol), a 241 mM solution of CPETC (2.0 mL in toluene, 0.48 mM), and a 100 mM solution of AIBN (0.96 mL in toluene, 0.096 mmol) at room temperature. The total volume of the reaction mixture was 12.0 mL ($[MA]_0/[CPETC]_0/[AIBN]_0 = 4000/40/8.0$ mM). The flask was immersed in a thermostatic oil bath at 60 °C. After 145 min, the polymerization was terminated by cooling the reaction mixture to -78 °C. The monomer conversion was determined from the concentration of residual monomer as measured by 1H NMR spectroscopy with toluene as the internal standard (62%). The quenched reaction solutions were concentrated to dryness to give poly(MA) with CPETC end groups ($M_n = 6000$, $M_w/M_n = 1.11$). The M_n (NMR) was

determined to be 6100 based on the ratio of the intensities of the RAFT ω -terminal peaks to the main-chain protons.

The RAFT block copolymerization of CAME and MAn was carried out by the syringe technique under dry nitrogen in sealed glass tubes using poly(MA)-CPETC, which was obtained by RAFT polymerization, as the macro RAFT agent in the presence of AIBN. After MAn (0.49 g, 5.0 mmol) and poly(MA) (0.61 g, 0.10 mmol as the RAFT terminal) were placed in a baked 25-mL graduated Schlenk flask, a three-way stopcock was attached. After degassing and filling the flask with dry nitrogen, CAME (0.78 mL, 5.0 mmol), a 100 mM solution of AIBN (0.20 mL in toluene, 0.02 mmol), and toluene were added at room temperature to a total volume of 5.0 mL ($[CAME]_0/[MAn]_0/[poly(MA)-CPETC]_0/[AIBN]_0 = 1000/1000/20/4.0$ mM). Immediately after mixing, aliquots (0.6 mL each) of the solution were distributed via syringe into baked glass tubes, which were then sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C. At predetermined intervals, the polymerizations were terminated by cooling the reaction mixtures to -78 °C. The monomer conversion was determined from the concentration of residual monomer as measured by 1H NMR spectroscopy with toluene as the internal standard (50 h, 35% for CAME and 38% for MAn). The obtained polymer was similarly hydrolyzed and esterified to give the product ($M_n = 8000$, $M_w/M_n = 1.38$).

2.6. Measurements

The monomer conversion was determined from the concentration of residual monomer as measured by 1H NMR spectroscopy with the reaction solvent as the internal standard. The 1H NMR spectra for the monomer conversion and product copolymer were recorded in $CDCl_3$ at 25 °C on a JEOL ECS-400 spectrometer operating at 400 MHz. The MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR Plus mass spectrometer (linear mode) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the ionizing matrix and sodium trifluoroacetate as the ion source. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the product polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Tosoh Multipore H_{XL}-M (7.8 mm i.d. \times 30 cm) \times 2; flow rate 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against standard polystyrene samples (Agilent Technologies; $M_p = 580$ -3,053,000, $M_w/M_n = 1.02$ -1.23). The polymer samples for 1H NMR analysis were purified by preparative SEC (column: Shodex KF-2002) to remove remaining unreacted

monomer. The glass-transition temperatures (T_g values: midpoint of the transition) of the polymers were recorded on a Q200 differential scanning calorimeter (DSC) (TA Instruments Inc.). Certified indium and sapphire were used to calibrate the temperature and heat flow. The samples were first heated to 240 °C at 10 °C/min, equilibrated at this temperature for 5 min, and then cooled to 40 °C at 10 °C/min. After being held at this temperature for 5 min, the samples were then reheated to 240 °C at 5 °C/min. All T_g values were obtained from the second scan after removing the thermal history. Thermogravimetric analysis (TGA) of each sample was performed on a Q500 system (TA Instruments Inc.) at 5 °C/min under flowing N_2 gas.

3. Results and discussion

3.1. Free radical copolymerization of methyl cinnamate and maleic anhydride and post-polymerization reactions

The free radical copolymerization of CAME and MAn was investigated at a 1:1 feed ratio using AIBN in toluene and 1,4-dioxane (DO) at 60 °C (Fig. 1).

