1:2-Sequence-Regulated Radical Copolymerization of Naturally Occurring Terpenes with Maleimide Derivatives in Fluorinated Alcohol

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ABSTRACT: Naturally occurring bulky terpenes, such as (+)- and (–)-limonene and (–)-*β*-pinene, were quantitatively copolymerized with maleimide (MI) derivatives (i.e., phenyl-, cyclohexyl-, ethyl-, and unsubstituted-MI) in $PhC(CF_3)_2OH$ solvent via selective 1:2-alternating propagation governed by the penultimate effect, which resulted in 1:2-sequence regulated polymers with relatively high glass transition temperatures and optical activities. Similar petroleum-derived bulky olefins possessing cyclohexenyl, cyclohexyl, or additional *α*-methyl substituents were copolymerized with phenylmaleimide via preferential 1:2-alternating propagation with a slightly lower selectivity. A further decrease in the bulkiness of nonpolar olefins increased the 1:1-alternating sequence. The copolymerization of limonene and acrylonitrile also proceeded approximately via 1:1-alternating propagation, in which the penultimate effect was less observable. Furthermore, when methylene chloride was used instead of fluorinated alcohol for the copolymerization of limonene and phenylmaleimide, the length of the sequence of MI units increased. Thus, in addition to the characteristic MI skeleton, the bulky and rather specific structure of either limonene or *β*-pinene induces 1:2-selective propagation via the penultimate effect, whereas the fluoroalcohol diminishes the homopropagation of MI via a hydrogen bonding interaction with the MI unit. RAFT copolymerization of limonene and various MI derivatives in $PhC(CF_3)_2OH$ successfully proceeded to give the end-to-end 1:2-sequence-regulated copolymer with a selective initiating sequence and predominant capping sequence using an appropriate RAFT agent. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1774–1785

KEYWORDS: bio-based polymer; copolymerization; limonene; monomer sequence control; pinene; radical polymerization; RAFT; renewable resources

INTRODUCTION Monomer sequence control in synthetic polymers is one of the most challenging topics in polymer chemistry, especially in the area of chain-growth polymerization.[1–5] Radical copolymerization allows the incorporation of nearly all types of vinyl compounds into copolymer products, whereas monomers react statistically in accordance with monomer reactivity ratios, which are determined by the electronic and steric factors of the substituents, producing statistical or "random" copolymers.[6,7] However, in some exceptional cases, a combination of monomers, the vinyl groups of which are electron-deficient and donating, alternating sequences can be obtained; this is particularly true when both monomers are either non- or hardly homopolymerizable. The former group includes 1,2-disubstituted monomers possessing electron-withdrawing groups, such as maleic anhydride,[8–12] maleimides,[13–22] fumarates,[23,24] and fumaronitrile,[25,26] whereas the latter group includes vinyl ethers,[27,28] vinyl sulfides,[29] and non-polar olefins.[30] In addition to the occurrence of such spontaneous alternating sequences governed by the inherent monomer reactivities, the use of Lewis acid additives or polar solvents can enhance the formation of alternating sequences. This process is the result of coordination of the Lewis acid or the solvent to the polar substituent of the former monomer or formation of a charge-transfer complex between these components, even when one or both of the monomers are homopolymerizable.[6,7,31–39] However, higher-ordered sequence control is generally difficult in chain-growth copolymerization, especially in the radical copolymerization of vinyl monomers.

Recently, we reported a selective 1:2 sequence-regulated radical copolymerization of (+)-*d*-limonene [(+)-Lim] and phenylmaleimide (PhMI) in a fluorinated alcohol,[40] which is an important result in the development of novel bio-based polymers from renewable resources. Additionally, this result offers unprecedented sequence control of polymers in chain-growth polymerization reactions. In particular, we showed not only the first quantitative polymerization of limonene, which is one of the most abundant naturally occurring terpenes and is obtained from the nonedible parts of plants such as lemon and orange peel[41–44] but also the highly

Additional Supporting Information may be found in the online version of this article.

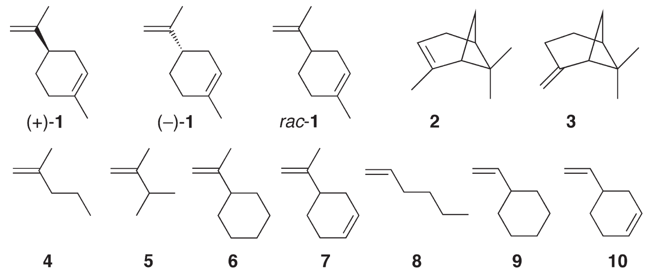


CHART 1 Various non-polar olefins used in this study.

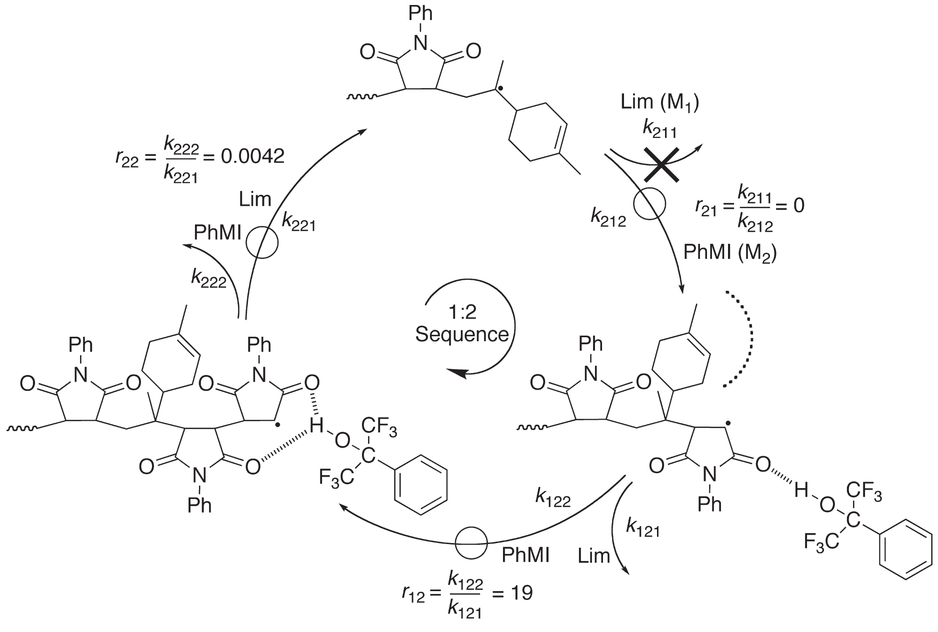
selective 1:2-copolymerization of a range of chain-growth polymerization reactions, including ionic and coordination polymerizations, which is unprecedented. Mechanistically, the copolymerization was well characterized by the penultimate model,[7] although the comonomer factors that induce such selective 1:2-copolymerization remain unknown; specifically, the comonomers used included non-polar olefins, such as (+)-Lim, and electron-deficient monomers such as PhMI. Additionally, from the perspective of the development of novel bio-based polymers,[45–48] other possibilities for combination should be investigated, including other major terpenes such as α- and β-pinenes (Pin)[19,36,37,49] and other maleimide (MI) derivatives.[50–52]

In this study, we investigated radical copolymerization to determine the effects of monomer structure on monomer reactivity or the resultant polymer sequences. Copolymerization reactions were conducted between various non-polar olefins (including terpenes such as (+)- and (–)-Lim and α- and β-Pin, in addition to petroleum-derived olefins (with both similar and dissimilar structures)) (Chart 1) and electron-deficient monomers [such as various MI derivatives and acrylonitrile (AN)]. The reactions were conducted in $PhC(CF_3)_2OH$. This approach analyzed copolymerization with the penultimate model with the further goal of revealing the mechanism underlying selective 1:2-copolymerization (Scheme 1). Additionally, the polymer properties and reversible addition-fragmentation chain-transfer (RAFT) copolymerization[53–56] were examined; in particular, combinations of Lim or β-Pin and MI derivatives were used to generate the desired 1:2-sequence-regulated structures.

