Radical Copolymerization of *N*-Phenylmaleimide and Diene Monomers in Competition with Diels–Alder Reaction

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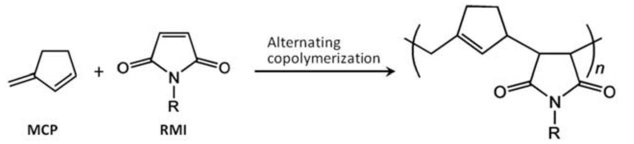
ABSTRACT: Radical copolymerization of *N*-phenylmaleimide (PhMI) is carried out with various diene monomers including naturally occurring compounds and the copolymers are efficiently produced by the suppression of Diels–Alder reaction as the competitive side reaction. Diene monomers with an exomethylene moiety and a fixed s-trans diene structure, such as 3-methylenecyclopentene and 4-isopropyl-1-methyl-3-methylenecyclohexene, exhibit high copolymerization reactivity to produce a high-molecular-weight copolymer in a high yield. The copolymerization of sterically hindered noncyclic diene monomers, such as 2,4-dimethyl-1,3-pentadiene and 2,4-hexadiene, also results in the formation of a high-molecular-weight copolymer in a moderate yield. The NMR spectroscopy reveals that the obtained copolymers consist of predominant 1,4-repeating structures for the corresponding diene unit. The copolymers have excellent thermal stability, that is, an onset temperature of decomposition over 330 °C and a glass transition temperature over 130 °C. The copolymerization reactivity of these diene monomers is discussed based on the results of the DFT calculations. The efficient copolymer formation in competition with Diels–Alder addition is investigated under various conditions of the temperature, solvents, and initiators used for the copolymerization. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

KEYWORDS: alternating copolymer; DFT calculations; glass transition temperature; naturally occurring materials; radical copolymerization; thermal stability

INTRODUCTION Alternating radical copolymerization has many advantages for polymer synthesis, such as the production of a high-molecular-weight copolymer in a high yield, well-defined alternating sequence structures independent of the comonomer ratio in the feed, and the use of various monomers.[1] N-Substituted maleimides (RMI) as the electron-accepting monomers readily provide alternating copolymers with excellent thermal, optical, and mechanical properties during radical copolymerization with electron-donating monomers, such as styrene, vinyl ethers, and isobutene.[2–28] In contrast to the facile copolymerization of the RMIs with olefins, they react with 1,3-diene compounds, such as butadiene, cyclopentadiene, and furan to predominantly yield Diels–Alder adducts rather than alternating copolymers.[29–31] We previously reported the production of an alternating copolymer of 3-methylenecyclopentene (MCP) as the cyclic 1,3-diene monomer containing a reactive exomethylene moiety during radical copolymerization with the RMIs,[32] because Diels–Alder reaction of MCP was totally suppressed due to the fixed s-trans conformation of this cyclic monomer (Scheme 1). More recently, we succeeded in the synthesis of alternating copolymers of maleic anhydride (MAn) and noncyclic 1,3-diene monomers by simple molecular design based on the DFT calculations for the conformational analysis of various kinds of diene compounds.[33] Actually, we demonstrated that the copolymerization of 2,4-dimethyl-1,3-pentadiene (DMPD) with MAn produced an alternating copolymer in the highest copolymer yield among various diene monomers[33] (Scheme 2). The anhydride moiety and carbon-to-carbon double bond in the repeating unit of the copolymer were available for postpolymerization reactions; for example, crosslinking using epoxy compounds, dialcohols, and diamines as the polyfunctional crosslinkers, as well as the oxidative ozonolysis of the carbon-to-carbon double bonds in the main chain, leading to the polymer chain scission, decrosslinking of cured resins, and polymer surface modification.[33–35]

In this study, we synthesized the copolymers of *N*-phenylmaleimide (PhMI) with various diene monomers including

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



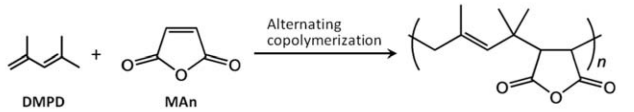
SCHEME 1 Radical alternating copolymerization of MCP and RMI.

DMPD, as shown in Figure 1. The diene monomers used in this study were commercially available as the chemicals or conveniently obtained by the one-step transformation of chemical sources including naturally occurring materials.[36–40] For example, DMPD, 2,4-hexadiene (HD), and isoprene (IP) as the hydrocarbon diene monomers were commercially available as well as methyl sorbate (MS). Several terpenes and the related chemicals, that is, myrcene (Myr), abietic acid (AA), α-phellandrene (T3), and α-terpinene (T4), were available as the naturally occurring materials. The other terpenoids, 4-isopropyl-1-methyl-3-methylenecyclohexene (T1) and (-)-2-methylene-4,6,6-trimethylbicyclo[3.1.1]-3-heptene (T2) were transformed from the corresponding ketones as the naturally occurring compounds, that is, piperitone and verbenone, respectively. MCP was obtained by the metathesis reaction of Myr using the Grubbs catalyst.[41] The reaction behavior of these diene monomers during radical copolymerization with PhMI and the structure and properties of the obtained copolymers were investigated.

