# Sequence-Controlled Radical Polymerization of N-Substituted Maleimides with 1-Methylenebenzocycloalkanes and the Characterization of the Obtained Copolymers with Excellent Thermal Resistance and Transparency

Miki Hisano,<sup>†</sup> Kyota Takeda,<sup>†</sup> Tsutomu Takashima,<sup>‡</sup> Zhengzhe Jin,<sup>‡</sup> Akira Shiibashi,<sup>‡</sup> and Akikazu Matsumoto<sup>†,</sup>\*

<sup>†</sup>Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

<sup>‡</sup>Central Technical Research Laboratory, Research & Development Division, JX Nippon Oil & Energy Corporation, 8, Chidoricho, Naka-ku, Yokohama 231-0815, Japan

Supporting Information

**ABSTRACT:** The radical copolymerization of *N*-methyl, ethyl, *n*-butyl, and 2-ethylhexylmaleimides (RMIs) with 1methylenebenzocycloalkanes (BCms) was carried out to fabricate thermally stable and transparent polymer materials. The copolymerization reactivity of BCms significantly depended on the carbon number of the ring structure of BCms. The analyses of the comonomer–copolymer composition curves and theoretical calculations results revealed that the sequence-controlled copolymerization of RMIs with BCms occurred in alternating and 2:1 fashions according to the BCms reactivity, which depends on the coplanarity of the exomethylene moiety and the benzene ring. The alternating and high-molecular-weight copolymers of BCms and RMIs



exhibited excellent thermal and optical properties. We have demonstrated that the radical copolymerization of RMIs is useful not only as the method for high-performance transparent polymer production but also as the tool for the fundamental research of radical polymerization mechanism.

# INTRODUCTION

N-substituted maleimides (RMIs) readily polymerize in the presence of a radical initiator to give a high-molecular-weight polymer with excellent thermal stabilities,<sup>1-9</sup> although they are one of the 1,2-disubstituted ethylenic monomers including a high steric hindrance between the propagating radical and the reacting monomer during polymerization.<sup>10-13</sup> The high glass transition temperatures  $(T_{\sigma})$  of the poly(RMI)s originate in the rigid poly(substituted methylene) structure, which has no methylene spacer as a flexible joint in their main chain, <sup>10,14–21</sup> and the high onset temperatures of decomposition arise from a robust imide-ring structure included in the repeating units of the polymers.<sup>22-27</sup> Poly(RMI)s are difficult to use as films and sheets because of their brittleness, while the RMI monomers have often been used as comonomers in order to modify the thermal properties of conventional polymers. In 1996, Doi et al. reported that the alternating copolymerization of the RMIs with isobutene (IB) produced high-molecular-weight copolymers with an excellent thermal stability, transparency, high strength, and high modulus.<sup>28,29</sup> For example, the alternating copolymer of N-methylmaleimide (MMI) and IB [poly(MMI-

alt-IB)] exhibited excellent properties superior to those of the conventional transparent polymers such as poly(methyl methacrylate) and polycarbonates.<sup>30-32</sup> Electron-donating monomers, such as IB and other olefins, styrenes, and vinyl ethers, are favorably combined with the electron-accepting RMIs for the facile production of alternating copolymers.<sup>33–40</sup> Omayu et al. previously demonstrated that exomethylene monomers had a copolymerization reactivity higher than those of cycloalkenes with an internal olefin structure during the copolymerization with the RMIs, and that the introduction of bulky substituents, such as the alicyclic group next to the main chain, effectively increased the  $T_{\rm g}$  values of the obtained copolymers.<sup>41</sup> Recently, it was demonstrated that the RMI monomers are useful for the sequence regulated radical copolymerization in alternating and 2:1-sequence controlled fashions.<sup>42-45</sup> Sequence-controlled radical polymerization has

```
        Received:
        March 4, 2013

        Revised:
        March 29, 2013

        Published:
        April 16, 2013
```

attracted significant attention in the research fields of polymer synthesis and radical polymerization.  $^{46-52}$ 

In this study, the radical copolymerization of the RMIs with 1-methylenebenzocycloalkanes (BCms) was carried out in order to fabricate the maleimide copolymer with more superior thermal properties (Scheme 1). The BCm monomers are  $\alpha$ -

#### Scheme 1



substituted styrene derivatives with a reactive exomethylene group. The m indicates the carbon number of the ring structure of the BCm molecules. It has been reported that cyclic 1,1disubstituted ethylene monomers with an exomethylene moiety have a high polymerization reactivity during the radical homo-and copolymerizations.<sup>53–56</sup> The homopolymerization of the BCms and the alternating copolymerization with maleic anhydride were previously reported,<sup>56,57</sup> but there is no report on the copolymerization of the BCms with the RMIs in the literature. During the course of our studies on the copolymerization of the RMIs with olefins, we found that the sequence-controlled radical copolymerization occurred and the copolymers consisting of the AB- and AAB-repeating units (alternating and 2:1 sequence controls, respectively) were produced depending on the m number of the BCms. We now discuss the ring-size effects of the BCms on the copolymerization reactivity and the sequence control based on the results of the monomer reactivity analysis during copolymerization as well as their theoretical calculations using model reactions. The thermal and optical properties of the copolymers were also investigated.

#### EXPERIMENTAL SECTION

General Procedures. The NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker AV300N spectrometer. The number-average molecular weight  $(M_n)$ , weight-average molecular weight  $(M_w)$ , and polydispersity  $(M_w/M_n)$  were determined by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The FT-IR spectra were recorded by a JASCO FT/IR 430 spectrometer using the KBr pellet method. The thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Seiko TG/DTA 6200 in a nitrogen stream at the heating rate of 10  $^{\circ}$ C/min. The onset temperature of decomposition ( $T_{d5}$ ) was determined as the 5% weight-loss temperature in the TG curves. The differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the heating and cooling rates of 10 °C/min. The UV-vis spectra were recorded using a JASCO V-550 spectrophotometer. The refractive index and Abbe number  $(\nu_{\rm D})$  were determined using an Abbe-type refractometer (Atago Co., Ltd., Model DR-M2). The  $\nu_{\rm D}$  value is represented by the following equation.

 $\nu_{\rm D} = (n_{\rm D} - 1) / (n_{\rm F} - n_{\rm C}) \tag{1}$ 

Theoretical calculations were carried out using density functional theory (DFT) at the B3LYP/6-31G\*//B3LYP/6-31G\* for the activation energy, and at the B3LYP/6-311+G\*\*//B3LYP/6-31G\* level for the energy difference of the reactant and the product. A Spartan'10 software package (Wave function, Inc.) was used for all the calculations.