RESULTS AND DISCUSSION

Radical Copolymerization of Various Non-Polar Olefins and Phenylmaleimide

A series of non-polar olefins was copolymerized with PhMI, which is a typical electron-deficient monomer. AIBN was used as the initiator, and the reactions were conducted in $PhC(CF_3)_2OH$ at 60 °C; the initial monomer feed ratio was 1:2 ($[\text{olefin}]_0/[\text{PhMI}]_0 = 1/2$) (Table 1). The nonpolar olefins studied included not only naturally occurring terpenes, such as (+)-Lim (**1**), (+)-α-Pin (**2**), and (–)-β-Pin (**3**) but also petroleum-derived isopropenyl (**4–7**) (α-methyl olefin) and vinyl compounds (**8–10**), each with a different pendent structure. As reported in our previous publication,[40] at the 1:2 feed ratio, both **1** and PhMI achieved nearly quantitative conversions to yield copolymers with an incorporation ratio of approximately 1:2 [entry 1 in Table 1 and Fig. S1(A) in Supporting Information]. Irrespective of the structures, all of the terpenes (**1–3**) were copolymerized with PhMI in $PhC(CF_3)_2OH$ to afford various copolymers [entries 1–3 in Table 1 and Supporting Information Fig. S1(A)]. In particular, (–)-β-Pin (**3**) was consumed at almost the same rate as PhMI to give the 1:2 copolymers, which suggests a 1:2-alternating copolymerization similar to that of **1** and PhMI, whereas the tri-substituted **2** exhibited a lower reactivity that resulted in a low terpene conversion (<30%). With respect to the



SCHEME 1 Schematics of 1:2 alternating copolymerization of *d*-limonene (**1**: M_1) and PhMI (M_2).

TABLE 1 Radical Copolymerization of Various Olefins (M_1) and PhMI (M_2)[a]

Entry	Olefin (M_1)	Conv. (%)[b] M_1/M_2	M_n[c]	M_w/M_n[c]	Incorp. (%)[d] M_1/M_2	r_{12}	$1/r_{12}$	r_{22}
1	(+)–**1**	88/92	9,700	2.16	34/66	19	0.053	0.0042
2	(+)–**2**	29/49	2,700	1.61	20/80	–	–	–
3	(–)–**3**	94/93	16,800	2.93	33/67	7.6	0.13	0.0011
4	**4**	100/78	33,500	4.15	40/60	2.7	0.37	0.0010
5	**5**	91/61	2,900	1.89	39/61	3.0	0.33	0.067
6	**6**	90/62	4,300	2.28	39/61	2.8	0.36	0.030
7	*rac*-**7**	83/85	6,600	2.72	30/70	30	0.033	0.25
8	**8**	96/83	17,500	2.27	34/66	2.1	0.48	0.11
9	**9**	71/63	3,400	1.67	35/65	1.9	0.53	0.21
10	*rac*-**10**	66/84	4,500	1.93	30/70	56	0.018	0.47

[a] Polymerization condition: $PhC(CF_3)_2OH$, 60 °C, $[M_1]_0 + [PhMI]_0 = 1{,}200$ mM, $[M_1]_0/[PhMI]_0 = 0.50$, $([M_1]_0+[PhMI]_0)/[AIBN]_0 = 150$.
[b] Determined by ^1H NMR analysis of residual monomers in the reaction mixture.[c] The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by size-exclusion chromatography.[d] Determined by ^1H NMR analysis of the isolated copolymers.

petroleum-derived olefins, the consumption rate of both monomers became more similar when the pendent groups of the olefin were bulkier. The monomers with less hindered linear aliphatic groups (**4** and **8**) were consumed faster than PhMI to reach 100% conversion of the olefin; additionally, this resulted in copolymers that contained higher olefin amounts, which was probably the result of conventional 1:1-alternating cross-propagation.[39] However, the bulkier olefin (**7**), which has a structure similar to that of **1**, led to a 1:2 consumption of the olefin and PhMI of which the conversions were 83 and 85%, respectively, and yielded copolymers with an approximate 1:2 incorporation. These results indicate that the bulkiness of the olefin pendent groups plays a significant role in inducing the 1:2-alternating copolymerization with PhMI. As the olefin bulkiness was increased, the incorporation ratio of olefin to PhMI gradually changed from 1:1 to 1:2 and reached a final value of nearly 1:2 for the bulky terpenes, **1** and **3**.

For further investigation of the copolymerizability of the unconjugated olefins (M_1) and PhMI (M_2), the respective monomer reactivity ratios were determined by copolymerization at various comonomer feed ratios ($[\text{olefin}]_0 + [\text{PhMI}]_0 = 1200$ mM, $[\text{AIBN}]_0 = 8$ mM in $PhC(CF_3)_2OH$ at 60 °C). Figure 1 shows copolymer composition curves in which the olefin incorporation ratios in the resulting copolymers were plotted as functions of the comonomer feed ratio. In particular, the curve should be constant at 0.33 for 1:2 copolymerization; however, for the conventional 1:1-alternating copolymerization, the curve should be 0.50, irrespective of the comonomer feed ratio. Incorporation of the less hindered olefins, such as **4**, **5**, **8**, and **9**, into the copolymers was apparently higher than 0.33, with values approaching 0.50 at the higher olefin feed ratios. This result also indicates that the bulkiness of the pendent groups is a significant factor for 1:2 propagation. As in the case of **1** and PhMI in the previous study,[40] for all of the copolymerization reactions, the monomer reactivity ratios were insufficiently described by the ordinary chain-end model, which uses r_1 and r_2. However, the monomer reactivity ratios were best fit by the penultimate model, which was used to calculate r_{12} and r_{22} based on the modified Kelen–Tüdõs or curve-fitting method, assuming that homopropagation of the unconjugated olefin does not occur and then the r_{11} and r_{21} are 0. The r_{12} and r_{22} values, which represent the relative reactivity of the $\sim\sim M_1M_2\cdot$ and $\sim\sim M_2M_2\cdot$ growing termini to M_2 in comparison to M_1, respectively, are significantly different, which indicates that the penultimate monomer unit (M_1 or M_2) significantly affects the reactivity of the terminal $\sim\sim M_2\cdot$ radical, as summarized in Table 1.

As previously reported,[40] the use of fluorinated alcohol as the solvent is critical for achieving the 1:2-alternating copolymerization. The copolymerization of **1** or **9** with PhMI was also performed in CH_2Cl_2 at varying comonomer feed ratios [open circles in Fig. 2(A,H)]. In both cases, incorporation of the olefins in the produced copolymers was lower than 0.33, even at a high olefin loading; additionally, the r_{22} values were significantly higher in CH_2Cl_2 [$r_{22} = 0.83$ (for **1**) and 1.3 (**9**)] than in $PhC(CF_3)_2OH$ [$r_{22} = 0.0042$ (for **1**) and 0.21 (**9**)]. These results indicate that $PhC(CF_3)_2OH$ increased the copolymerizability of these particular olefins in comparison to CH_2Cl_2, in which the lower copolymerizability of the olefins resulted in longer homopolymerizable MI sequences (Scheme 2; Path C). As reported previously,[40] the higher copolymerizability of non-polar olefins in $PhC(CF_3)_2OH$ likely can be attributed to hydrogen bonding interactions of $PhC(CF_3)_2OH$ with the carbonyl groups of the PhMI units, which enhances the cross-propagation to the electron-donating unconjugated olefins.