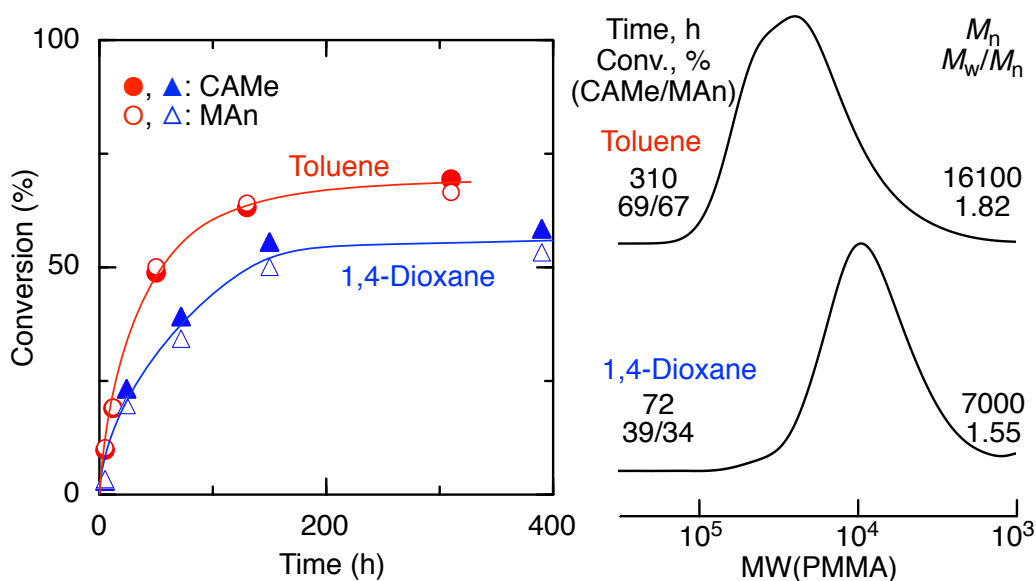


Fig. 1. Time-conversion curves for radical copolymerization of methyl cinnamate (CAME) and maleic anhydride (MAn) at 1:1 monomer feed ratio in toluene and 1,4-dioxane at 60 °C and size-exclusion chromatography (SEC) curves of the obtained copolymers: $[CAME]_0 = [MAn]_0 = 1000$ mM, $[AIBN]_0 = 10$ mM.

In toluene and DO, the two monomers were consumed at the same rate, affording copolymers. The number-average molecular weight (M_n) of the copolymers obtained in toluene was 16,100, whereas that obtained in DO was low due to chain-transfer reactions to

the solvent. These results indicate that CAME and MAn, which are both non-homopolymerizable, can be radically copolymerized in toluene to give relatively high-molecular-weight polymers.

To further evaluate the copolymerizabilities of these monomers in toluene, the monomer reactivity ratios were determined by analyzing the comonomer compositions of the copolymers obtained in the initial stages (total conversion $\leq 15\%$) in the radical copolymerizations at various monomer feed ratios. Fig. 2 shows the relationship between the CAME feed in the monomers and CAME incorporation into the copolymers (M_1 : CAME, M_2 : MAn). The plots were almost constant and close to 0.5 regardless of the monomer feed ratio.

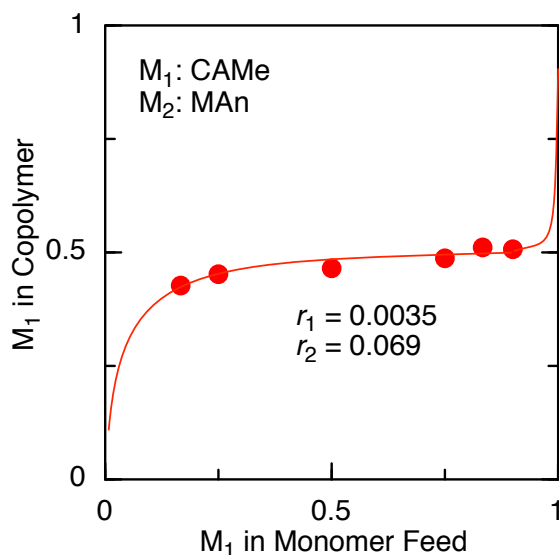


Fig. 2. Copolymer composition curves for radical copolymerization of methyl cinnamate (CAME) as M_1 and maleic anhydride (MAn) as M_2 in toluene at 60 °C obtained at varying the monomer feed ratios: $[M_1]_0 + [M_2]_0 = 2.0$ M, $[AIBN]_0 = 10$ mM. The curved line was fitted by the Kelen-Tüdös method for the terminal model.

The copolymerization was analyzed using the terminal model, and the plots were fitted by the Kelen-Tüdös method [32,33]. The obtained r_1 and r_2 values were 0.0035 and 0.069, respectively, which are both close to 0, indicating that nearly alternating radical copolymerization was achieved for CAME and MAn. A similar alternating copolymerization of non-homopolymerizable 1,2-disubstituted monomers has been reported for *trans*-anethole (*p*-methoxy- β -methylstyrene) and MAn, and their e values in the Q - e scheme of Alfrey and Price are -1.4 and 2.25 , respectively [19]. A combination of such low (negative) and high (positive) e values is generally suitable for forming alternating sequences.