**Materials.** 2,2'-Azobis(isobutyronitrile) (AIBN) (Wako Pure Chemical Industries, Ltd.) was recrystallized from methanol. *N*-Methylmaleimide (MMI, mp 97 °C), *N*-*n*-butylmaleimide (BMI), and *N*-(2-ethylhexyl)maleimide (EHMI) were synthesized according to the methods reported in previous papers.<sup>58,59</sup> *N*-Ethylmaleimide (EMI, mp 46 °C) (Tokyo Chemical Industry Co., Ltd.) was used as received without further purification. 1-Methylenebenzocyclobutane (BC4) was synthesized according to the method reported in a previous paper.<sup>57</sup> 1-Methyleneindane (BC5), 1-methylenetetralin (BC6), and 1-methylenebenzocycloheptane (BC7) were synthesized by the Wittig reaction of the respective precursor ketones, i.e., 1-indanone, 1-tetralon, and 1-benzosuberone, which were commercially available (Tokyo Chemical Industry Co., Ltd.).

Synthesis of BCms. A four-necked flask was charged with methyltriphenylphosphonium bromide (32.0 g, 90 mmol) (Wako Pure Chemical Industries, Ltd.) suspended in dry THF (200 mL) under argon. Potassium tert-butoxide (14.6 g, 0.13 mol) (Tokyo Chemical Industry Co., Ltd.) was then added, and the yellow mixture was stirred at ambient temperature for 30 min. The mixture was cooled to 0 °C, and the corresponding ketone, i.e., 1-indanone (11.9 g, 90 mmol), 1-tetralon (13.2 g, 90 mmol), or 1-benzosuberon (14.4 g, 90 mmol) was dropwise added. After being warmed to room temperature, the mixture was stirred overnight. A small amount of water (2-3 mL) was added to quench the excess reagent, and the mixture was filtered through silica gel. The silica was rinsed with THF, and the solvent was evaporated under reduced pressure. The residue was poured into n-hexane (ca. 1 L) to precipitate the triphenylphosphine oxide as the byproduct. The mixture was filtered and the solvent was evaporated under reduced pressure. The residual crude yellow oil was purified by silica gel column chromatography with *n*-hexane as the eluent. The obtained BCms were colorless oils.

BC4. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.25–7.16 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 5.31 (t, C=CH<sub>2</sub>, 1H), 4.94 (s, C=CH<sub>2</sub>, 1H), 3.63 (s, CH<sub>2</sub>, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  145.2 (C=CH<sub>2</sub>), 145.3, 144.8, 128.8, 127.2, 122.8, and 118.5 (C<sub>6</sub>H<sub>4</sub>), 103.2 (C=CH<sub>2</sub>), 38.8 (CH<sub>2</sub>).

*BC5.* Yield: 53.2%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.54–7.46 (m, C<sub>6</sub>H<sub>4</sub>, 1H), 7.30–7.15 (m, C<sub>6</sub>H<sub>4</sub>, 3H), 5.45 (t, C=CH<sub>2</sub>, 1H), 5.03 (t, C=CH<sub>2</sub>, 1H), 3.02–2.92 (m, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2H), 2.84–2.75 (m, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  151.0 (*C*=CH<sub>2</sub>), 147.1, 141.4, 128.6, 126.8, 125.8, and 121.0 (C<sub>6</sub>H<sub>4</sub>), 102.8 (C=CH<sub>2</sub>), 31.6 (CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 30.5 (CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>C<sub>4</sub>).

BC6. Yield: 60.3%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.68–7.60 (m, C<sub>6</sub>H<sub>4</sub>, 1H), 7.21–7.17 (m, C<sub>6</sub>H<sub>4</sub>, 3H), 5.47 (d, C=CH<sub>2</sub>, 1H), 4.95 (dd, C=CH<sub>2</sub>, 1H), 2.85 (t, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2H) 2.55 (m, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2H), 1.89 (m, CH<sub>2</sub>= CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 143.4 (C=CH<sub>2</sub>), 137.3, 134.7, 129.2, 127.6, 125.9, and 124.2 (C<sub>6</sub>H<sub>4</sub>), 107.9 (C=CH<sub>2</sub>), 33.2, 30.4, and 23.8 (CH<sub>2</sub>).

*BC7.* Yield: 38.9%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.22–7.07 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 5.10 (dt, C=CH<sub>2</sub>, 1H), 4.98 (d, C=CH<sub>2</sub>, 1H), 2.76 (t, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CG<sub>4</sub>H<sub>4</sub>, 2H), 2.39 (t, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CG<sub>4</sub>H<sub>4</sub>, 2H), 1.90–1.67 (m, CH<sub>2</sub>=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CG<sub>4</sub>H<sub>4</sub>, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  152.8 (C=CH<sub>2</sub>), 144.2, 140.2, 128.9, 128.1, 127.0, and 126.1 (C<sub>6</sub>H<sub>4</sub>), 113.7 (C=CH<sub>2</sub>), 36.5, 36.3, 31.5, and 27.3 (CH<sub>2</sub>).

**Polymerization Procedures.** RMI, BC*m*, AIBN, and 1,2dichloroethane (for solution polymerization) were placed in a glass ampule. After the freeze-thaw cycles, the ampule was sealed. The solution was heated at 60  $^{\circ}$ C for a given time, and then the polymerization mixture was poured into a large amount of methanol to precipitate the copolymers with BC4 and BC5, a methanol/water

Table	1.	Synthesis	and	Thermal	Properties	of Po	oly(MMI-co-BCm)s'	ı
-------	----	-----------	-----	---------	------------	-------	-------------------	---

BCm	yield (%)	$M_{\rm n}/10^{3}$	$M_{\rm w}/10^{3}$	$M_{ m w}/M_{ m n}$	BC <i>m</i> mol % in copolymer <sup>b</sup>	$T_{d5}$ (°C)	$T_{\rm max}$ (°C)	$T_{g}(^{\circ}C)$
BC4	89.9	24.9	67.2	2.7	48.2	346	368	143
BC5	36.6	10.3	18.5	1.6	51.3	345	385	212
BC6	1.4	2.6	3.1	1.3	47.3	с	с	200
BC7	0.5	1.0	1.6	1.7	25.6	с	с	с
			[	1/7 [		1 (2.0.0	and the base	

<sup>*a*</sup>Copolymerization conditions:  $[MMI] = [BCm] = 0.2 \text{ mol/L}, [AIBN] = 10 \text{ mmol/L in 1,2-dichloroethane at 60 °C for 5 h. <sup>$ *b*</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>*c*</sup>Not determined.

mixture (4/1 in volume) for the copolymers with BC6, and *n*-hexane for the copolymers with BC7. The copolymers were filtered out, washed, and then dried in vacuo. The yield of the copolymers was gravimetrically determined. The copolymers were purified by repeated precipitation procedures using chloroform as the solvent and the appropriate precipitants. The composition of the obtained copolymers was determined by <sup>1</sup>H NMR spectroscopy.

*Poly(MMI-alt-BC4).* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.80–5.72 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 4.36–0.65 (m, CHCH, CH<sub>2</sub>, and CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 179.2 and 177.2 (C=O), 146.3, 141.4, 128.8, 127.3, 123.5, 122.1, and 120.5 (C<sub>6</sub>H<sub>4</sub>), 55.2–45.5 (CC<sub>6</sub>H<sub>4</sub>, CH<sub>2</sub>, and CH), 45.2–25.4 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and CH<sub>3</sub>). IR (KBr):  $\nu_{C=O}$  (cm<sup>-1</sup>) 1699.