EXPERIMENTAL

General Procedures

The NMR spectra were recorded in $CDCl_3$ using a Bruker AV300N spectrometer (Bruker-Biospin, Ltd., Yokohama). 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 CCPD RE-8020 system (Tosoh Co., Ltd., Tokyo) and calibration with standard polystyrenes. The thermogravimetric (TG) analysis was carried out using a Seiko TG 6200 (Seiko Instruments Co., Tokyo) in a nitrogen stream at the heating rate of 10 °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 rate of 10 °C/min. Theoretical calculations were carried out using the Spartan'10 software package (Wavefunction, Inc., Irvine, CA). The production of the initial molecular structure and the preliminary optimization of the structure were carried out using molecular mechanics (MMFF) and the semiemprical method (PM3), then the density functional theory (DFT) was used for the final structure determination and the calculations of the energy and electron densities at the B3LYP/6-31G* level.



SCHEME 2 Radical alternating copolymerization of DMPD and MAn.

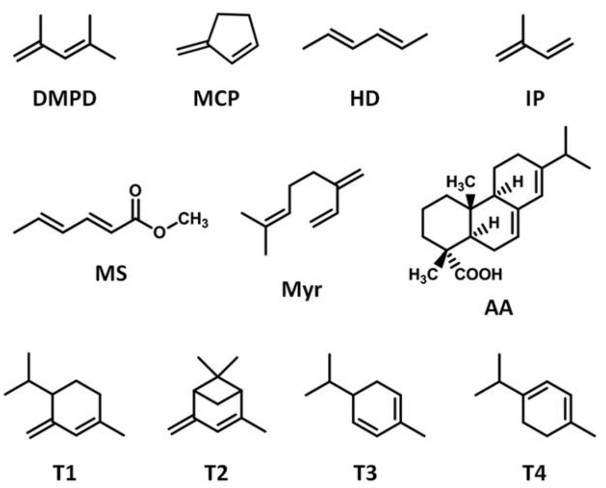


FIGURE 1 Chemical structures of diene monomers used in this study.

Materials

2,2′-Azobis(isobutyronitrile) (AIBN; Wako Pure Chemical Industries, Ltd., Osaka) and dimethyl 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN; Wako Pure Chemical Industries, Ltd., Osaka) were recrystallized from methanol. 2,2′-Azobis(2,4,4-trimethylpentane) (ATMP) was supplied from Wako Pure Chemical Industries, Ltd., Osaka and used without further purification. Commercially available *N*-phenylmaleimide (PhMI; Wako Pure Chemical Industries, Ltd., Osaka) was used after recrystallization. All solvents were distilled before use. Myrcene (Myr; Tokyo Chemical Industry Co., Ltd., Tokyo) as the mixture of two isomers was distilled before use. The composition of the isomers was determined to be α-Myr/β-Myr = 16/84 by ^{1}H NMR spectroscopy (Fig. S1 in Supporting Information). MCP was synthesized by the ring-closure metathesis reaction of Myr according to the method described in the literature.[41] (−)-α-Phellandrene (T3) and α-terpinene (T4) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, and used without further purification. Abietic acid (AA; Tokyo Chemical Industry Co., Ltd., Tokyo) was used after purification by the following procedure: 3 g of AA in 13 mL of ethanol was heated to 60 °C, then 4 mL of water was added and cooled to room temperature. The precipitated crystals were filtered, dried, then used for copolymerization. The isolated AA was the mixture of several compounds and the purity of AA was 95%. The predominant contaminant was dehydroabietic acid (Fig. S1 in Supporting Information), which was inert for the copolymerization and Diels–Alder reaction.

Synthesis of T1 and T2

A four-necked flask was charged with methyltriphenylphosphonium bromide (34.3 g, 0.1 mol) (Wako Pure Chemical Industries, Ltd., Osaka) suspended in dry THF (240 mL) under nitrogen. Potassium *tert*-butoxide (15.6 g, 0.14 mol; Tokyo Chemical Industry Co., Ltd., Tokyo) was then added, and the yellow mixture was stirred at ambient temperature for 30 min. The mixture was heated to 50 °C, and piperitone for the synthesis of T1 or verbenone for the synthesis of T2 (9.2 g, 0.1 mol) in 60 mL of anhydrous THF was dropwise added. After the mixture was stirred for 24 h at 50 °C, a small amount of water (2 mL) was added to quench the excess reagent. A large amount of *n*-hexane was added, then washed with water and saturated NaCl aqueous solution three times. The organic layer was dried on $\mathrm{Na_2SO_4}$ and purified by silica gel column chromatography (eluent: *n*-hexane). The solvent was removed at a reduced pressure (20 mmHg) and room temperature over 5 h, then T1 or T2 was distilled under the identical reduced pressure with an oil bath maintained at 90 °C. The isolated yield of T1 was 13% and the purity was 94%. The yield and purity of T2 were 14% and 98%, respectively.