In contrast to the low e value of *trans*-anethole, the e value of CAME is 0.49, and this positive value suggests that the carbon-carbon double bond is more or less electron deficient and less suitable for alternating radical copolymerization with MAn. Furthermore, it was reported that in the radical copolymerization of ethyl cinnamate (M_1) and MAn (M_2) in CHCl_3 , which is more polar than toluene, the r_1 and r_2 values were 10.8 and $<1.0 \times 10^{-4}$, respectively [16]. The relatively high r_1 value may be ascribed to the difference in polarity of the solvents, but it seems weird because ethyl cinnamate is not homopolymerizable. However, the results obtained in this study show that the radical copolymerization of CAME and MAn in toluene proceeded in a nearly 1:1 alternating fashion via the regioselective propagation of CAME via the styrenic radical, which has high reactivity with MAn, giving an alternating monomer sequence.

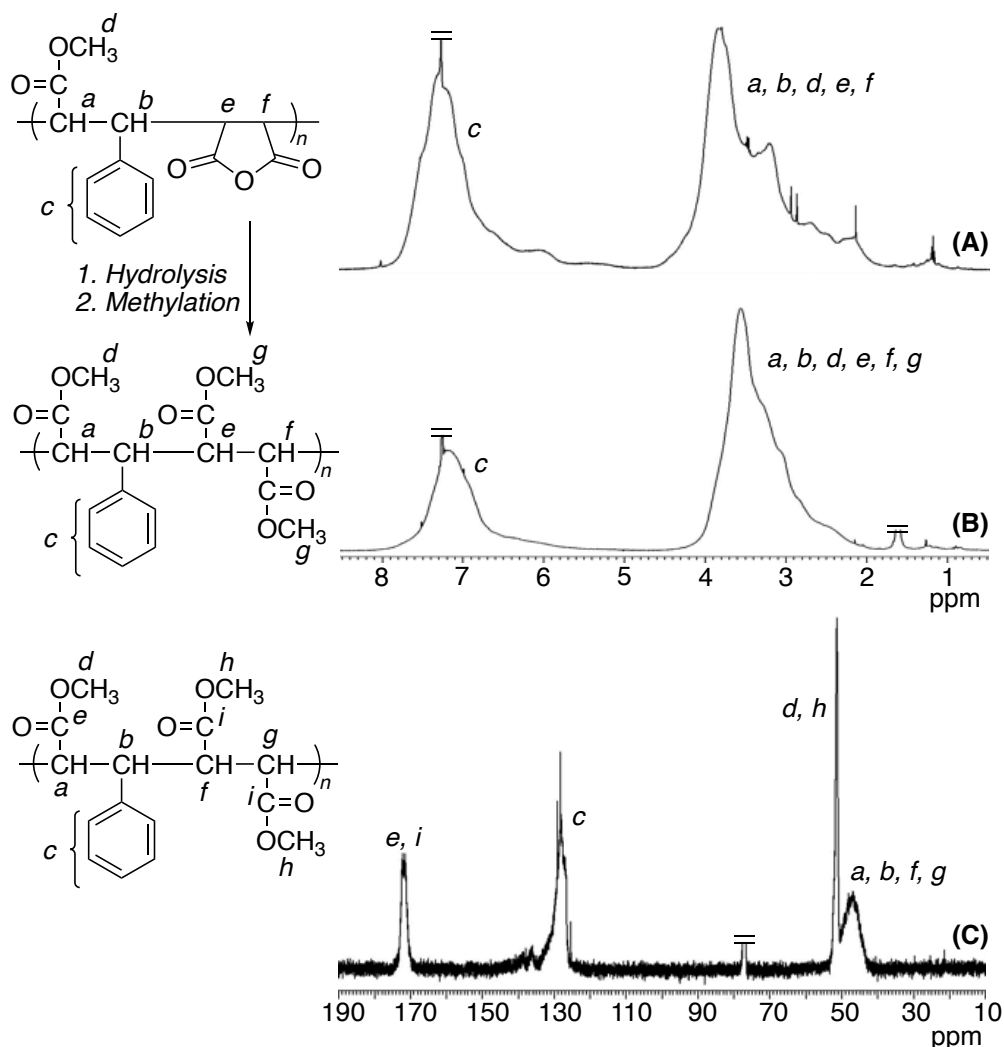


Fig. 3. (A) ^1H NMR spectrum (CDCl_3 , 55°C) of copolymers ($M_n = 16,100$, $M_w/M_n = 1.82$) obtained in radical copolymerization of methyl cinnamate (CAME) and maleic anhydride (MAN) at 1:1 monomer feed ratio in toluene at 60°C ($[\text{CAME}]_0 = [\text{MAN}]_0 = 1000\text{ mM}$, $[\text{AIBN}]_0 = 10\text{ mM}$). (B) ^1H and (C) ^{13}C NMR spectra (CDCl_3 , 55°C) of polymers ($M_n = 16,700$, $M_w/M_n = 1.46$) obtained after hydrolysis and methylation of the obtained copolymers.

Fig. 3A shows the ^1H NMR spectrum of the copolymer, which is the same as that obtained at a 1:1 feed ratio in toluene at 60 °C shown in Fig. 1. Although the peaks were very broad, most likely due to the low stereoselectivity of the radical propagation and rigidity or low mobility of the substituted polymethylene structures, the incorporation of CAME was calculated based on the peak area ratio of aromatic protons (*c*) of the CAME units to the other protons assigned to the methyl ester (*d*) and the main-chain methine protons (*a*, *b*, *e*, and *f*) of the CAME and MAn units. The incorporation of CAME was 48%, suggesting the formation of alternating copolymers.

The anhydride unit was then hydrolyzed under acidic conditions and methylated with trimethylsilyl diazomethane. In the ^1H NMR spectrum of the obtained products (Fig. 3B), the relative intensities of the peak at approximately 3.6 ppm increased due to the formation of additional methyl ester units in the post-polymerization reactions. The incorporation of phenyl-substituted methylene units per main-chain substituted methylene units was 25%, indicating the formation of a 1:3 ratio of