For all copolymerizations in $PhC(CF_3)_2OH$, the inverse of r_{12} ($1/r_{12}$) and r_{22} values were less than 1.0. These results suggest that $\sim\sim M_1M_2\cdot$ apparently favors M_2 in the formation of

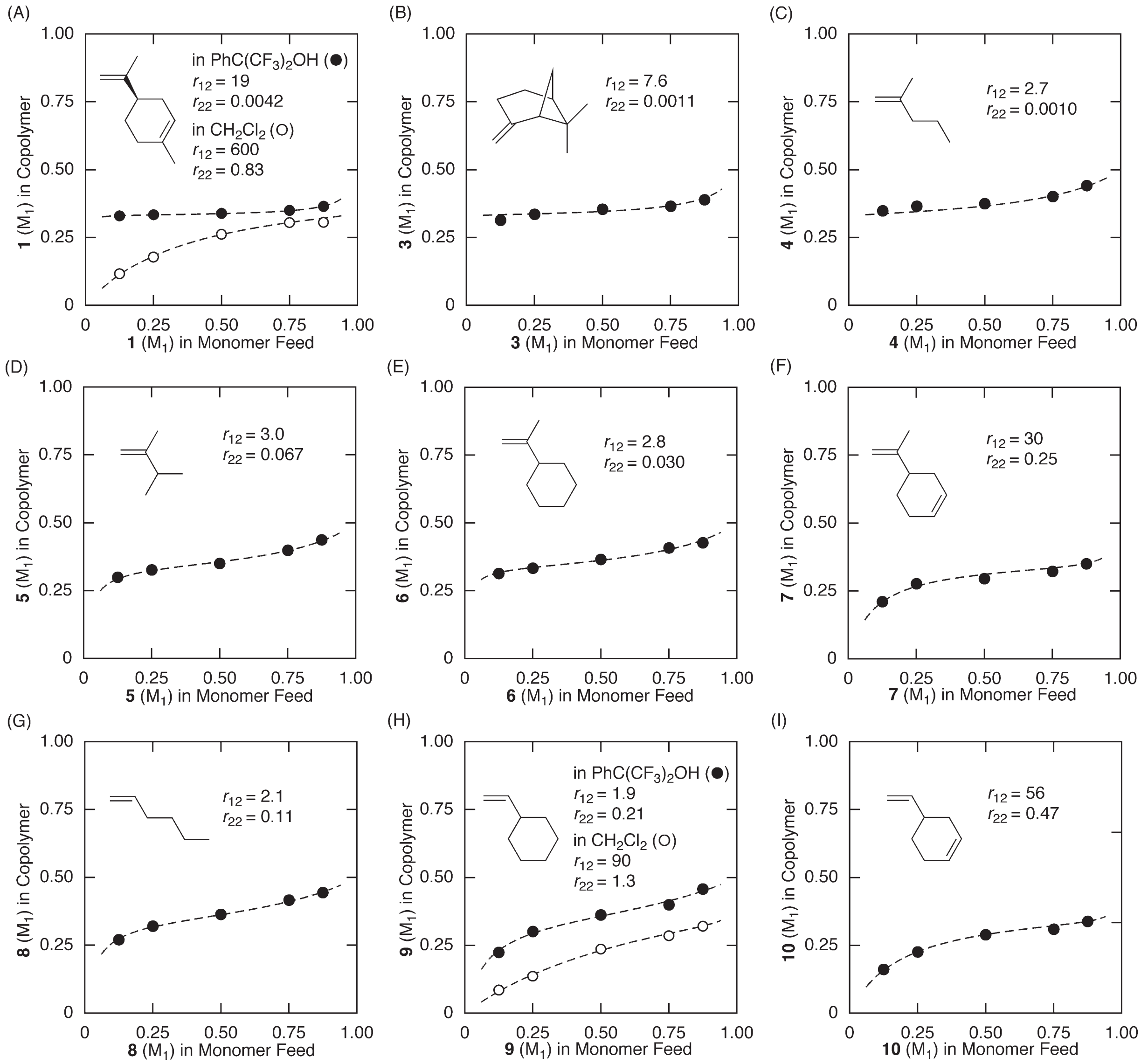


FIGURE 1 Copolymer composition curves for the copolymerization of various olefins and PhMI in $PhC(CF_3)_2OH$ (●) and CH_2Cl_2 (○) at 60 °C; $[\text{olefin}]_0 + [\text{PhMI}]_0 = 1200$ mM, $[\text{olefin}]_0/[\text{PhMI}]_0 = 1/7, 1/3, 1/1, 3/1, 7/1$, $[\text{AIBN}]_0 = 8.0$ mM. The dotted lines were fitted by the modified Kelen–Tüdõs method (for **1**, **3**, **5**, **6**, **8**, and **9**) or the curve fitting method (for **4**, **7**, and **10**), assuming that the values of r_{11} and r_{21} are 0.

repeating MI sequences, irrespective of the penultimate olefin structure. In contrast, the repeating $\sim\sim M_2M_2\cdot$ dominantly adds to the electron-rich olefin, M_1, as in the conventional 1:1 alternating copolymerization (Scheme 2). Among the various olefins, the naturally occurring Lim and β-Pin (**1** and **3**) gave particularly low $1/r_{12}$ and r_{22} values, which resulted in the selective 1:2-alternating propagation (Scheme 2; Path B). This is likely because the incorporated structure of **3** after the ring opening is quite similar to that of **1** in terms of bulkiness and residual C=C bonds, as shown in Scheme 3. The slightly higher $1/r_{12}$ value for **3** (0.13) relative to **1** (0.053) likely resulted from the higher reactivity of the strained bicyclic monomer, **3**.

For the other petrochemical-derived olefins, the $1/r_{12}$ values were lower than 1.0 but were not low enough to produce the selective 1:2 copolymers. The $1/r_{12}$ values of the isopropenyl compounds (**4**–**6**) were lower than those of the corresponding vinyl compounds (**8** and **9**), despite the higher electron density of the unsaturated C=C bonds, which originated from the α-methyl substituent. This also indicates that the steric hindrance results in a $\sim\sim M_1M_2M_2$ sequence rather than the conventional $\sim\sim M_1M_2M_1$ alternating sequence (Scheme 2; Path A). In addition to the bulkiness of the pendent group, the cyclohexenyl group was roughly effective to provide selective 1:2 cross-propagation. The $1/r_{12}$ values of **7** and **10** were significantly lower than those of the saturated cyclohexyl analogues (**6** and **9**), respectively, although the r_{22} values were slightly increased. Thus, not only the use of fluorinated alcohol as the solvent but also the steric hindrance and unsaturated pendent ring structure of the olefins was important for achieving unprecedented 1:2-alternating copolymerizability.