4-Isopropyl-1-methyl-3-methylenecyclohexene (T1): Colorless liquid, yield 13%, purity 94%, ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.89 (d, $\mathrm{CH_3}$, 3H), 0.92 (d, $\mathrm{CH_3}$, 3H), 1.74 (s, $\mathrm{CH_3}$, 3H), 1.50–2.20 (m, $\mathrm{CH_2}$, CH, 6H), 4.63 (s, $\mathrm{=CH_2}$, 1H), 4.74 (s, $\mathrm{=CH_2}$, 1H), 5.86 (s, =CH, 1H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 20.0, 21.9, and 23.7 ($\mathrm{CH_3}$), 24.7 and 26.9 ($\mathrm{CH_2}$), 27.7 and 46.1 (CH), 109.3 ($\mathrm{=CH_2}$), 124.9 (=CH), 138.1 and 146.6 (=C).

(−)-2-Methylene-4,6,6-trimethylbicyclo[3.1.1]-3-heptene (T2): Colorless liquid, yield 14%, purity 98%, ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.82 (s, $\mathrm{CH_3}$, 3H), 1.35 (s, $\mathrm{CH_3}$, 3H), 1.45 (d, $\mathrm{CH_2}$, 1H), 1.78 (d, $\mathrm{CH_3}$, 3H), 2.10 (dt, $\mathrm{CH_2}$, 1H), 2.51 (dt, CH, 1H), 2.59 (dt, CH, 1H), 4.57 (s, $\mathrm{CH_2}$, 2H), 5.78 (s, $\mathrm{CH_2}$, 1H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 21.9, 23.0, and 26.3 ($\mathrm{CH_{3.}}$), 35.7 ($\mathrm{CH_2}$), 43.7 (C), 48.3 and 51.4 (CH), 104.5 ($\mathrm{=CH_2}$), 120.7 (=CH), 148.6 and 150.3 (=C).

Copolymerization Procedures

PhMI, a diene monomer, a radical initiator, and a solvent were placed in a glass ampoule. After the freeze–thaw cycles, the ampoule was sealed. The solution was heated at a determined temperature for a given time, then the polymerization mixture was poured into a large amount of methanol to precipitate the copolymers, which were filtered out, washed, then dried *in vacuo*. The yield of the copolymers was gravimetrically determined. The copolymers were purified by a precipitation method using chloroform and methanol as the solvent and non-solvent, respectively. The composition of the repeating units in the copolymers was determined by ^{1}H NMR spectroscopy. Photopolymerization was carried out in the presence of an azo initiator under UV irradiation at a distance of 10 cm from a high-pressure Hg lamp (Toshiba SHL-100UVQ-2) at 0 °C.

Diels–Alder Reactions

The reaction of PhMI with diene monomers was carried out in various solvents at a determined temperature, then an aliquot was analyzed by NMR spectroscopy in order to determine the conversion of PhMI and the yield of the corresponding Diels–Alder adduct.

Diels–Alder Adduct of PhMI and DMPD: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.98 (s, $\mathrm{CH_3}$, 3H), 1.33 (s, $\mathrm{CH_3}$, 3H), 1.74 (s, $\mathrm{CH_3}$, 3H), 2.45 (dd, $\mathrm{CH_2}$, 1H), 2.50 (m, $\mathrm{CH_2}$, 1H), 2.74 (d, CCH, 1H), 3.27 (ddd, $\mathrm{CH_2CH}$, 1H), 5.38 (s, =CH, 1H), 7.22–7.45 (m, $\mathrm{C_6H_5}$, 5H); ^{13}C-NMR (75 MHz, $\mathrm{CDCl_3}$) δ 23.3, 23.6, and 25.7 ($\mathrm{CH_3}$), 29.5 ($\mathrm{CH_2}$), 34.6 and 39.2 (CH), 49.3 (C), 126.3, 128.4, and 129.0 ($\mathrm{C_6H_5}$), 131.8, 131.9, and 132.0 ($\mathrm{C_6H_5}$, =CH, =C), 177.3 and 179.3 (C=O).

Diels–Alder Adduct of PhMI and HD: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.50 (d, $\mathrm{CH_3}$, 3H), 2.52 (q, $\mathrm{CHCH_3}$, 2H), 3.17 (dd, CH, 2H), 5.77 (s, =CH, 2H), 7.14–7.52 (m, $\mathrm{C_6H_5}$, 5H); ^{13}C-NMR (75 MHz, $\mathrm{CDCl_3}$) δ 17.0 ($\mathrm{CH_3}$), 31.4 and 45.8 (CH), 126.8, 128.6, 129.2, and 132.1 ($\mathrm{C_6H_5}$), 134.3 (=CH), 176.8 (C=O).