phenyl- and methoxycarbonyl-substituted units. Fig. 3C shows the ^{13}C NMR spectrum of the products, which also indicates the formation of substituted polymethylene structures consisting of phenyl- and methoxycarbonyl-substituted units. These results and previous results on the regioselective propagation of CAME support that 1:3 sequence-regulated, ABAA polymethylene structures were constructed by the radical copolymerization of CAME and MAn followed by the post-polymerization reactions consisting of hydrolysis of the MAn units and methylation.

As a control experiment, in place of MAn, *N*-cyclohexylmaleimide (CyMI) was employed in a radical copolymerization with CAME at a 1:1 feed ratio in toluene and $\text{PhC}(\text{CF}_3)_2\text{OH}$ at 60 °C to observe the effects of the comonomer on the copolymerization with CAME (Fig. S1). Although the radical copolymerization did proceed, CyMI was consumed faster than CAME, indicating that the homopolymerization of CyMI occurred simultaneously because maleimide derivatives are homopolymerizable. The incorporation of CAME was approximately 40% in both solvents, indicating that homosequences of CyMI were produced due to the lower selectivity of the 1:1 alternating propagation (Fig. S2). These results indicate that both non-homopolymerizable monomers, CAME and MAn, are important for the selective 1:1 alternating radical copolymerization.

3.2. RAFT copolymerization of methyl cinnamate and maleic anhydride and block copolymerization from poly(methyl acrylate)

The RAFT copolymerization of CAME and MAn was investigated using 2-cyano-2-propyl ethyl trithiocarbonate (CPETC) as the RAFT agent, which is effective for

controlling the radical copolymerization of CAME and methyl acrylate (MA) [27], in toluene at 60 °C. Even in the radical copolymerization in the presence of the RAFT agent, both CAME and MAn were consumed at the same rate (Fig. 4). The obtained copolymers were similarly hydrolyzed under acidic conditions and methylated by trimethylsilyl diazomethane. The number-average molecular weight (M_n) of the resulting copolymers increased in direct proportion to total monomer conversion. In addition, the SEC curves shifted to higher molecular weights as the polymerization proceeded, and the molecular weight distribution (MWD) remained narrow ($M_w/M_n \sim 1.2$). The M_n values were slightly lower than the calculated values assuming that one molecule of CPETC generates one polymer chain. The observed lower molecular weights can be attributed to differences between the hydrodynamic volumes of the resulting copolymers and the standard poly(methyl methacrylate).