Poly(MMI-alt-BC5). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.68–5.41 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 4.44–0.20 (m, CHCH, CH<sub>2</sub>, and CH<sub>3</sub>, 11H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 179.4 and 177.7 (C=O), 152.3, 145.0, and 128.0–123.2 (C<sub>6</sub>H<sub>4</sub>), 62.5–49.1 (CH<sub>2</sub> and CH), 40.3 (CH), 36.8 (CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 30.9 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 24.3 (CH<sub>3</sub>). IR (KBr):  $\nu_{C=O}$  (cm<sup>-1</sup>) 1698.

*Poly(MMI-alt-BC6).* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.98–4.71 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 4.47–0.10 (m, CHCH, CH<sub>2</sub>, and CH<sub>3</sub>, 13H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  179.5–176.8 (C=O), 140.3, 136.6, 129.8, and 126.3 (C<sub>6</sub>H<sub>4</sub>), 60.7–53.1 (CH<sub>2</sub> and CH), 44.9–41.4 (CC<sub>6</sub>H<sub>4</sub> and CH), 31.4 and 30.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 24.6 (CH<sub>3</sub>), 18.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>). IR (KBr):  $\nu$ <sub>C=O</sub> (cm<sup>-1</sup>) 1697.

*Poly(MMI-per-MMI-per-BC7).* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.99–6.08 (m, C<sub>6</sub>H<sub>4</sub>, 4H), 4.86–0.33 (m, CHCH, CH<sub>2</sub>, and CH<sub>3</sub>, 15H).

# RESULTS AND DISCUSSION

Copolymerization of MMI with BCms. The radical copolymerization of MMI with the BCms (m = 4-7) was carried out in the presence of AIBN as the radical initiator at 60  $^{\circ}$ C for 5 h under equimolar comonomer conditions ([MMI] = [BCm] = 0.2 mol/L in 1,2-dichloroethane). All the copolymers were isolated as colorless powders after reprecipitation. The copolymer yield, the  $M_n$ ,  $M_w$ , and  $M_w/M_n$  values determined by SEC measurement, and the  $T_{d5}$ ,  $T_{max}$ , and  $T_{g}$  values determined by TG and DSC measurements are summarized in Table 1. The BC4 monomer gave a copolymer with the highest molecular weight in the highest copolymer yield. The yield and the  $M_{\rm n}$  value varied in the ranges of 0.5–90% and 1–25 ×  $10^3$ , respectively, sensitive to the structure of the BCms. Both values drastically decreased with an increase in the ring size of the BCms. The NMR spectroscopy revealed the formation of copolymers with an equimolar composition during the copolymerization of MMI with all the BCms except for BC7 (Figures S1-S7 in Supporting Information). The polymerization reactivity significantly depended on the BCm structure, and similar results were observed during the homopolymerization (Table 2). The BC4 and BC5 monomers gave the corresponding homopolymers with an  $M_{\rm n}$  of  $5-10 \times 10^3$  in low yields (4-10%), while the BCms with a higher m number provided no polymer even during bulk polymerization.

The obtained copolymers exhibited excellent thermal properties. The  $T_{dS}$  and  $T_{max}$  values were over 345 and 365 °C, respectively. The  $T_g$  value of the copolymers with BC4 was

BCm	$\begin{bmatrix} BCm \end{bmatrix} \\ (mol/L)$	yield (%)	$\frac{M_{\rm n}}{10^3}$	$\frac{M_{\rm w}}{10^3}$	${M_{ m w}}/{M_{ m n}}$	$\stackrel{T_{d5}}{(^{\circ}C)}$	$T_{\max}$ (°C)	$\overset{T_{g}}{(^{\circ}C)}$
BC4	1.0	10.3	4.6	65	1.4	305	397	133

19.6

2.1

228

339

119

Table 2. Synthesis and Thermal Properties of Poly(BCm)s<sup>a</sup>

BC5	1.0	4.0	9.5
BC6	1.0	0	
BC7	1.0	0	

0

BC7 bulk

<sup>*a*</sup>Polymerization conditions: [AIBN] = 10 mmol/L in 1,2-dichloroethane or bulk, at 60  $^{\circ}$ C for 20 h.

143 °C, similar to the previously reported values for poly(MMIalt-IB).<sup>30</sup> It is noted that the  $T_{\rm g}$  values were over 200 °C for the copolymers with BC5 and BC6 in spite of their decreased molecular weights by the increase in the m number. The  $T_{\rm d5}$ and  $T_{\rm g}$  values for poly(BC4) and poly(BC5) as the homopolymers were lower than those for the copolymers with MMI.

Determination of Monomer Reactivity Ratios. To clarify the monomer reactivity depending on the ring size of the BCms, the copolymerization of BMI with the BCms (m =5-7) was carried out over various compositions in the feed, and the monomer reactivity ratios were determined based on the analysis of the obtained comonomer-copolymer composition curves. The liquid BMI monomer enabled us to perform a copolymerization in bulk, and consequently, we obtained sufficiently high-molecular-weight copolymers to accurately estimate their copolymer composition, while MMI with a melting point at 97 °C was only used for the solution polymerization. The copolymerization with the highly reactive BCms was carried out in 1,2-dichloroethane under a high monomer concentration ([BMI] + [BCm] = 2 mol/L). The results are summarized in Table 3. The comonomer-copolymer composition curves are shown in Figure 1.

All the copolymers were recovered at a low conversion to allow the analysis of the copolymerization parameters using the Mayo-Lewis equation (eq 2). The copolymer compositions were determined by <sup>1</sup>H NMR spectroscopy. For the copolymerizations of BMI with BC5 and BC6 (Scheme 2), the monomer reactivity ratios,  $r_1$  and  $r_2$ , were successfully determined by the terminal unit model (Scheme 3). The  $r_1$  and  $r_2$  values, which are defined by eqs 3 and 4, respectively, were determined by the nonlinear least-squares curve fitting method,<sup>60</sup> as shown in Figure 1. The monomer reactivity ratios were also estimated by the Fineman-Ross<sup>61</sup> and Kelen-Tüdõs<sup>62</sup> methods, but these methods gave scattered plots and the comonomer-copolymer composition curves based on the calculated values partially failed to fit the experimental data (Table S1 and Figure S8-S10, Supporting Information). In contrast, the curve fitting method resulted in good results over the whole range of compositions.