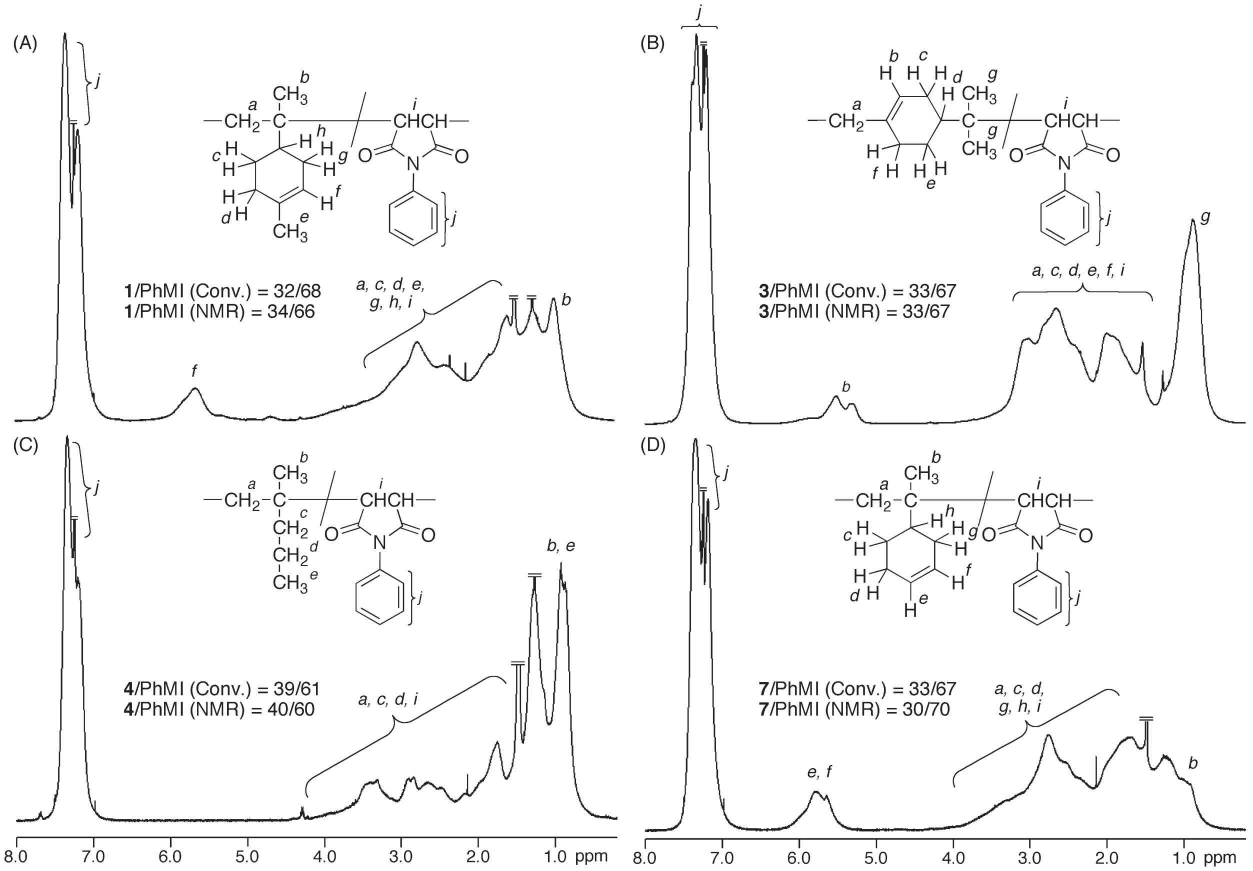
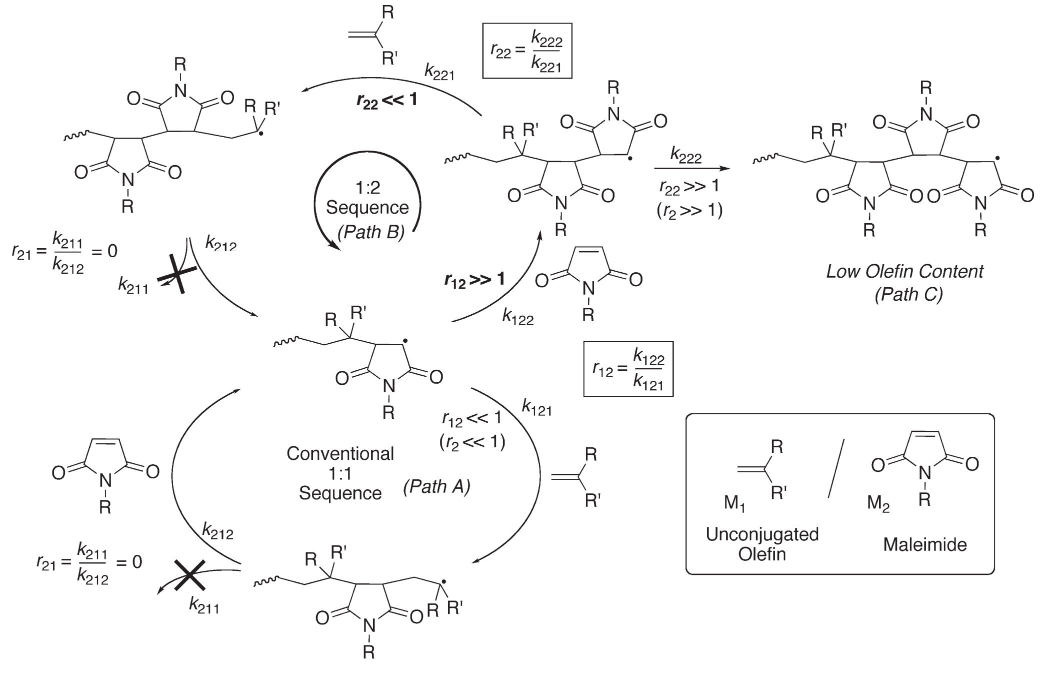
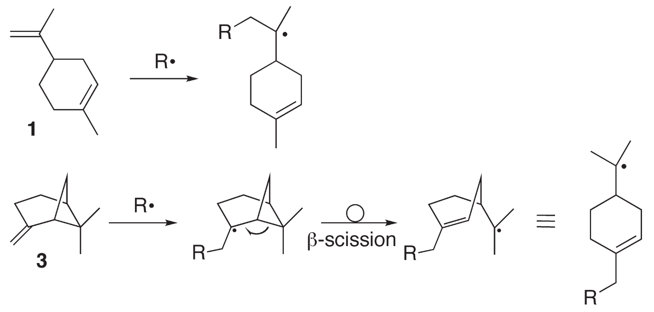


FIGURE 2 ^{1}H NMR spectra of (CDCl$_3$, 55 °C) of the copolymers of **1** (A), **3** (B), **4** (C), and **7** (D) with PhMI obtained in PhC(CF$_3$)$_2$OH at 60 °C; [olefin]$_0$/[PhMI]$_0$ = 400/800 mM; [AIBN]$_0$ = 8.0 mM.



SCHEME 2 Mechanism for radical copolymerization of various unconjugated olefins and MI derivatives in various solvents.

The structures of the copolymers as obtained from the various unconjugated olefins and PhMI in PhC(CF$_3$)$_2$OH were analyzed by ^{1}H NMR spectroscopy (Fig. 2 and Fig. S2 in Supporting Information). Figure 2 shows the ^{1}H NMR spectra of poly(**1**-*co*-PhMI), poly(**3**-*co*-PhMI), poly(**4**-*co*-PhMI), and poly(**7**-*co*-PhMI). In all spectra, the large signals were



SCHEME 3 Propagation of limonene (**1**) and β-pinene (**3**) during radical copolymerization.

assigned to the protons in the main chains of the olefins/PhMI copolymers; the methine (*i*) and phenyl (*j*) protons in the PhMI units absorbed at 1.2−4.5 and 6.5–7.6 ppm, respectively, whereas the residual olefin (*f* for **1**, *b* for **3** and *e*, *f* for **7**), aliphatic (*a*, *c-e*, *g*, and *h* for **1**, *a*, *c–f* for **3**, *a*, *c*, and *d* for **4**, and *a*, *c*, *d*, *g*, and *h* for **7**), and methyl (*b* for **1**, *g* for **3**, *b, e* for **4**, and *b* for **7**) protons in the olefin units absorbed at 5.0–6.2, 1.2–4.5, and 0.5–1.2 ppm, respectively. The copolymer compositions, that is, the PhMI/olefin ratios, were calculated from the peak intensities of the phenyl (*j* for PhMI), the residual olefin (*f* for **1**, *b* for **3**, and *e*, *f* for **7**), and aliphatic and methyl protons (*a–e* for **4**, and *a, c, d, g*, and *h* for **7**), which agreed well with the values calculated from the initial charge ratio and conversions of the two monomers. Thus, all of the consumed monomers were incorporated into the copolymers. These ^{1}H NMR analyses further confirmed the 1:2 alternating copolymerizations of **1** or **3** and PhMI.