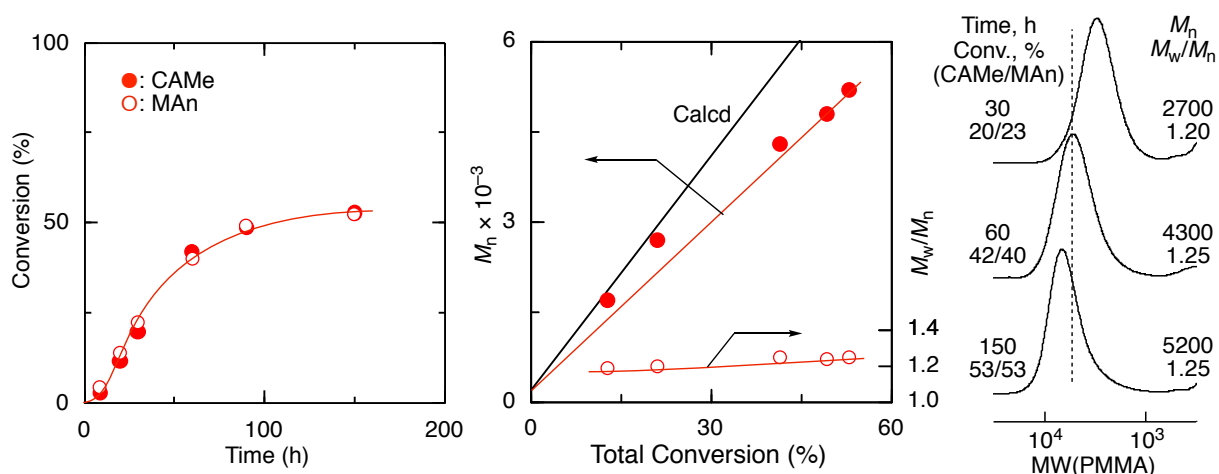


Fig. 4. Time-conversion curves for RAFT copolymerization of methyl cinnamate (CAME) and maleic anhydride (MAn) at 1:1 monomer feed ratio with 2-cyano-2-propyl ethyl trithiocarbonate (CPETC) and AIBN in toluene at 60 °C and plots for M_n and M_w/M_n vs. total monomer conversion and size-exclusion chromatography (SEC) curves of polymers obtained after hydrolysis and methylation of the obtained copolymers: $[CAME]_0 = [MAn]_0 = 1000$ mM, $[CPETC]_0 = 20$ mM, $[AIBN]_0 = 10$ mM.

The ^1H NMR spectrum of the copolymers obtained in the RAFT copolymerization showed relatively small signals at 1–2 ppm that can be attributed to the methyl protons of both the α - and ω -RAFT terminals, in addition to large signals for the main-chain repeating units (Fig. S3A). The incorporation of CAME units was similarly calculated to be 49%, indicating that alternating copolymerization also occurred in the RAFT process. The hydrolysis and methylation were successfully achieved as shown in Fig. S3B. The incorporation of phenyl-substituted methylene units per main-chain substituted methylene unit was also calculated to be 25% based on the ratio of the intensity of the ^1H NMR peaks.

The M_n (NMR) calculated from the ratio of the intensities of the α -RAFT terminal peaks to peaks of the repeating units was 3000, which was closer to the calculated value than the M_n (SEC). However, the intensity peak of the ω -RAFT terminal group decreased due to the loss of the trithiocarbonate group during the modification reactions. These results indicate that CPETC is suitable for controlling the alternating RAFT copolymerization of CAME and MAN to afford polymers with controlled molecular weights and chain-end groups.