Table 3. Radical Copolymerization of BMI  $(M_2)$  with BCms  $(M_1)$  at 60 °C<sup>*a*</sup>

BC <i>m</i> (M <sub>1</sub> )	BC <i>m</i> mol % in comonomer	time (h)	yield (%)	$M_{ m n} / 10^4$	$M_{ m w} / 10^4$	${M_{ m w}}/{M_{ m n}}$	BC <i>m</i> mol 9 in copolymer
BC5 <sup>a</sup>	8.6	0.5	7.7	7.1	13.5	1.9	48.2
	17.5	0.5	7.4	7.1	13.5	1.9	50.5
	26.7	0.5	7.4	5.3	10.9	2.1	51.9
	36.1	0.5	5.6	4.4	8.9	2.0	49.5
	46.0	0.5	5.0	3.4	6.6	1.8	50.5
	56.0	1	8.0	3.0	5.6	1.9	55.0
	66.5	1	4.9	1.9	3.4	1.7	50.7
	77.2	2	5.3	1.2	1.9	1.6	53.1
	88.4	2	2.0	0.7	0.9	1.3	57.3
BC6 <sup>a</sup>	9.5	2	3.4	1.0	1.6	1.5	42.5
	19.0	5	7.3	0.9	1.3	1.5	45.4
	28.7	5	4.6	0.7	1.0	1.3	45.5
	38.5	5	4.8	0.8	1.0	1.4	46.5
	48.5	12	7.9	0.6	0.9	1.2	47.0
	58.5	12	4.8	0.6	0.7	1.2	47.6
	68.4	24	4.0	0.5	0.6	1.2	51.0
	79.0	48	1.0	0.4	0.5	1.2	53.0
	89.4	48	0.8	0.1	0.2	1.4	52.8
$BC7^b$	10.3	1	1.8	1.0	1.3	1.3	18.0
	20.5	5	6.4	0.8	1.0	1.3	26.1
	30.7	5	4.6	0.8	0.9	1.2	32.3
	40.8	5	3.6	0.7	0.9	1.2	32.9
	50.8	5	2.4	0.7	0.8	1.2	32.5
	60.8	5	1.9	0.7	0.8	1.2	39.4
	70.7	12	3.5	0.6	0.7	1.2	39.3
	80.3	48	5.8	0.5	0.6	1.2	41.6
	90.3	48	1.5	0.5	0.6	1.2	39.9
757	[ ]		• /-	F7			

a[BMI] + [BCm] = 2.0 mol/L, [AIBN] = 20 mmol/L in 1,2dichloroethane. b([BMI] + [BC7])/[AIBN] = 100/1 in bulk.



**Figure 1.** Comonomer-copolymer composition curves for the radical copolymerization of BMI ( $M_2$ ) with BC5 ( $\bullet$ ), BC6 ( $\Box$ ), and BC7 ( $\blacklozenge$ ) ( $M_1$ ) in 1,2-dichloroethane at 60 °C.

#### Scheme 2

Scheme 3

$\mathcal{M}_{1}^{\bullet} + M_{1} \xrightarrow{k_{11}} \mathcal{M}_{1}^{\bullet}$
$\mathcal{M}_{1}^{\bullet} + M_{2} \xrightarrow{k_{12}} \mathcal{M}_{2}^{\bullet}$
$\mathcal{M}_{2}^{\bullet} + M_{1} \xrightarrow{k_{21}} \mathcal{M}_{1}^{\bullet}$
$\mathcal{M}_2^{\bullet} + M_2 \xrightarrow{k_{22}} \mathcal{M}_2^{\bullet}$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])}$$
(2)

$$r_1 = k_{11}/k_{12} \tag{3}$$

$$r_2 = k_{22}/k_{21} \tag{4}$$

where  $M_1$  and  $M_2$  are BCm and BMI, respectively.

Both the  $r_1$  and  $r_2$  values determined for the copolymerizations with BC5 and BC6 were close to zero;  $r_1 = 0.046$  and  $r_2 =$ 0.0043 for the BC5(M<sub>1</sub>)-BMI(M<sub>2</sub>) system and  $r_1 = 0.019$  and  $r_2 = 0.047$  for the BC6(M<sub>1</sub>)-BMI(M<sub>2</sub>) system, as summarized in Table 4. This indicates the production of the copolymers with highly controlled alternating repeating structures. The value of  $1/r_2$  represents the relative reactivity of the BMI radical to the BCm monomers. The  $1/r_2$  value for the BC5 copolymerization  $(1/r_2 = 233)$  was ten times higher than that for BC6 ( $1/r_2 = 21$ ). The lower reactivity of BC6 was reflected in the yield and molecular weight of the resulting copolymers shown in Table 3. For the copolymerization of BMI with BC7, the copolymerization behavior was entirely different from the alternating one observed for the cases with BC5 and BC6. The monomer reactivity ratios were determined using the penultimate unit model<sup>42-45,63,64</sup> for the BMI-BC7 copolymerization, while appropriate values were not obtained using the terminal model. Similar penultimate group effects were reported for the copolymerization of RMIs with various olefins containing bulky substitutents, leading to the formation of the 2:1 sequence controlled copolymers.<sup>4</sup>

In general, the penultimate unit model involves the use of eight propagation reactions (Scheme 4) with four monomer reactivity ratios (eqs 5-8)

$$r_{11} = k_{111} / k_{112} \tag{5}$$

$$_{12} = k_{122} / k_{121} \tag{6}$$

$$k_{21} = k_{211} / k_{212} \tag{7}$$

$$r_{22} = k_{222} / k_{221} \tag{8}$$

With these four monomer reactivity ratios, the copolymer composition is represented as eq 9.



r

olefin $(M_1)$	RMI $(M_2)$	solvent	$r_1$	$r_2$	$r_{11}$	r <sub>12</sub>	$r_{21}$	r <sub>22</sub>	ref
BC5	BMI	1,2-dichloroethane	0.046	0.0043					this work
BC6	BMI	1,2-dichloroethane	0.019	0.047					this work
BC7	BMI	bulk			0	2.92	0	0.252	this work
limonene	PhMI	$PhC(CF_3)_2OH$			0	18.7	0	0.0042	42
eta-pinene	MMI	1,2-dichloroethane			0	7.09	0	0.20	43
$\beta$ -pinene	PhMI	1,2-dichloroethane			0	10.3	0	0.236	44

Table 4. Monomer Reactivity Ratios for Radical Copolymerization of RMIs (M2) with BCms and Other Olefins (M1) at 60 °C

#### Scheme 4



$$f = \frac{1 + r_{21}F\left(\frac{r_{11}F + 1}{r_{21}F + 1}\right)}{1 + \frac{r_{12}}{F}\left(\frac{r_{22} + F}{r_{12} + F}\right)}$$
(9)

where  $F = [M_1]/[M_2]$  and  $f = d[M_1]/d[M_2]$ . In this case, the  $r_{11}$  and  $r_{21}$  values can be regarded as zero due to the lack of the homopolymerization ability of BC7 (Table 2). Therefore, eq 9 is reformulated as eq 10.

$$\frac{1-2f}{F(1-f)} = \frac{f}{F^2(1-f)}r_{22} - \frac{1}{r_{12}}$$
(10)

The monomer reactivity ratios,  $r_{12}$  and  $r_{22}$ , were determined as  $r_{12} = 2.9$  and  $r_{22} = 0.25$  by the curve fitting method. The values of  $r_{12} > 1$  and  $r_{22} < 1$  agreed well with the fact that the AAB-type periodic copolymer with a 2:1 composition of BMI and BC7, i.e., poly(BMI-*per*-BMI-*per*-BC7), was predominantly produced. The penultimate group effect was indispensable for the production of the 2:1 sequence-controlled copolymers, but the origin of the effect has not been revealed yet.<sup>63,64</sup> Both the polar and steric effects are important to determine the monomer reactivity, and a significant solvent effect was also pointed out for the RMI–olefin copolymerization systems.<sup>28,44,65,66</sup> In this study, we found that the coplanarity of the exomethylene moiety and the benzene ring of BC*ms* significantly determined the reactivity of the monomer and the corresponding propagating radicals as follows.