Diels–Alder Adduct of PhMI and IP: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.75 (s, $\mathrm{CH_3}$, 3H), 2.15–2.37 (m, $\mathrm{=CHCH_2CH}$, 2H), 2.53–2.66 (m, $\mathrm{=CCH_2CH}$, 2H), 3.13–3.25 (m, CH, 2H), 5.55–5.64 (m, =CH, 1H), 7.14–7.52 (m, $\mathrm{C_6H_5}$, 5H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 23.5 ($\mathrm{CH_3}$), 24.5 and 28.8 ($\mathrm{CH_2}$), 39.2 and 39.6 (CH), 120.1 (CH=C), 126.4, 128.5, 129.0, and 132.1 ($\mathrm{C_6H_5}$), 136.5 ($\mathrm{CH_2{=}C}$), 179.1 and 179.4 (C=O).

Diels–Alder Adduct of PhMI and MS: ^{1}H-NMR (300 MHz, $\mathrm{CDCl_3}$) δ 1.45 (d, $\mathrm{CH_3}$, 3H), 2.40–2.56 (m, CH, 1H), 3.14–3.24 (m, CHC=O, 1H), 3.25 (dd, CH, 1H), 3.82 (s, $\mathrm{OCH_3}$, 3H), 3.86 (dd, CH, 1H), 5.84 (ddd, CH, 1H), 6.43 (ddd, CH, 1H), 7.14–7.46 (m, $\mathrm{C_6H_5}$, 5H); ^{13}C-NMR (75 MHz, $\mathrm{CDCl_3}$) δ 16.7 ($\mathrm{CH_3}$), 31.6, 40.5, 43.8, and 52.4 (CH), 126.4, 128.6, 129.1, and 131.6 ($\mathrm{C_6H_5}$), 134.7 (=CH), 171.2, 175.8, and 176.3 (C=O).

RESULTS AND DISCUSSION

We carried out the radical copolymerization of PhMI with various diene monomers shown in Figure 1 under the conditions of [PhMI] = [Diene] = 0.5 mol/L (50/50 in a molar ratio) and [AIBN] = 0.01 mol/L in 1,2-dichloroethane at 60 °C for various polymerization times (1–24 h). The results of the copolymerization are summarized in Table 1. The copolymers with a high molecular weight were produced in a high yield during the copolymerizations of DMPD, MCP, HD, and T1 with PhMI. Among these diene monomers, MCP and T1 with a fixed s-trans conformation due to their cyclic monomer structure showed the highest copolymerization reactivity ($M_\mathrm{n} = 6.5$–15×10^4, 82%–97% yield), as was expected. The copolymerization of DMPD and HD as the noncyclic diene monomers also resulted in the formation of a high-molecular-weight copolymer in a moderate yield ($M_\mathrm{n} = 1.6$–3.6×10^4, 47%–51% yield), being consistent with the previously reported results for the copolymerization with MAn.[33] The copolymerization of IP with PhMI produced a copolymer in a lower yield ($M_\mathrm{n} = 1.8$–2.4×10^4, 13%–20% yield).

In Table 1, the obtained polymer yields were almost constant, independent of the time for several copolymerizations. This was because the copolymer yield already reached a certain value after polymerization for several hours and the

TABLE 1 Results of the Copolymerization of PhMI with Various Diene Monomers and Thermal Properties of the Obtained Copolymers[a]

Diene	Time (h)	Copolymer Yield[b] (%)	PhMI Content in Copolymer (mol %)	$M_n \times 10^{-3}$	M_w/M_n	T_{d5} (°C)	T_g (°C)
DMPD	2.5	16.5 (34.9)		35.8	1.57		
	5	26.3 (51.7)		31.7	1.57		
	10	37.9 (68.1)		27.1	1.62		
	15	43.3 (76.1)		24.8	1.64		
	20	50.7 (80.2)	49.5	22.5	1.67	331	130
MCP	6	97.3	50.1	147	2.97	364	159
HD	2	28.2 (71.0)		25.8	1.67		
	6	33.6 (84.7)		22.5	1.82		
	12	41.7 (91.8)		18.1	1.94		
	15	44.8 (92.9)		17.2	1.96		
	20	47.3 (93.7)	51.1	15.8	2.06	355	144
IP	2	13.1 (87.6)	49.4	23.9	1.67		
	19	19.6 (99.9)	49.4	18.0	2.26		
MS	1	2.5 (28.5)		10.0	1.26		
	3	5.3 (40.5)		8.3	1.24		
	20	6.1 (90.8)	49.0	7.0	1.24	339	142
Myr[c]	4.5	9.3	52.3	9.8	3.90	340	142
AA[d]	4.5	2.0	51.4	6.1	1.24	348	210
T1	7	82.1	49.0	64.6	2.21	340	189
T2	7	8.9	53.8	6.6	1.29	339	[e]
T3	24	8.0 [16.0][f]	62.4	2.4 [3.6][f]	1.63 [1.99][f]	349	208
T4	24 [10][f]	1.0 [3.8][f]	61.8	1.5 [3.9][f]	1.39 [2.54][f]	380	151

[a] [PhMI] = [Diene] = 0.5 mol/L, [AIBN] = 0.01 mol/L, in 1,2-dichloroethane at 60 °C.