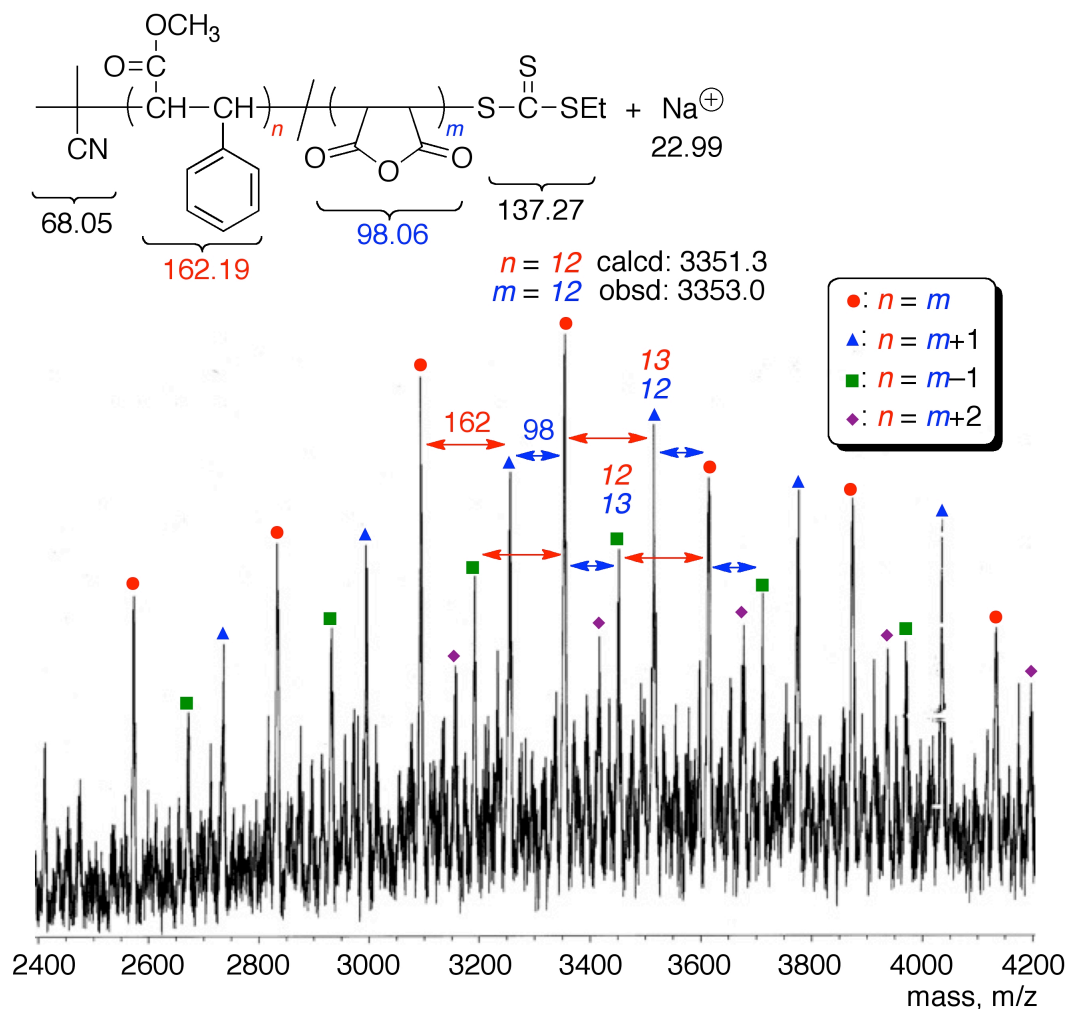


Fig. 5. MALDI-TOF-MS spectrum of copolymers of methyl cinnamate (CAME) and maleic anhydride (MAN) (M_n (NMR) = 2600) obtained at conversion of CAME/MAN = 20%/23% in RAFT copolymerization with 2-cyano-2-propyl ethyl trithiocarbonate (CPETC) and AIBN in toluene at 60 °C: $[\text{CAME}]_0 = [\text{MAN}]_0 = 1000 \text{ mM}$, $[\text{CPETC}]_0 = 20 \text{ mM}$, $[\text{AIBN}]_0 = 10 \text{ mM}$.

To clarify the monomer sequence, the copolymer obtained by RAFT copolymerization was subjected to MALDI-TOF-MS analysis (Fig. 5). The molar mass of the highest peak, marked by a red circle, was 3353, which is very close to the absolute molar mass, 3351.3, of the copolymer of CAME and MAN with the same number of units ($n = m = 12$) and a CPETC

unit at the α - and ω -termini with sodium ions originating from $\text{CF}_3\text{CO}_2\text{Na}$ as the ionizing agent. The main series of other peaks, also marked by red circles, are attributed to polymers that also have the same number of CAME and MAn units and RAFT chain-ends. In addition, for the series of peaks marked by blue triangles, there was one more CAME unit than there was MAn unit, and for those marked by green squares, there was one fewer CAME unit than there was MAn unit. Each member of these two series of polymers, marked by blue triangles or green squares, can still be attributed to alternating copolymers though they have the same monomer unit, i.e., CAME or MAn, respectively, at both chain ends. However, a much smaller series of peaks, marked by pink diamonds, are attributed to the polymers in which the number of CAME units was higher than that of MAn, indicating a small amount of homosequence statistically occurring during the 1:1 alternating propagation. In total, the MALDI-TOF-MS analysis also supports that the copolymers obtained by the RAFT copolymerization mainly have 1:1 alternating monomer sequences and RAFT terminal groups.