1:2 Radical Copolymerization of Terpenes and Various MI Derivatives

Optically active Lim (**1**) can be found in nature as (+)-, (−)-, and racemic forms, although (+)-**1** occurs most abundantly in citrus peel, leaf oil, and camphor oil.[43,44] The effect of the stereochemistry of **1** also was examined by the copolymerization of (+)-, (−)-, and *rac*-**1** with PhMI (Fig. 3 and Table S1 in Supporting Information). Irrespective of differences in monomer stereochemistry, copolymerization proceeded in the 1:2-alternating fashion. Copolymers obtained from chiral (+)- and (−)-**1** exhibited mirror images of circular dichroism (CD) and specific optical rotation, whereas no optical activity was observed in the copolymer of *rac*-**1**. Additionally, the copolymer obtained from (−)-**3** exhibited characteristic CD and a specific optical rotation. These results indicate that the configuration of the chiral centers in (+)-**1**, (−)-**1**, and (−)-**3** was retained during the copolymerization. The thermal properties of the obtained copolymers were evaluated by differential scanning calorimetry (DSC) under a nitrogen atmosphere. All of the obtained copolymers also exhibited relatively high glass-transition temperatures (T_gs) because of the rigid MI and the bulky terpene backbone.[50]

The effects of the MI unit pendent groups on 1:2-alternating copolymerization and polymer properties were also investigated using various MI derivatives such as cyclohexylmaleimide (CyMI), ethylmaleimide (EtMI), and unsubstituted MI rather than PhMI. The MI derivatives also were copolymerized with Lim (**1**) or β-Pin (**3**) ($[\text{terpene}]_0/[\text{MI}]_0 = 1/2$) using AIBN as the initiator in $PhC(CF_3)_2OH$ at 60 °C. Similar to PhMI, the copolymerization of these maleimides proceeded smoothly irrespective of their structure: both monomers were simultaneously and quantitatively consumed at the same rate with a consumption ratio of approximately 1:2 (Fig. S3 in Supporting Information). Table 2 summarizes the copolymerizations with various MI derivatives as well as AN, which is an electron-deficient vinyl monomer that is often used in conventional 1:1-alternating copolymerization with non-polar olefins such as propylene.[31,32] Irrespective of the substituents, the monomer compositions in the copolymers obtained from the MI

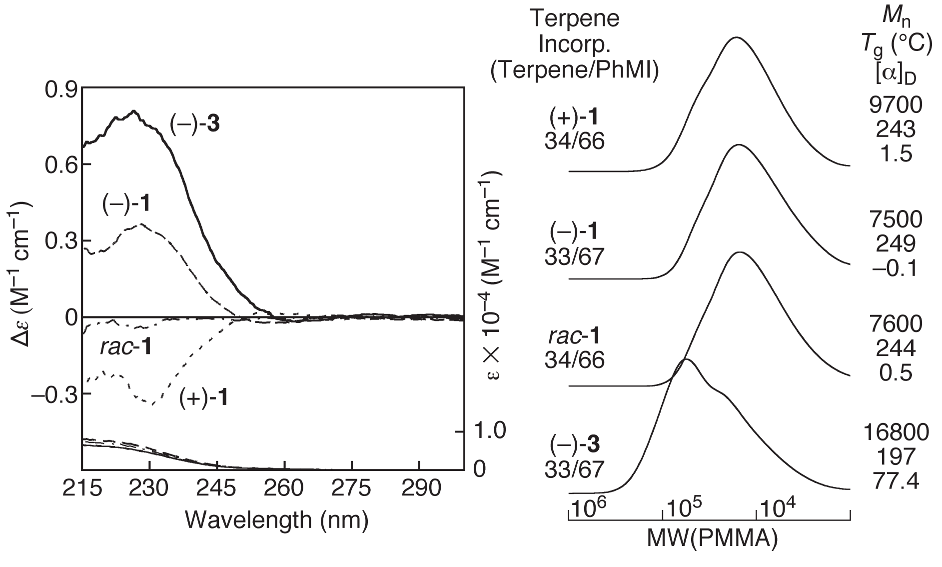


FIGURE 3 CD spectra (A) and SEC curves (B) of poly(terpene-*co*-PhMI) obtained in the radical copolymerization of chiral or racemic terpene and PhMI in $PhC(CF_3)_2OH$ at 60 °C; $[\text{terpene}]_0/[\text{PhMI}]_0 = 400/800$ mM, $[\text{AIBN}]_0 = 8.0$ mM.

TABLE 2 Radical Copolymerization of Terpenes (M_1) and Polar Monomers (M_2)[a]

Entry	M_1	M_2	Conv. (%)[b] M_1/M_2	M_n[c]	M_w/M_n[c]	Incorp. (%)[d] M_1/M_2	T_g (°C)[e]
1	**1**	AN	34/39	4,300	1.99	29/71	–
2		PhMI	88/92	9,700	2.16	34/66	243
3		CyMI	85/88	8,700	1.96	33/67	226
4		EtMI	77/81	7,000	1.99	35/65	182
5		MI	85/86	10,700	2.79	39/61	275
6	**3**	PhMI	94/93	16,800	2.93	33/67	197
7		CyMI	91/92	15,800	2.57	34/66	181
8		EtMI	92/93	12,600	3.21	35/65	152
9		MI	89/76	25,700	2.64	35/65	–

[a] Polymerization condition: $PhC(CF_3)_2OH$, 60 °C, $[M_1]_0 + [M_2]_0 = 1{,}200$ mM (for PhMI) or 3,000 mM (for AN), $[M_1]_0/[M_2]_0 = 0.50$, $([M_1]_0 + [M_2]_0)/[AIBN]_0 = 150$.

[b] Determined by ^1H NMR analysis of residual monomers in the reaction mixture.

[c] The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by size-exclusion chromatography.

[d] Determined by ^1H NMR analysis of the isolated copolymers.[e] Evaluated by a differential scanning calorimetry.

derivatives were nearly 1:2, which agrees with the values calculated from the initial charge ratio and conversions. In contrast, AN afforded copolymers with smaller amounts of terpene units. Additionally, all maleimides and Lim or β-Pin afforded copolymers with relatively high T_g due to the rigid backbone chains although it slightly decreased in the order of R = Ph > Cy > Et. All these copolymers of maleimides and Lim or β-Pin in Table 2 showed only one thermal transitions (T_g) and no decompositions between 40 and 350 °C.

The 1:2-alternating copolymerization of the maleimides (M_2) with **1** (M_1) was further addressed in terms of the monomer reactivity ratio determined for copolymerization at varying comonomer feed ratios in $PhC(CF_3)_2OH$ at 60 °C: $[\mathbf{1}]_0 + [MI]_0 = 1200$ mM, $[AIBN]_0 = 8.0$ mM (Fig. 4). The copolymer composition curves for the MI copolymerization show a characteristic plateau in which the content of **1** (M_1) in the obtained copolymers was constant at approximately one-third (0.33) irrespective of the feed ratio and the MI structure. Similar to PhMI, by using the penultimate model, r_{12} and r_{22} were calculated as 21 and 0.0059, respectively, for CyMI and as 17 and 0.029, respectively, for EtMI, based on the modified Kelen–Tüdõs method. These results again indicate that the penultimate model governs the selective 1:2-alternating copolymerizations and that the side groups of the MI derivatives did not significantly affect the 1:2 selectivity.

However, the r_{12} and r_{22} values for the copolymerization of **1** and AN (M_2) were 0.72 and 0.61, respectively; these values are both less than 1.0 and are almost the same, which suggests that the reactivity of the terminal AN radical is nearly independent of the penultimate monomer unit and that no 1:2 selectivity occurred for AN.[39] Thus, the MI structure was also crucial for the 1:2-alternating copolymerization of terpene, whereas the effect of the MI derivative pendent group on selectivity was small.