**Theoretical Calculations.** In order to discuss the copolymerization reactivity of the BC*ms*, we estimated the activation energies ( $E_{act}$ ) and energy differences between the reactant and the product ( $\Delta E$ ) by the DFT calculations using model reactions for the homo- and cross-propagations of MMI and the BC*ms* (Scheme 5). The  $E_{act-22}$  value represents the activation energy for the homopropagation of MMI and the  $E_{act-12}$  and  $E_{act-21}$  values are activation energies for the cross-propagations. Similarly, the  $\Delta E_{11}$  and  $\Delta E_{22}$  values indicate

Scheme 5



energy differences between the reactant and the product for the homopropagations and the  $\Delta E_{12}$  and  $\Delta E_{21}$  values correspond to those for the cross-propagations. The results are summarized in Table 5.

Table 5. Activation Energies  $(E_{act})$  and Energy Differences in Reactant and Product  $(\Delta E)$  for Propagations during Copolymerization of MMI with BCms<sup>*a*</sup> (Unit is kJ/mol)

		cross-pro		homopropagation	
BCm	E <sub>act-12</sub>	$\Delta E_{12}$	$E_{\rm act-21}$	$\Delta E_{21}$	$\Delta E_{11}$
BC4	18.3	-61.3	9.2	-85.4	-60.9
BC5	29.4	-27.7	8.2	-97.9	-35.5
BC6	38.8	-14.4	7.1	-97.3	24.4
BC7	74.5	-2.5	33.4	-71.6	19.7

<sup>*a*</sup>Calculated by the DFT method at the B3LYP/6-31G\*//B3LYP/6-31G\* and B3LYP/6-311+G\*\*//B3LYP/6-31G\* levels of theory for the  $E_{\rm act}$  and  $\Delta E$  values, respectively, using the model reactions in Scheme 5. For the MMI homopropagation, the  $E_{\rm act-22}$  and  $\Delta E_{22}$  values were calculated to be 20.9 and -79.1 kcal/mol, respectively.

The calculated  $E_{\rm act}$  and  $\Delta E$  values were closely related to each other; i.e., the lower the  $E_{\rm act}$  values, the negatively larger the  $\Delta E$  values. This tendency satisfies a common rule accepted for many reactions. The  $E_{\rm act-21}$  values (7.1–9.2 kJ/mol) for the cross-propagation of the MMI radical to BCms (m = 4-6) were lower than the  $E_{\rm act-22}$  value (20.9 kJ/mol) for the MMI homopropagation, while the  $E_{\rm act-21}$  value (33.4 kJ/mol) for BC7 was far greater than the  $E_{\rm act-22}$  one. The  $\Delta E_{21}$  and  $\Delta E_{22}$  values showed similar results; the  $\Delta E_{21}$  values were in the range of -85.4 to -97.9 kJ/mol for BC4 to BC6 and  $\Delta E_{21} = -71.6$  kJ/

mol for BC7, while the  $\Delta E_{22}$  was -79.1 kJ/mol for the MMI homopropagation. Typical energy diagrams are shown in Figure 2. This result indicates that the cross-propagation of



**Figure 2.** Energy profiles for the homopropagation of the MMI radical and the cross-propagation to the BCms (m = 5 and 7). BC4 and BC6 provide diagrams similar to that for BC5. M and M<sup>•</sup> indicate the MMI monomer and radical, respectively.

the MMI radical predominantly occurs rather than the homopropagation of MMI for the cases of BCms (m = 4-6). In contrast, the MMI homopropagation is preferred to the cross-propagation for the BC7 case. The formation of the copolymers with the 2:1 sequence is based on the reduced reactivity of the BC7 radical during the cross-propagation to BMI.

Each  $E_{act-12}$  value (18.3–74.5 kJ/mol) was higher than the corresponding  $E_{act-21}$  one (7.1–33.4 kJ/mol) for all the BCms, indicating that the cross-propagation of the BCm radical to RMI is the rate-determining step. Therefore, the copolymerization rate is significantly affected by the cross-propagation to the RMI monomers during the copolymerization of the BCms and RMIs. This suggests the order of the copolymerization reactivity as follows: BC4 > BC5 > BC6  $\gg$  BC7. Actually, it

is quite consistent with the fact that the copolymerization reactivity (deduced from the yield and the molecular weight of the produced copolymers) decreased with an increase in the ring size of the BC*ms*, as already shown in Table 1. The  $\Delta E_{11}$ values calculated for the homopropagation of the BC*ms* also well agreed with the homopolymerization results in Table 2. No polymer was produced during the polymerization systems exhibiting a positive  $\Delta E$  value, i.e., for the cases of the endothermic homopropagation of the BC*ms*.

We further investigated the molecular conformations in the transition state during the cross-propagations in order to discuss the reactivities of the BCm monomers and their radicals (m = 5-7). The molecular structures in the transition state are shown in Figure 3. The carbon-to-carbon distances between the carbon atoms making a new covalent bond during the reaction were almost the same ( $R_{CC} = 2.22-2.37$  Å) in the transition states. No steric interaction was observed during the reaction of the MMI radical to the BCms (Figure 3a-c). This is consistent with the low  $E_{act-21}$  values and the fast addition of the MMI radical to the BCms. During the reactions of the BCm radicals to the MMI monomer (Figure 3d-f), the distances between the closest hydrogen atoms on the maleimide carbon-to-carbon double bond and the cyclic methylene moieties of the BCm radicals decreased according to the increased ring size. This suggests the enhanced steric repulsion during the transition state leading to an increase in the  $E_{\rm act}$  values with an increase in the m number.

It was revealed that the conformation of the exomethylene moieties varied from a planar structure for BC5 and BC6 to a nonplanar structure for BC7, as noted by the dihedral angles ( $\angle$ C1-C2-C3-C4) in Table 6. In this table, the values estimated based on the <sup>13</sup>C coupling constants in the NMR spectra are also shown.<sup>67</sup> The BC7 monomer had large dihedral angles in the ground and transition states;  $\angle$ C1-C2-C3-C4 = 55.3 and 44.3°, respectively. The electron density on the C1 carbon of the exomethylene group of BC7 was slightly lower than those for BC5 and BC6 with a coplanar molecular conformation. The deviation from the coplanar structure of the BC*m* monomers was reduced by the radical addition due to a



**Figure 3.** Transition-state structures determined by the DFT calculations for (a) the MMI radical···BC5 ( $R_{CC} = 2.37$  Å), (b) the MMI radical···BC6 ( $R_{CC} = 2.37$  Å), (c) the MMI radical···BC7 ( $R_{CC} = 2.26$  Å), the MMI radical, (d) the BC5 radical···MMI ( $R_{CC} = 2.26$  Å), (e) the BC6 radical···MMI ( $R_{CC} = 2.22$  Å), and (f) the BC7 radical···MMI ( $R_{CC} = 2.29$  Å).  $R_{CC}$  is the distance between the carbons which make a new covalent bond.