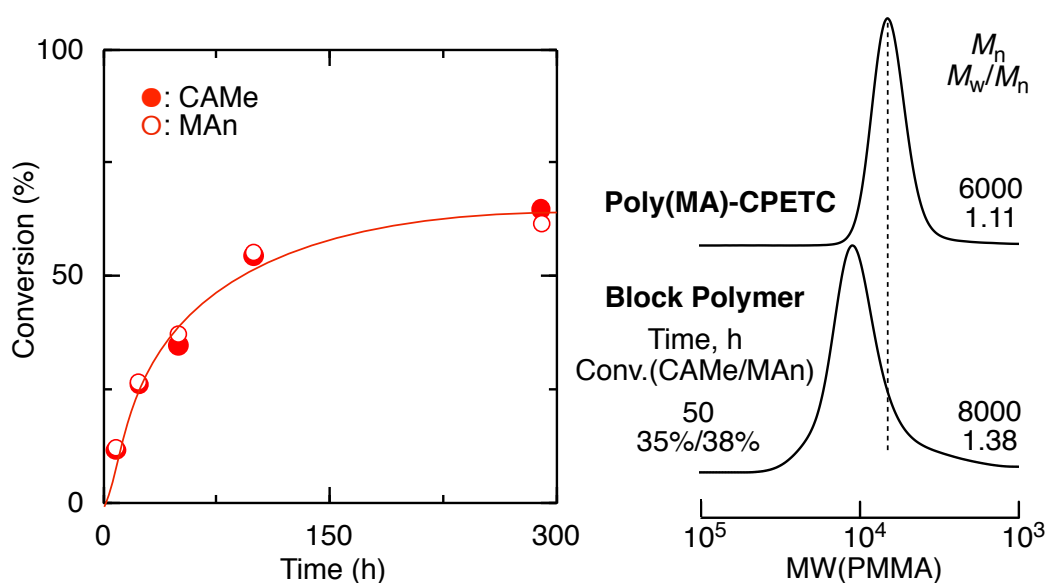


Fig. 6. Time-conversion curves for block RAFT copolymerization of methyl cinnamate (CAME) and maleic anhydride (MAn) at 1:1 monomer feed ratio using poly(MA)-CPETC as macro RAFT agent in the presence of AIBN in toluene at 60 °C size-exclusion chromatography (SEC) curves of poly(MA)-CPETC and polymers obtained after hydrolysis and methylation of the block copolymers: $[\text{CAME}]_0 = [\text{MAn}]_0 = 1000 \text{ mM}$, $[\text{poly(MA)-CPETC}]_0 = 20 \text{ mM}$, $[\text{AIBN}]_0 = 4.0 \text{ mM}$.

The success of the RAFT radical copolymerization of CAME and MAn, which results in a rigid polymer structure, prompted us to investigate the block copolymerization with MA, which results in relatively soft segments, for the synthesis of rigid-soft block copolymers.

MA was thus first polymerized with AIBN in the presence of CPETC in toluene at 60 °C to afford well-defined poly(MA) with controlled molecular weights ($M_n(\text{SEC}) = 6000$, $M_w/M_n = 1.11$) and RAFT chain ends ($M_n(\text{NMR}) = 6100$). The obtained poly(MA) was then used as the macro-RAFT agent for the RAFT block copolymerization of CAME and MAn with AIBN in toluene at 60 °C (Fig. 6). The consumption of CAME and MAn in the copolymerization occurred at the same rates, suggesting formation of a 1:1 alternating sequence in the second block. The obtained products were similarly subjected to the post-polymerization reactions, i.e., hydrolysis and methylation. The SEC curves of the final products shifted to higher molecular weights, keeping the narrow MWDs, indicating the formation of block copolymers consisting of soft poly(MA) and rigid sequence-regulated ABAA polymethylene segments.

3.3. Thermal properties of the copolymers

The thermal properties of the copolymers were analyzed using TGA and DSC. TGA showed that the 5% decomposition temperature (T_{d5}) of poly(CAME-*alt*-MAn) was 280 °C, whereas that of the polymers after the post-polymerization reactions was 323 °C (Fig. 7A). The lower thermal stability of poly(CAME-*alt*-MAn) was thus improved by the transformation of the anhydride group into the two methyl ester groups. In addition, the T_{d5} of the 1:3 sequence-regulated, substituted polymethylene possessing one phenyl and three methyl ester groups in the repeating units was higher than those of the homopolymers of diisopropyl fumarate (267 °C) [8] and other dialkyl fumarates [1,2].