[b] Values in parentheses indicate PhMI conversion in % determined in $CDCl_3$.

[c] [PhMI] = [Myr] = 1.0 mol/L.

[d] [PhMI] = [AA] = 0.7 mol/L.

[e] Not detected in a temperature range below the T_{d5} by DSC.

[f] Values in brackets indicate the values for photopolymerization: [ATMP] = 0.01 mol/L in 1,2-dichloroethane at 0 °C under UV irradiation with a high-pressure Hg lamp.

copolymerization occurred in competition with Diels–Alder reaction. In Figure 2, the yields of the copolymers and the Diels–Alder adducts were plotted as the function of a reaction time during the reaction of various diene monomers at 60 °C. The conversion of PhMI was simultaneously monitored by ^{1}H-NMR spectroscopy.

As a result, the rates of the both reactions of copolymerization and Diels–Alder addition depended on the diene monomer structure. The total rate of the both reactions, which is also deduced from the consumption of PhMI, decreased according to the steric bulkiness of the substituents of the diene monomers in the order of IP > HD > DMPD. The yield of the copolymers increased with a decrease in the total reactivity of the diene monomers. The main product was a copolymer during the reaction of DMPD, while Diels–Alder reaction of HD rapidly proceeded in competition with the copolymer formation. The Diels–Alder adduct was the main product throughout the reaction of IP. The introduction of an electron-withdrawing substituent also resulted in the suppressed copolymer formation, as was seen in the reaction of MS. It was concluded that MS was not suitable to the copolymerization with PhMI, although it readily reacted with molecular oxygen to produce an alternating copolymer.[42–44]

The PhMI contents in the copolymers were revealed to be close to 50 mol %, which was determined from the peak intensity ratios of the aromatic hydrogens and the others in the ^{1}H-NMR spectra of the copolymers (Fig. 3). It was also clarified that the diene units in the copolymers consisted of mainly 1,4-repeating units, based on the chemical shifts and the intensity of the peaks due to the unsaturated groups observed at 4–6 ppm in the NMR spectra. It was previously revealed that the peaks due to the 1,2- and 3,4-repeating units of the copolymers of the RMIs or MAn with diene monomers were observed as those with chemical shifts clearly different from the 1,4-repeating one.[32,33] In this study, the peaks due to the 1,4-repeating units with a relatively large intensity were observed at 5–5.5 ppm for the all copolymers and minor several peaks were additionally