Tuble of Diffediat Inigles Exhibiting Coplanaticy of Exomethytene Group and Denzene Idings of Domo and Dom Idadeaus	Table 6. Dihedral Angles Exhibiting	Coplanarity of Exomethylen	e Group and Benzene Ring	gs of BCms and BCm Radicals <sup>a</sup>
---	-------------------------------------	----------------------------	--------------------------	--

	_	dihedral angles (∠C1−C2−C3−C4, deg)								
	-	iı	n the ground state	in the transition state						
	Mulliken atomic charge <sup>b</sup>	BCm	BCm•	MMI−BCm <sup>•</sup>	BC <i>m</i> <sup>●</sup> ···MMI	$MMI^{\bullet} \cdots BCm$				
BC5	-0.433	9.3 $(1.4)^c$	1.6	1.4	26.7	6.3				
BC6	-0.433	19.8 $(1.8)^c$	6.7	5.4	31.8	9.2				
BC7	-0.385	$55.3 (59.0)^c$	34.0	23.1	5.9	44.3				
<sup><i>a</i></sup> Dihedral angles	$(\angle C1 - C2 - C3 - C4)$ are defined	ned as in Figure 4. (	Calculated by DFT	method at the	B3LYP/6-31G*//B3LYI	P/6-31G* levels of				

theory. <sup>b</sup>C1 carbon of the exomethylene moiety of the BCms (see Table S2, Supporting Information). <sup>c</sup>Reference 67.

change in the sp<sub>2</sub> carbon to the benzyl-type conjugated radicals, of which the dihedral angle values decreased to 34.0 and 23.1° when the adduct radicals, BCm<sup>•</sup> and MMI–BCm<sup>•</sup> were formed, respectively. A smaller deviation from the planar structure was observed for both the monomers (9.3–19.8°) and the radicals (1.4–6.7°) of BC5 and BC6. Ring strain can be released during the radical addition reactions. The MMI<sup>•</sup>···BCm in the transition state exhibited intermediate molecular structures ( $\angle C1-C2-C3-C4 = 6.3-44.3^\circ$ ), as shown in Table 6. The BCm radicals in the transition state (BCm···MMI) were revealed to have a molecular structure entirely different from the BCm radicals in the ground state due to their late transition state during the slow cross-propagation reactions as the rate-determining steps.



**Figure 4.** Numbering for the carbons for dihedral angle determination of the BC*ms* and the related radicals.

Synthesis and Properties of High-Molecular-Weight Copolymers. The bulk and solution polymerizations at a high monomer concentration were carried out to obtain highmolecular-weight copolymers using BC5 and BC6 as the BCms and MMI, EMI, BMI, and EHMI as the RMIs. The results are summarized in Table 7. The yield and  $M_w$  values of the copolymers produced during the copolymerization with BC5 were high at 55–67% and 9–22 × 10<sup>4</sup>, respectively. The lower values were obtained during the BC6 copolymerization due to the reduced monomer reactivity, i.e., 16–18% yields and 0.4–2 × 10<sup>4</sup>  $M_{\rm w}$  values. All the poly(RMI-*alt*-BC*m*)s were confirmed to be thermally stable and the  $T_{\rm d5}$  and  $T_{\rm max}$  values were high enough. The decomposition of the copolymers proceeded via a one-step reaction and a trace amount of residue was observed after heating to 420 °C, independent of the *N*-alkyl substituents and the m number (Figure 5, see also Figures S11 and S12,



Figure 5. TG curves of (---) poly(MMI-alt-BC5), (---) poly(EHMI-alt-BC5), and (----) poly(MMI-alt-BC6) in a nitrogen stream at the heating rate of 10 °C/min.

Supporting Information, for details). The  $T_g$  values of poly(MMI-*alt*-BC5) and poly(MMI-*alt*-BC6) were 212 and 213 °C, respectively, being higher than the  $T_g$  values previously reported for poly(MMI-*alt*-IB) (152 °C),<sup>30</sup> poly(MMI-*alt*-

Table 7. Thermal and Optical Properties of Poly	r(RMI-alt-BC5)s and Poly(RMI-alt-BC6)s <sup>c</sup>
---	---

1.0		([olefin] + [RMI])/	yield	$M_{\rm w}/$	$M_{\rm w}/$	olefin mol % in	$T_{d5}$	$T_{\text{max}}$	$T_{g}$		b
olefin	KMI (mol/L)	[AIBN]	(%)	10.	M <sub>n</sub>	copolymer	(C)	(C)	(-C)	$n_{\rm D}$	$ u_{\mathrm{D}} $
BC5	MMI(0.2)	40	36.6	1.9	1.8	51.3	345	385	212		
	EMI(2.0)	100	54.6	8.5	2.1	50.6	344	381	203	1.559	38
	BMI(bulk)	100	66.7	16.6	2.1	50.3	341	381	158	1.554	40
	EHMI(bulk)	100	60.6	21.7	1.7	49.3	330	377	109	1.543	43
BC6	MMI(0.4)	40	17.6	0.4	1.4	47.7	330	362	213		
	EMI(2.0)	100	16.0	1.0	1.5	51.8	320	359	221		
	BMI(bullk)	100	16.3	2.0	1.7	49.3	317	350	194		
	EHMI(bulk)	100	17.9	1.9	1.7	50.3	319	348	139		
IB <sup>c</sup>	MMI			22.0		50.0	396		157	1.53	51
$CA5^d$	MMI			0.4		49.5	334	416	178		
$CA6^d$	MMI			0.3		48.8	307	395	198		
poly(MMA) <sup>c</sup>							303		100	1.49	53
polycarbonate <sup>c</sup>							454		140	1.58	29

<sup>*a*</sup>Copolymerization conditions: [BC*m*]/[MMI] = 1/1 in 1,2-dichloroethane or in bulk at 60 °C for 5 h (BC5) or 20 h (BC6). <sup>*b*</sup>Abbe number:  $\nu_{\rm D} = (n_{\rm D} - 1)/(n_{\rm F} - n_{\rm C})$ . The  $n_{\rm F}$ ,  $n_{\rm D}$ , and  $n_{\rm C}$  values were determined at 486, 589, and 656 nm, respectively. <sup>c</sup>Reference 30. <sup>*d*</sup>Reference 41.

CA5) (178 °C),<sup>41</sup> and poly(MMI-*alt*-CA6) (198 °C),<sup>41</sup> of which the repeating structures are shown in Figure 6. The CA5



**Figure 6.** Repeating structures and the  $T_g$  values of poly(MMI-*alt*-BC*m*)s and poly(MMI-*alt*-CAm)s.

and CA6 are exomethylene cyclic olefin monomers containing no benzene ring. These results indicate that the introduction of the benzene moiety into the position closest to the polymer main chain effectively increases the  $T_g$  values of the polymers. Furthermore, the copolymers containing the BC6 and CA6 unit with bulkier structures resulted in the higher  $T_g$  values than the corresponding copolymer containing the BC5 and CA5 units.