RAFT Copolymerization of Limonene and MI Derivatives

The copolymerization of **1** and PhMI in fluoroalcohol produced not only 1:2-alternating copolymers with quantitative

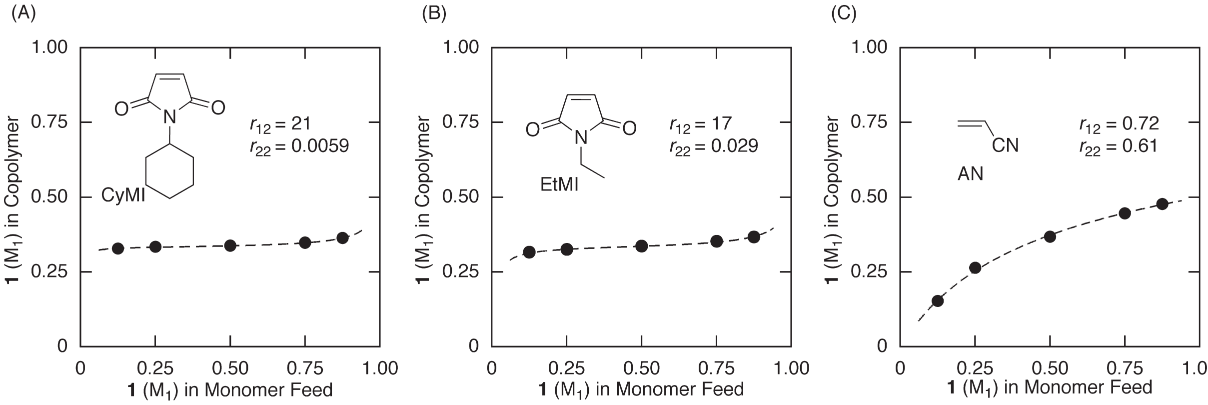


FIGURE 4 Copolymer composition curves for the copolymerization of **1** and CyMI (A), EtMI (B), and AN (C) in $PhC(CF_3)_2OH$ at 60 °C; $[M_{total}]_0 = 1200$ mM (for CyMI and EtMI), $[M_{total}]_0 = 3000$ mM (for AN), $[\mathbf{1}]_0/([MI]_0$ or $[AN]_0) = 1/7, 1/3, 1/1, 3/1, 7/1$, $[AIBN]_0 = 8.0$ mM (for CyMI and EtMI), 20 mM (for AN). The dotted lines were fitted by the modified Kelen–Tüdõs method, assuming that the values of r_{11} and r_{21} are 0.

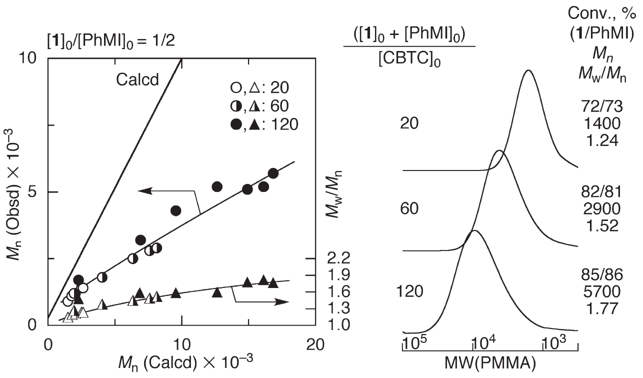


FIGURE 5 M_n, M_w/M_n, and SEC curves of poly(**1**-*co*-PhMI) obtained with varying the $[M_{total}]_0/[CBTC]_0$ ratio in $PhC(CF_3)_2OH$ at 60 °C; $[\mathbf{1}]_0/[PhMI]_0 = 1/2$, $[M_{total}]_0 = [\mathbf{1}]_0 + [PhMI]_0 = 1200$ mM, $[M_{total}]_0/[AIBN]_0 = 240$, $[M_{total}]_0/[CBTC]_0 = 20$, 60, or 120. The diagonal line indicates the calculated M_n assuming the formation of one living polymer per one CBTC molecule.

conversions of both monomers but also a regulated sequence from the initiating end to the growing end when coupled with an appropriate RAFT agent, as reported previously.[40] For simultaneous control of molecular weight and monomer sequence during copolymerization of **1** and the various maleimides in $PhC(CF_3)_2OH$, RAFT copolymerization was investigated with *S*-cumyl *S′*-buthyl trithiocarbonate (CBTC)[57] as the RAFT agent by varying the $([\mathbf{1}]_0 + [PhMI]_0)/[CBTC]_0$ ratio from 20 to 120. The monomer feed ratio of **1** and PhMI was constant at 1:2.

The copolymerization proceeded smoothly irrespective of the monomer-to-RAFT agent ratios, and the two monomers were simultaneously consumed at approximately the same rate, as observed in the above free radical copolymerizations without RAFT agents. Figure 5 shows the M_n, M_w/M_n, and size-exclusion chromatography (SEC) curves of the resultant copolymers obtained from the RAFT copolymerization of **1** and PhMI by varying the monomer-to-RAFT agent ratio from 20 to 120. The M_n values of the obtained copolymers (the circles in Fig. 5) were measured by SEC, based on the standard poly(methyl methacrylate) (PMMA) calibration, and were found to increase in direct proportion to the monomer conversion. However, the M_n values were lower than the calculated values, which were generated by assuming that one CBTC molecule generates one living polymer chain, mainly because of the difference in hydrodynamic volume with respect to the PMMA standards. The absolute M_n value was then determined using multiangle laser light scattering (MALLS), which yielded a value of $M_n(\text{MALLS}) = 8400$ that was similar to the value calculated from the monomer-to-RAFT agent ratio and the monomer conversion, $M_n(\text{calcd}) = 9500$. Although the molecular weight distribution (MWD) became broader as the concentration of the RAFT agent was decreased, a copolymer with a relatively high molecular weight was obtained at a high $([\mathbf{1}]_0 + [PhMI]_0)/[CBTC]_0$ ratio. Thus, the molecular weight of the 1:2 sequence-regulated copolymer of limonene and PhMI can be controlled using the RAFT system.

RAFT copolymerizations also were conducted for other combinations with **1** and various MI derivatives, CyMI and EtMI (Fig. 6). The M_n of the obtained copolymers (the circles in Fig. 6), which were measured by SEC on PMMA standards, was found to increase similarly in direct proportion to the monomer conversion, although the obtained values were lower than the calculated values, as in the case of **1** and PhMI. The copolymer of **1** and CyMI obtained with CBTC was analyzed by ^1H NMR spectroscopy (Fig. S6 in Supporting Information). In addition to the characteristic main-chain signals of poly(**1**-*co*-CyMI), the polymer gave small signals of cumyl protons at the α-end that originated from CBTC at 7.0–7.5 ppm. The M_n values calculated from those peaks were in good agreement with the calculated values irrespective of the monomer conversion (the open squares in Fig. 6). Thus, the controlled radical copolymerization of maleimide derivatives was achieved by using CBTC, which served as the RAFT agent in the formation of one polymer chain.

The copolymers of **1** and various MI derivatives obtained with CBTC were further analyzed by matrix-assisted laser-desorption-ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) in the presence of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix and CF_3CO_2Na as the ionizing agent (Fig. 7). The spectra show a series of the selective —M—M—L— sequence (M: MI derivatives, L: limonene) in which each peak is separated by intervals of 173 Da for PhMI, 179 Da for CyMI, 125 Da for EtMI, and 136 Da for **1**. Although a few series of peaks that did not have the ideal structure were observed because of the loss of the chain-end S [S: S—C(=S)—SBu] group, which was derived from the RAFT agent during the ionization process, the molecular weights of each individual peak are in good agreement with the calculated values: that is, the molecular weight of both monomers plus the sodium ion from the salt for the MS analysis.