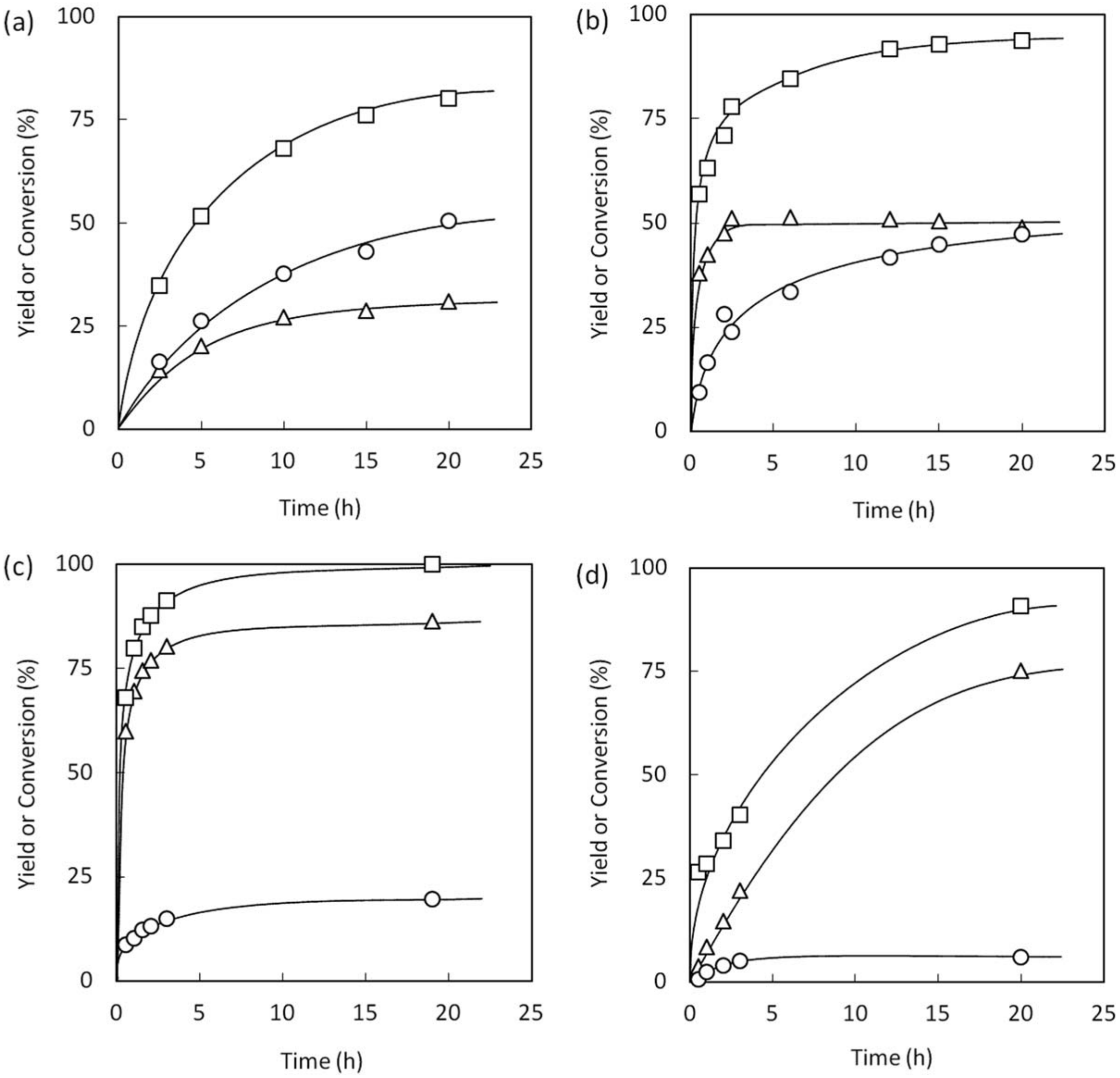


FIGURE 2 Relationship between polymerization time and the copolymer yield (○), the yield of Diels–Alder adduct (△), and the conversion of PhMI (□) during the radical copolymerization of PhMI with (a) DMPD, (b) HD, (c) IP, and (d) MS in the presence of AIBN (0.01 mol/L) in 1,2-dichloroethane or $CDCl_3$ at 60 °C.

observed in some cases, as is shown in Figure 3. It was concluded that the copolymers obtained in this study consisted of mainly 1,4-repeating structures, that is, approximately more than 90%.

On the other hand, the copolymerization with other diene monomers resulted in the formation of copolymers with M_n less than 10^4 in a copolymer yield lower than 10% (Table 1). The ^{1}H-NMR spectra of the copolymers with MS and Myr in Figure 3 indicated the formation of the copolymer with almost equimolar comonomer contents, but the other copolymer compositions varied in a range of 54–62 mol % as the PhMI content, depending on the reactivity of the diene monomers. As a result of the homopolymerization of Myr under the conditions of $[\text{Myr}] = 0.5$ mol/L, $[\text{AIBN}] = 0.01$ mol/L in 1,2-dichloroethane at 60 °C for 18 h, we confirmed the formation of a homopolymer with a molecular weight of 3000 in 1.2% yield (see Fig. S9 in Supporting Information). The contribution of the both diene and vinyl moieties should also be taken in consideration during the propagation of Myr. It may produce a branched and partly crosslinked polymer. In fact, a large M_w/M_n value was observed for the copolymer with Myr ($M_w/M_n = 3.90$), as was shown in Table 1. In addition, the intramolecular cross-propagation of the diene and vinyl moieties might produce a cyclic repeating structure in the main chain during the propagation of Myr (Scheme 3). On the other hand, AA produced no homopolymer under similar polymerization conditions, and no occurrence of Diels–Alder reaction because of its fixed s-trans conformation. Several less-reactive diene monomers with considerable steric hindrance, such as T3 and T4, led to the formation of the PhMI-rich