In DSC, no glass transition was observed for poly(CAME-*alt*-MAn) up to 250 °C, where decomposition of the polymer started, due to the rigid polymer chain. However, the 1:3 sequence-regulated substituted polymethylene showed a clear glass transition due to the softer chain, and the temperature of the transition increased from 144 °C to 192 °C as M_n increased (Fig. 7B). In addition, the T_g linearly decreased with the reciprocal of M_n ($1/M_n$) (Fig. 7C). From the plots for the Flory and Fox equation ($T_g = T_g^\infty - K/M_n$), T_g^∞ of the 1:3 sequence-regulated substituted polymethylene was estimated to be 204 °C. The T_g values were higher than those (-15~160 °C) of poly(dialkyl fumarates) prepared by the radical polymerization of dialkyl fumarates [1,2,8,9], although there were differences in the molecular weights of the polymers, and in some cases, the T_g of the main-chain poly(dialkyl fumarates) was not observed before the decomposition of the polymers. The T_g of the polymethylene with phenyl substituents being higher than those of poly(dialkyl fumarates) consisting only of ester substituents can be expected by analogy to the higher T_g of polystyrene (~100 °C) relative to that of poly(methyl acrylate) (~10 °C). In addition, the T_g was higher than that of previously prepared copolymers of *trans*-anethole and diethyl

fumarate with 47:53 ratios (86 °C) [21], which may have one methyl, one 4-methoxyphenyl, and two ethyl ester substituents in the repeating units. These results indicate that the sequence-regulated substituted polymethylene with one phenyl and three methyl ester substituents in the repeating units has good thermal properties compared with other alkyl fumarate-derived substituted polymethylenes.

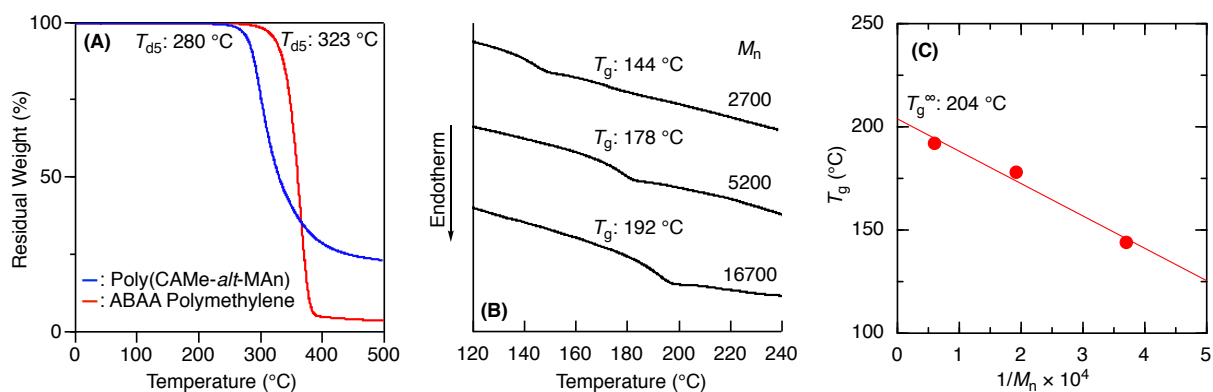


Fig. 7. (A) Thermogravimetric analysis (TGA) of poly(CAMe-*alt*-MAN) ($M_n = 16,100$, $M_w/M_n = 1.82$) and ABAA polymethylene ($M_n = 16,700$, $M_w/M_n = 1.46$) obtained after hydrolysis and methylation. (B) Differential scanning calorimetry (DSC) of ABAA polymethylene with different molecular weights obtained by RAFT copolymerization followed by post-polymerization reactions. (C) $1/M_n$ vs. T_g plots for Flory and Fox equation for ABAA polymethylene in (B).

4. Conclusion

In conclusion, 1,2-disubstituted CAME and Man, which are both non-homopolymerizable, were radically copolymerized to result in nearly 1:1 alternating copolymers. The 1:1 alternating radical copolymerization also proceeded in the presence of a RAFT agent, resulting in alternating copolymers with controlled molecular weights and RAFT terminal groups. Block copolymerization with MA was also successful and enabled the synthesis of well-defined block copolymers consisting of soft poly(MA) and rigid polymethylene segments. The MAN units were transformed into two methyl ester groups to afford ABAA sequence-regulated polymethylene structures (A: methyl ester, B: phenyl) with good thermal properties ($T_{d5} = 323\text{ °C}$, $T_g \geq 192\text{ °C}$). This study will lead to other sequence-regulated polymethylenes with unique properties, which can be accessed via 1:1 alternating radical copolymerizations of 1,2-disubstituted vinyl monomers.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Number JP18H04647 in Hybrid

Catalysis for Enabling Molecular Synthesis on Demand, JP18H03917, the JSPS Core-to-Core Program B, the Asia-Africa Science Programs, the JST-Mirai Program “Development for Innovative Adhesion Technologies for Realizing Society 5.0”.

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