Additionally, irrespective of the substituents in the MI units, the highest series of peaks are separated by the total masses of one limonene and two MI units, which can be assigned to a

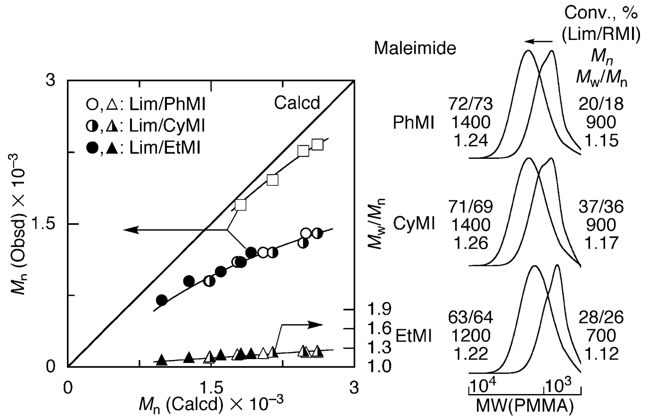
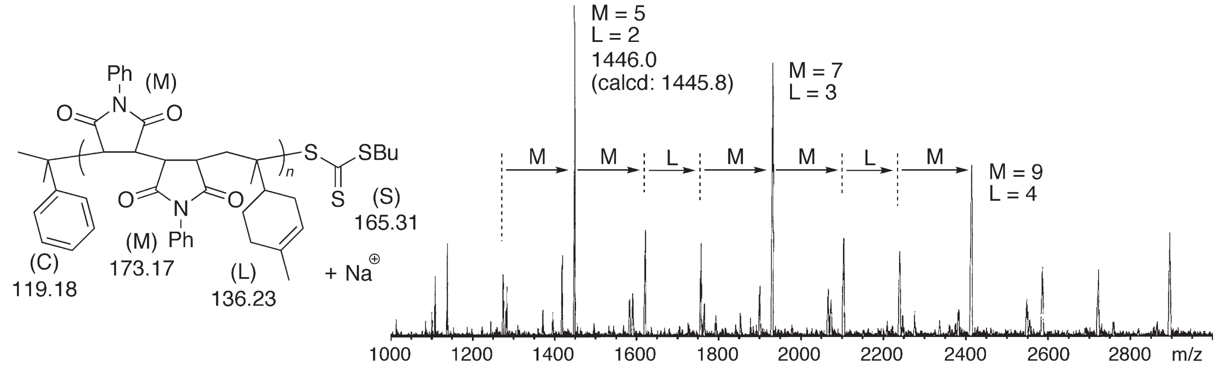
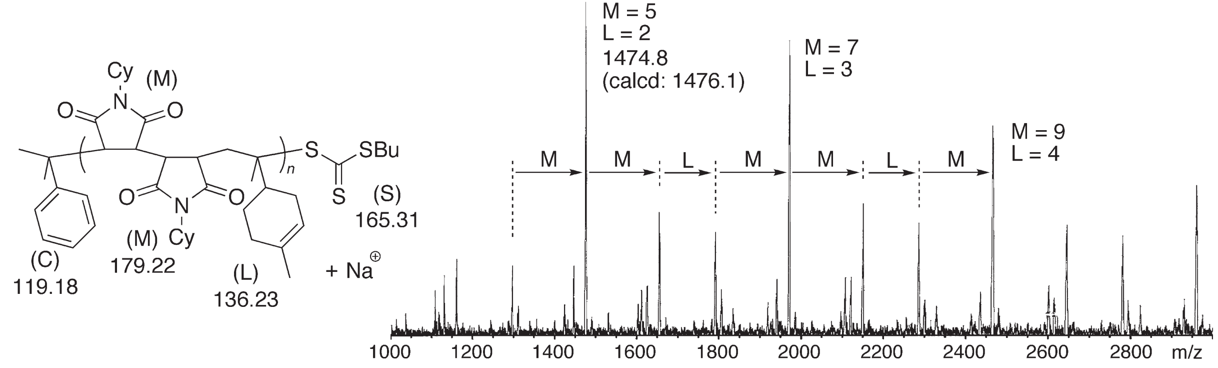


FIGURE 6 M_n, M_w/M_n, and SEC curves of copolymer obtained in the radical copolymerization of **1** and various MI in $PhC(CF_3)_2OH$ at 60 °C; $[\mathbf{1}]_0/[MI]_0 = 1/2$, $[\mathbf{1}]_0 + [MI]_0 = 1200$ mM, $[CBTC]_0 = 60$ mM, $[AIBN]_0 = 5.0$ mM. The open square indicate the molecular weights of poly(**1**-*co*-CyMI) calculated by ^1H NMR from the α-end peaks.

(A) Poly(Lim-*co*-PhMI)



(B) Poly(Lim-*co*-CyMI)



(C) Poly(Lim-*co*-EtMI)

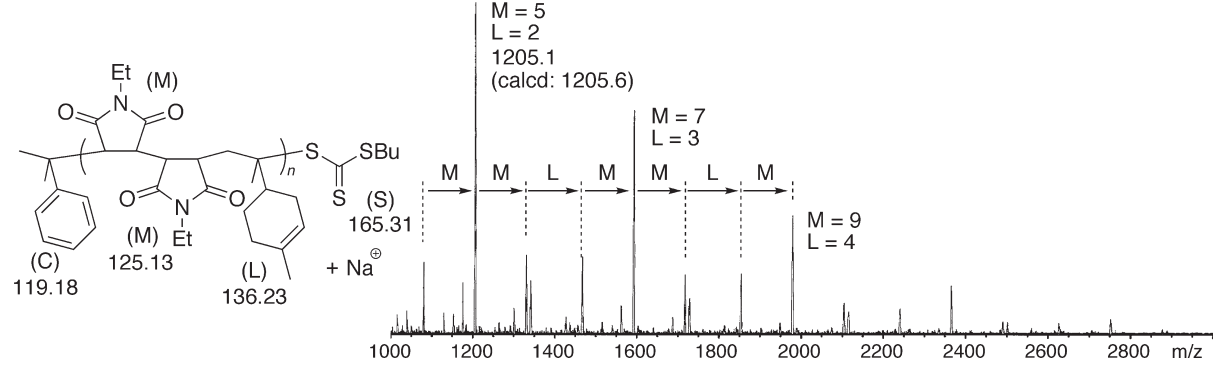


FIGURE 7 MALDI-TOF-MS spectra of poly(**1**-*co*-MI) in $PhC(CF_3)_2OH$ at 60 °C; $[\mathbf{1}]_0/[MI]_0 = 400/800$ mM, $[CBTC]_0 = 60$ mM, $[AIBN]_0 = 5.0$ mM.

series of end-to-end sequenced copolymers [C—(M—M—L)$_n$—M—S] (C: cumyl group; S: trithiocarbonyl group) starting with the C—M—M—L—unit at the initiating terminal and the —M—M—L—M—S unit at the capping terminal in addition to the —M—M—L— main-chain repeating sequence. These results again indicate that the copolymerization of limonene and various MI derivatives produces copolymers with 1:2-alternating sequences irrespective of the MI structure.

CONCLUSIONS

In conclusion, this study revealed the effects of the structure of various unconjugated olefins and MI derivatives on 1:2-alternating copolymerization in $PhC(CF_3)_2OH$. The bulky and specific structures originating from naturally occurring limonene and β-pinene proved to be crucial factors for inducing selective 1:2-alternating copolymerization; hydrogen-bonding interactions of the $PhC(CF_3)_2OH$ solvent with the MI units also proved to be important. Thus, these various factors work synergistically to produce an unprecedented 1:2-alternating copolymerization of naturally occurring bulky terpenes and MI derivatives. A special function can be imparted to the novel bio-based sequence-regulated copolymers by functionalizing the residual double bonds in the terpene units or by introducing functional groups in the MI units.