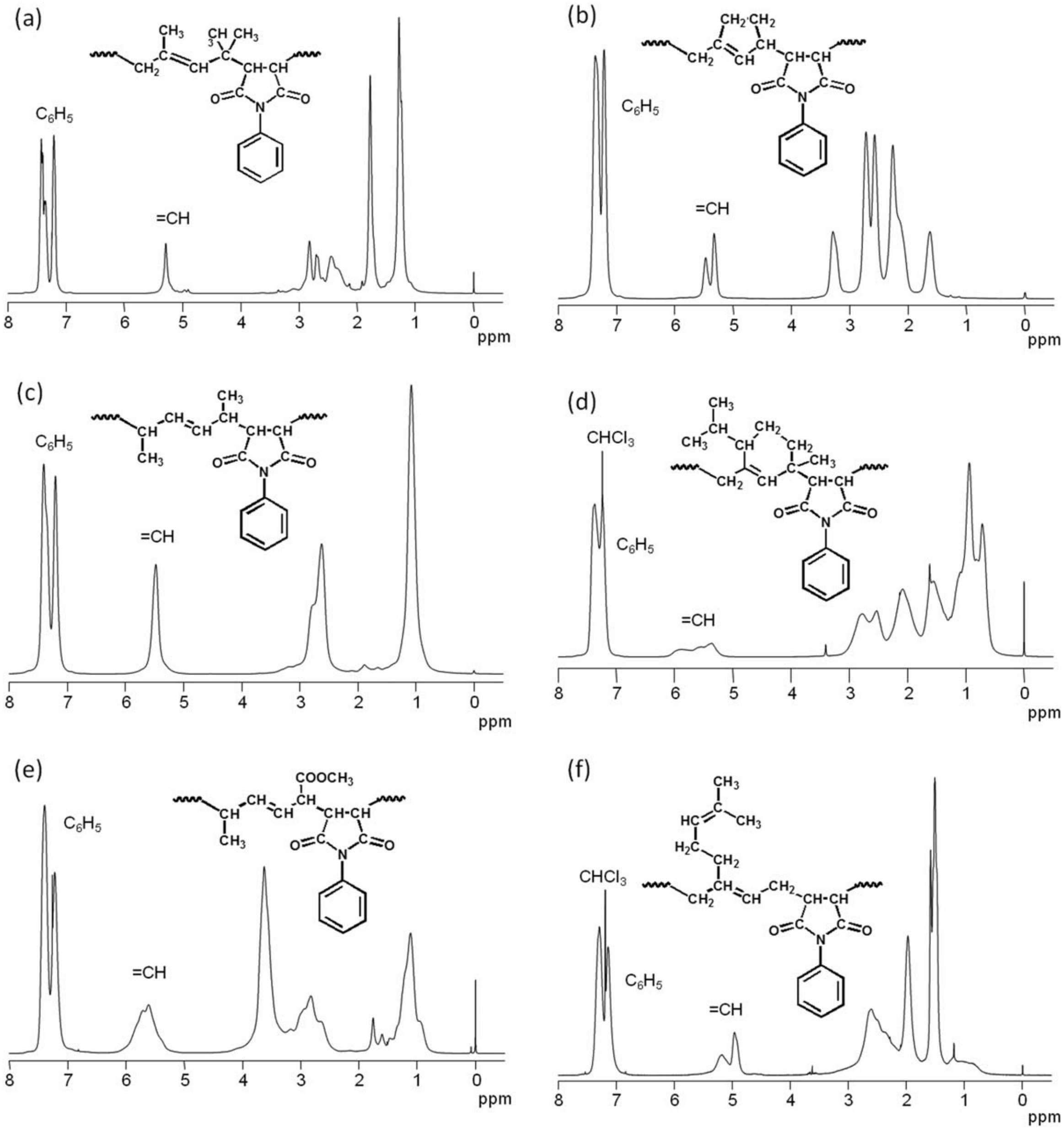
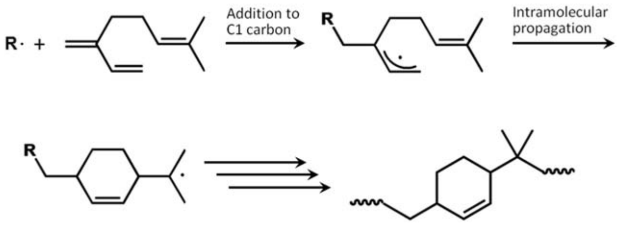


FIGURE 3 ^{1}H-NMR spectra of the copolymers of PhMI with (a) DMPD, (b) MCP, (c) HD, (d) T1, (e) MS, and (f) Myr. Measured in $CDCl_3$. The chemical structures indicate 1,4-repeating units as the predominant structures for each copolymer.

copolymers (61.8–62.4 mol % as the PhMI content in the copolymers). The control of copolymer sequences has been reported for the copolymerizations of RMI with bulky olefin monomers including *β*-pinene (BP), limonene, diisobutene by several research groups.[45–48] It was pointed out that the penultimate unit effect played an important role for the formation of the sequence-controlled copolymers including an AAB-type repeating unit and that the suppressed copolymerization rate was observed during the copolymerization under the penultimate unit control. The copolymer production with the high PhMI content may be due to the penultimate unit effect of the sterically hindered diene monomers. We carried out the photopolymerization of T3 and T4 as the less reactive monomers with sterically ernal diene structures at 0 °C in order to check the effect of a ceiling temperature. As a result, the low-molecular-weight copolymers (M_n less than 4 × 10^3) were produced during the copolymerization with



SCHEME 3 Possible intramolecular 1,4-propagation of Myr.

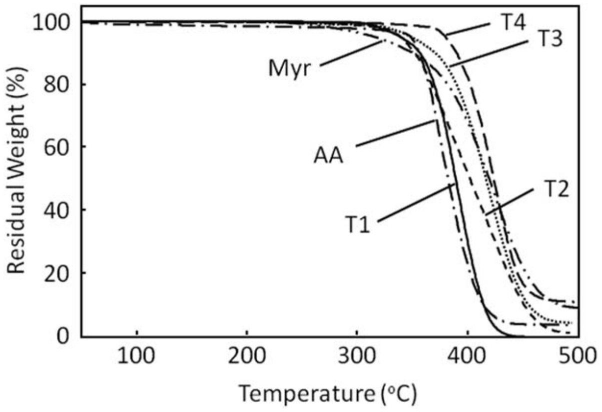


FIGURE 4 TG curves for the copolymers obtained by the radical copolymerization of PhMI with various diene monomers at the heating rate of 10 °C/min in a nitrogen stream.