The poly(RMI-*alt*-BC*m*)s were soluble in many organic solvents, such as chloroform, THF, toluene, and acetone, and transparent thin films were obtained by casting the solution and drying, as shown Figure 7. The film strength, i.e., brittleness, was dependent on the *N*-alkyl groups. The flexibility of the poly(RMI-*alt*-BC*m*)s films increased in the order of MMI < EMI < BMI < EHMI due to the increased free volume. On the basis of the transmittance experiments of visible light using the films (ca. 60- $\mu$ m thickness), the excellent transparency of poly(BMI-*alt*-BC5) and poly(EHMI-*alt*-BC5) was confirmed. The *n*<sub>D</sub> values of the poly(RMI-*alt*-BC*m*)s (1.54–1.56) were higher than that of poly(MMA) and the  $\nu$ <sub>D</sub> values of the poly(RMI-*alt*-BC*m*)s (38–43) were lower (Table 7). In Figure 7c, the dispersion was fitted by the simplified Cauchy's formula,

$$n_{\lambda} = n_{\infty} + D/\lambda^2 \tag{11}$$

where  $n_{\infty}$  and *D* are the estimated refractive index at the infinite wavelength and the dispersion coefficient. The  $n_{\infty}$  values were 1.537, 1.533, and 1.524, and the *D* values were 7781, 7335, and 6752 nm<sup>2</sup>, for poly(EMI-*alt*-BC5), poly(BMI-*alt*-BC5), and poly(EHMI-*alt*-BC5), respectively. The poly(MMI-*alt*-BC*m*)s with the highest  $T_{g}$  values provided transparent films, but they were too brittle to determine the  $n_{D}$  and  $\nu_{D}$  values.

# CONCLUSIONS

The copolymers of RMI with BCms (m = 4-7) were synthesized by the radical copolymerization process. The yield and molecular weight of the resulting copolymers decreased with an increase in the ring size of the BCm. In order to investigate the copolymerization reactivity of the BCms, we determined the monomer reactivity ratios for the



**Figure** 7. (a) Photographs of poly(EHMI-*alt*-BC5) film. (b) Transmittance of poly(RMI-*alt*-BC5) films (thickness ca. 60  $\mu$ m) in the UV and visible regions (——) poly(BMI-*alt*-BC5) and (--) poly(EHMI-*alt*-BC5). (c) Wavelength dispersion of the poly(EMI-*alt*-BC5) ( $\blacksquare$ ), poly(BMI-*alt*-BC5) ( $\blacksquare$ ), and poly(EHMI-*alt*-BC5) ( $\blacktriangle$ ).

copolymerization of BMI with the BCms. As a result, highly alternating copolymers were produced during the copolymerizations of BMI with BC5 and BC6, while the copolymerization of BMI with BC7 produced copolymers with a 2:1 composition. The monomer reactivity ratios were determined by the terminal and penultimate group models based on the obtained comonomer-copolymer composition curves. The DFT calculations for the propagation reactions were carried out in order to clarify the difference in the copolymerization reactivity and fashion of the copolymerization, i.e., alternating or 2:1 sequence controlled, depending on the ring size of the BCms. It was revealed that the coplanarity of the exomethylene group and the benzene ring of the BCms was important for the determination of the reactivity of the BCm monomers and the corresponding radicals. We also investigated the polymer properties, such as the thermal stability and transparency. The introduction of the benzocycloalkane units neighboring the main chain improved the  $T_{\rm g}$  values of the copolymers, as was expected. We concluded that the high-molecular-weight and high- $T_{g}$  poly(RMI-alt-BCm)s were produced during the copolymerization of BC5 and BC6 combined with the RMIs with an appropriate N-alkyl substituent and the transparent and thermally stable films were readily obtained by casting the polymer solutions. It is noted that the radical copolymerization of the RMIs is useful not only as the method for highperformance polymer production, but also as the tool for the fundamental research of radical polymerizations.

# ASSOCIATED CONTENT

#### **S** Supporting Information

NMR spectra, monomer reactivity ratios data, DFT calculation data, Kelen–Tüdõs and Fineman–Ross plots for the BMI–BC5 copolymerization, and TG and DSC curves. This material is available free of charge via the Internet at http://pubs.acs. org/.

#### AUTHOR INFORMATION

# **Corresponding Author**

\*(A.M.) Present address: Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai 599-8531, Japan. Phone and Fax: +81-72-254-9292; E-mail: matsumoto@chem.eng.osakafuu.ac.jp.

#### Notes

The authors declare no competing financial interest.

#### REFERENCES

- (1) Cubbon, R. C. P. Polymer 1965, 6, 419-426.
- (2) Yamada, M.; Takase, I.; Koutou, N. J. Polym. Sci., Polym. Lett. Ed. **1968**, 6, 883–888.
- (3) Barrales-Rienda, J. M.; Gonzalez Ramos, J.; Sanchez Chaves, M. J. Polym. Sci., Polym. Chem. Ed. 1979, 17, 81–96.
- (4) Otsu, T.; Matsumoto, A.; Kubota, T.; Mori, S. Polym. Bull. 1990, 23, 43-50.
- (5) Matsumoto, A.; Kubota, T.; Otsu, T. Macromolecules 1990, 23, 4508-4513.
- (6) Oishi, T.; Yamasaki, H.; Fujimoto, M. Polym. J. **1991**, 23, 795–804.
- (7) Ahn, K. D.; Lee, Y. H.; Koo, D. I. Polymer 1992, 33, 4851–4856.
  (8) Hill, D. J. T.; Shao, L. Y.; Pomery, P. J.; Whittaker, A. Polymer
- **2001**, 42, 4791–4802.
- (9) Gacal, B.; Cianga, L.; Aga, T.; Takeichi, T.; Yagci, Y. J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 2774–2786.
- (10) Otsu, T.; Yasuhara, T.; Matsumoto, A. J. Macromol. Sci.—Chem. 1988, A25, 537-554.
- (11) Matsumoto, A.; Otsu, T. Macromol. Symp. 1995, 98, 139–152.
  (12) Yoshioka, M.; Matsumoto, A.; Otsu, T. Polym. J. 1991, 23,
- 1249–1252. (13) Matsumoto, A.; Shimizu, K.; Mizuta, K.; Otsu, T. J. Polym. Sci.,
- Part A: Polym. Chem. 1994, 32, 1957–1968. (14) Kitano, T.; Fujimoto, T.; Nagasawa, M. Macromolecules 1974, 7,
- 719–724. (15) Otsu, T.; Yasuhara, T.; Shiraishi, K.; Mori, S. Polym. Bull. 1984, 12, 449–456.
- (16) Yamada, K.; Takayanagi, M.; Murata, Y. Polymer 1986, 27, 1054–1057.
- (17) Matsumoto, A.; Tarui, T.; Otsu, T. Macromolecules 1990, 23, 5102-5105.
- (18) Matsumoto, A.; Kubota, T.; Otsu, T. Polym. Bull. 1990, 24, 459-466.
- (19) Kurosu, H.; Yamada, T.; Ando, I.; Seto, K.; Otsu, T. J. Mol. Struct. 1993, 300, 303-311.
- (20) Matsumoto, A.; Nakagawa, E. Eur. Polym. J. **1999**, 35, 2107–2113.
- (21) Nakatsuji, M.; Hyakutake, M.; Osaka, M.; Yoshizaki, T. *Polym. J.* 2008, 40, 566–571.
- (22) Otsu, T.; Watanabe, H.; Yang, J. -Z.; Yoshioka, M.; Matsumoto, A. Makromol. Chem., Macromol. Symp. 1992, 63, 87–104.