EXPERIMENTAL

Materials

α,α-Azobisisobutyronitrile (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. *N*-Phenylmaleimide (PhMI) (Aldrich, 97%), *N*-CyMI (Aldrich, 97%), *N*-EtMI (Tokyo

Kasei, >98%) and unsubstituted MI (Aldrich, 97%) were purified by recrystallization from acetone, toluene, or methanol. (+)-*d*-Limonene (**(+)-1**) (Aldrich, 97%), (–)-*l*-limonene (**(–)-1**) (Aldrich, 96%), (±)-limonene (***rac*-1**) (Tokyo Kasei, >95%), (+)-α-pinene (**2**) (Aldrich, ≥99%), (–)-β-pinene (**3**) (Aldrich, ≥99%), 2-methyl-1-pentene (**4**) (Tokyo Kasei, 98%), 2,3-dimethyl-1-butene (**5**) (Aldrich, 97%), 1-hexene (**8**) (Tokyo Kasei, >95%), vinylcyclohexane (**9**) (Aldrich, ≥99%), 4-vinyl-1-cyclohexene (**10**) (Aldrich, 97%), $PhC(CF_3)_2OH$ (Wako, >99%), and AN (Aldrich, ≥99%) were distilled from calcium hydride under reduced pressure before use. CBTC was synthesized according to the literature.[40]

Synthesis of Isopropenylcyclohexane (6)

The monomer syntheses were carried out by a syringe technique under a dry argon atmosphere in an oven-dried glass tube equipped with three-way stopcocks. Isopropenylcyclohexane (**6**) was synthesized by a Wittig reaction as follows. Methyltriphenylphosphonium iodide (133.4 g, 0.33 mol) was dispersed in dry THF (1200 mL). In to the suspension, *n*BuLi (204 mL of 1.62 M solution in *n*-hexane) was added at 0 °C. After stirring at 0 °C for 30 min, the solution was cooled to −78 °C, and then cyclohexylmethylketone (0.33 mol in THF, 150 mL) was added dropwise. After stirring at ambient temperature for additional 20 h, the aqueous solution of NH_4Cl was added. The aqueous phase was extracted with Et_2O and then all the organic phase was corrected. The crude product was purified by repeating fractional distillation to give **6** (10.9 g, 0.088 mol; yield = 27%, purity >99%). ^1H NMR ($CDCl_3$, r.t.): δ 1.01–1.34 (m, 5H), 1.65–1.89 (m, 6H), 1.70 (m, 3H, $CH_2{=}C{-}CH_3$), 4.64 (m, 1H, *cis*—$CH_2{=}C{-}CH_3$), 4.64 (m, 1H, *trans*-$CH_2{=}C{-}CH_3$).

Synthesis of 4-Isopropenylcyclohexene (7)

4-Isopropenylcyclohexene (**7**) was synthesized by two-step reactions. First, the corresponding ketone was synthesized from 3-cyclohexenecarboxylic acid, and then **7** was obtained by Wittig reaction of the ketone. MeLi (140 mL of 1.07 M solution in *n*-hexane) was added dropwise to a solution of 3-cyclohexenecarboxylic acid (37 mL, 0.317 mol) in dry Et_2O at 0 °C under stirring. After 14 h at ambient temperature, the mixture was added dropwise to HCl aqueous solution. The mixture was neutralized and washed with the aqueous solution of $NaHCO_3$ and then NaCl. The crude product was purified by fractional distillation to give 4-cyclohexenylmethylketone (28.9 g, 0.23 mol; yield = 73%, purity >98%). *n*BuLi (84 mL of 2.62 M solution in *n*-hexane) was added dropwise to a suspension of methyltriphenylphosphonium iodide (89 g, 0.22 mol) in dry THF at 0 °C. After stirring at 0 °C for 30 min, a solution of 3-cyclohexenylmethylketone (0.33 mol in THF, 150 mL) was added dropwise at −78 °C. After stirring at ambient temperature for 20 h, the aqueous solution of NH_4Cl was added at 0 °C. The aqueous phase was extracted with Et_2O and then all the organic phase were corrected. The crude product was purified by repeating fractional distillation to give **7** (10.9 g, 0.089 mol; yield = 41%, purity >98%). ^1H NMR ($CDCl_3$, r.t.): δ 1.41–2.63 (m, 7H), 1.70 (m, 3H, $CH_2{=}C{-}CH_3$), 4.71 (m, 1H, *cis*-$CH_2{=}C{-}CH_3$), 4.72 (m, 1H, *trans*-$CH_2{=}C{-}CH_3$), 5.69 (m, 2H, $-CH_2-CH{=}CH-CH_2-$).

Free Radical 1:2 Alternating Copolymerization

Copolymerization was carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example for Lim and PhMI copolymerization with AIBN in $PhC(CF_3)_2OH$ is given below. In a 50 mL round-bottomed flask were placed $PhC(CF_3)_2OH$ (0.85 mL), $PhC(CF_3)_2OH$ solution of PhMI (3.0 mL of 1200 mM solution, 3.6 mmol), Lim (0.29 mL, 1.8 mmol), and $PhC(CF_3)_2OH$ solution of AIBN (0.36 mL, 0.15 mmol) at room temperature. The total volume of the reaction mixture was 4.5 mL. 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 nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^1H NMR with $PhC(CF_3)_2OH$ as an internal standard (106 h, 88% for Limonene and 92% for PhMI, respectively). The quenched reaction solutions were evaporated to dry to give poly(Lim-*co*-PhMI).

RAFT 1:2 Alternating Copolymerization

RAFT copolymerization was carried out by the syringe technique under dry nitrogen in sealed glass tube. A typical example for (+)-Lim (**1**) and PhMI copolymerization with CBTC/AIBN in $PhC(CF_3)_2OH$ is given below. In a 50 mL round-bottomed flask were placed $PhC(CF_3)_2OH$ (1.2 mL), $PhC(CF_3)_2OH$ solution of PhMI (5.0 mL of 1200 mM solution, 6.0 mmol), **1** (0.49 mL, 3.0 mmol), and $PhC(CF_3)_2OH$ solution of AIBN (0.25 mL, 0.15 mmol) and CBTC (0.56 mL of 134 mM solution in $PhC(CF_3)_2OH$, 0.075 mmol) at room temperature. The total volume of the reaction mixture was 7.5 mL. Immediately after mixing, aliquots (1.0 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by the cooling of the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^1H NMR with $PhC(CF_3)_2OH$ as an internal standard (108 h, 85% for **1** and 86% for PhMI, respectively). The quenched reaction solutions were evaporated to dry to give poly(**1**-*co*-PhMI).

Measurements

Monomer conversion was determined from the concentration of residual monomer measured by ^1H NMR spectroscopy with reaction solvent as an internal standard. ^1H NMR spectra for monomer conversion were recorded in $CDCl_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300 MHz, and ^1H NMR spectra for the product copolymer were recorded in $CDCl_3$ at a 55 ° C DMSO-d_6 at 80 °C, or acetone-d_6 at 50 °C on a JEOL ECS-400 spectrometer, operating at 400 MHz. MALDI-TOF-MS spectra were measured on a

Shimazu 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 the MWD (M_w/M_n) of the product copolymers were determined by SEC in THF at 40 °C on two polystyrene gel columns [Shodex KF-805 L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 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 eight standard poly(MMA) samples (Shodex; M_p = 202–1950000; M_w/M_n = 1.02–1.09). The T_g (midpoint of the transition) of the polymers were recorded on Q200 DSC (TA Instruments). Certified indium and sapphire were used for temperature and heat flow calibration. Samples were first heated to 300 at 10 °C/min., equilibrated at this temperature for 5 min, and cooled to 40 at 10 °C/min. After being held at this temperature for 5 min., the sample was then reheated to 350 at 5 °C/min. All T_g values were obtained from the second scan, after removing the thermal history. Absorption and CD spectra were measured in a 1.0-mm quartz cell on a JASCO V-560 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The polymer concentration was calculated on the basis of the monomer units and was 4 mg/mL. Optical rotation was measured in a 10-cm quartz cell on a JASCO P-2300 polarimeter.

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