- (23) Matsumoto, A.; Umehara, S.; Watanabe, H.; Otsu, T. J. Polym. Sci., Part B: Polym. Phys. **1993**, 31, 527-535.
- (24) Omayu, A.; Ueno, T.; Matsumoto, A. Macromol. Chem. Phys. 2008, 209, 1503-1514.
- (25) Omayu, A.; Matsumoto, A. Polym. J. 2008, 40, 736-742.
- (26) Yukawa, S.; Omayu, A.; Matsumoto, A. Macromol. Chem. Phys. 2009, 210, 1776–1784.
- (27) Takeda, K.; Matsumoto, A. Macromol. Chem. Phys. 2010, 211, 782-790.
- (28) Doi, T.; Akimoto, A.; Matsumoto, A.; Otsu, T. J. Polym. Sci., Part A: Polym. Chem. **1996**, 34, 367–373.
- (29) Doi, T.; Akimoto, A.; Matsumoto, A.; Oki, Y.; Otsu, T. J. Polym. Sci., Part A: Polym. Chem. **1996**, 34, 2499–2505.
- (30) Doi, T.; Sugiura, Y.; Yukioka, S.; Akimoto, A. J. Appl. Polym. Sci. 1996, 61, 853–858.
- (31) Doi, T.; Ishikawa, N.; Akimoto, A. J. Appl. Polym. Sci. 1996, 61, 859–863.
- (32) Doi, T.; Yukioka, S.; Inoue, H.; Akimoto, A. J. Appl. Polym. Sci. 1997, 63, 925–929.
- (33) Alternating Copolymers; Cowie, J. M. G., Ed.; Plenum Press: New York, 1985.
- (34) Hirooka, M.; Yabuuchi, H.; Morita, S.; Kawasumi, S.; Nakaguchi, K. J. Polym. Sci., Part B: Polym. Lett. **196**7, 5, 47–55.
- (35) Barrales-Rienda, J. M.; Gonzalez de la Campa, J. I.; Ramos, G. J. Macromol. Sci.—Chem. 1977, A11, 267–286.
- (36) Olson, K. G.; Butler, G. B. Macromolecules 1984, 17, 2480-2486.
- (37) Jones, S. A.; Tirrell, D. A. Macromoelcules 1986, 19, 2080–2082.
- (38) Otsu, T.; Matsumoto, A.; Kubota, T. Polym. Int. 1991, 25, 179–184.
- (39) Wulff, G.; Krieger, S. Macromol. Chem. Phys. 1994, 195, 3665-3677.
- (40) Lange, R. F. M.; Meijer, E. W. Macromolecules 1995, 28, 782-783.
- (41) Omayu, A.; Matsumoto, A. Macromol. Chem. Phys. 2008, 209, 2312–2319.
- (42) Satoh, K.; Matsuda, M.; Nagai, K.; Kamigaito, M. J. Am. Chem. Soc. 2010, 132, 10003–10005.
- (43) Wang, Y.; Chen, Q.; Liang, H.; Lu, J. Polym. Int. 2007, 56, 1514–1520.
- (44) Yamamoto, D.; Matsumoto, A. Macromol. Chem. Phys. 2012, 213, 2479–2485.
- (45) Matsuda, M.; Satoh, K.; Nagai, K.; Kamigaito, M. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 1774–1785.
- (46) Sebastian, P.; Lutz, J.-F. J. Am. Chem. Soc. 2007, 129, 9542–9543.
- (47) Ida, S.; Terashima, T.; Ouchi, M.; Sawamoto, M. J. Am. Chem. Soc. 2009, 131, 10808–10809.
- (48) Lutz, J.-F. Polym. Chem. 2010, 1, 55-62.
- (49) Satoh, K.; Ozawa, S.; Mizutani, M.; Nagai, K.; Kamigaito, M. *Nat. Commun.* **2010**, *1*, 1–6.
- (50) Hibi, Y.; Ouchi, M.; Sawamoto, M. Angew. Chem., Int. Ed. 2011, 50, 7434–7437.
- (51) Lutz, J.-F.; Mirela, Z. Nat. Commun. 2012, 3, 2151/1-2151/8.
- (52) Badi, N.; Chan-Seng, D.; Lutz, J.-F. Macromol. Chem. Phys. 2013, 214, 135–142.
- (53) Klemm, E.; Schulze, T. Acta Polym. 1999, 50, 1-19.
- (54) Ito, H.; Ueda, M. Makromol. Chem., Macromol. Symp. 1992, 54/ 55, 551–560.
- (55) Iskander, G. M.; Ovenell, T. R.; Davis, T. P. Macromol. Chem. Phys. **1996**, 197, 3123–3133.
- (56) Ueda, M.; Mano, M.; Mori, H.; Ito, H. J. Polym. Sci., Part A: Polym. Chem. 1991, 29, 1779–1787.
- (57) Chino, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 5947–5950.
- (58) Mehta, N. B.; Phillips, A. P.; Lui, F. F.; Brooks, R. E. J. Org. Chem. 1960, 25, 1012–1015.
- (59) Tawney, P. O.; Snyder, R. H.; Conger, R. P.; Leibbrand, K. A.; Stiteler, C. H.; Williams, A. R. J. Org. Chem. **1961**, 26, 15–21.

(60) Yamada, B.; Itahashi, M.; Otsu, T. J. Polym. Sci., Part A: Polym. Chem. 1978, 16, 1719–1733.

(61) Fineman, M.; Ross, S. D. J. Polym. Sci. 1950, 5, 259-262.

(62) Kelen, T.; Tüdős, F. J. Macromol. Sci.—Chem. 1975, A9, 1–27. (63) Fukuda, T.; Kubo, K.; Ma, Y.-D. Prog. Polym. Sci. 1992, 17,

(5) Funda, 1., Kubb, K., Ma, 1.-D. *Frig. Folym. Sci.* 1992, 17, 875–916.

(64) Coote, M. L.; Davis, T. P. Prog. Polym. Sci. 1999, 24, 1217–1251.

(65) Sato, T.; Masaki, K.; Kondo, K.; Seno, M.; Tanaka, K. *Polym.* Bull. **1995**, 35, 345–350.

(66) Matsumoto, A.; Hiuke, R.; Otsu, T. J. Polym. Sci., Part A: Polym. Chem. 1997, 35, 1515–1525.

(67) Buchanan, G. W.; Selwyn, J.; Dawson, B. A. Can. J. Chem. 1979, 57, 3028–3033.