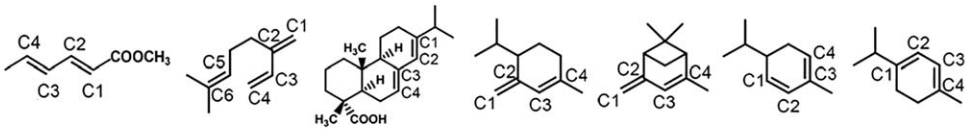
PhMI (Table 1), suggesting that the less reactivity of these monomers was not caused by a low ceiling temperature.

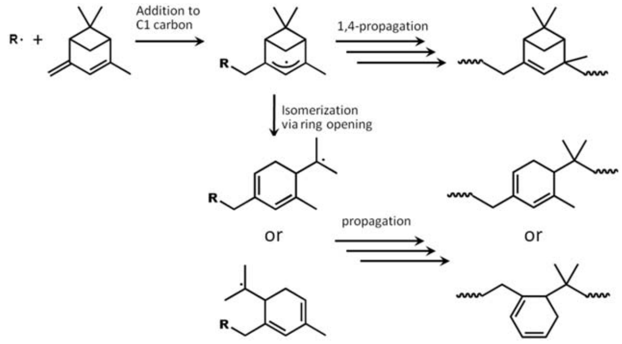
All the copolymers of PhMI with diene monomers obtained in this study were thermally stable and the T_{d5} values were higher than 330 °C, as is shown in Figure 4. The copolymer of T4 with PhMI showed the highest T_{d5} value of 380 °C despite the lowest molecular weight ($M_n = 1.5 \times 10^3$). The T_g values varied depending on the structure of the diene monomer units, as shown in Table 1. The T_g values of the copolymers including noncyclic diene units were 130 °C–144 °C and the copolymers including cyclic repeating units showed T_g values higher than 150 °C. Especially, the copolymers obtained from the terpenes and the related monomers, T1–T4 had high T_g values, being due to the rigid cyclic repeating structure with bulky alkyl substituents. The T_g value of the copolymer of T4 with PhMI ($T_g = 158$ °C) lower than those for the copolymers of other terpenes with PhMI might be due to the lowest molecular weight. The copolymers were soluble in organic solvents, such as toluene, chloroform, 1,2-dichloroethane, and THF. Highly transparent films were obtained by casting the solutions of the copolymers, but they were brittle due to the steric bulkiness of the substituents in the RMI and diene repeating units.

In order to clarify the reason for a difference in the reactivity of the diene monomers, we estimated the electron density of a diene moiety by the DFT calculations at the B3LYP level of theory with the 6-311G* basis set. The results are shown in Table 2. It was revealed that the highest electron density was observed on the C1 carbon of T1, well accounting for its high copolymerization reactivity. The calculations also revealed low electron density on the C1 carbon of AA and the C1 and C4 carbons of T4, due to the presence of methyl and isopropyl substituents. The addition of the PhMI radical to the C4 carbon of AA was confirmed to be more favored ($\Delta H_4 = -34.9$ kcal/mol) compared with that to the C1 carbon ($\Delta H_1 = -22.0$ kcal/mol). It was also considered that the 4,1-propagation predominantly proceeded rather than the 4,3-propagation during the reaction of the AA radical and the PhMI monomer. For the other monomers, Myr, T2, and T3, the moderate electron density values were obtained. Judging from the molecular structure of T2, it was expected to exhibit copolymerization reactivity similar to that of T1 with an exomethylene structure, but it produced a low-molecular-weight polymer in a low yield. The bicyclic structure of T2 may suppress the reactivity. The propagation proceeded via a ring-opening process in competition with the intermolecular 1,4-addition and led to the copolymer formation with complex repeating copolymer structures during the copolymerization of T2 (Scheme 4). The structure of the propagating radicals formed by the ring-opening reactions in Scheme 4 were similar to those for the radicals produced from the copolymerizations of β-pinene.[45] T4 showed the lowest copolymerization reactivity because of the disadvantageous addition of the PhMI radical to the C1 and C4 carbons of T4 due to the low electron densities and the steric hindrance of the alkyl substituents. The T_g value of the copolymer of T4 with PhMI (T_g =158 °C) lower than those for the other copolymers of terpenes with PhMI might be due to the lowest molecular weight.

TABLE 2 Mulliken Atomic Charge of Conjugated Diene Monomers at the B3LYP Level of Theory with the 6-311G* Basis Seta

	Mulliken Atomic Charge (Electron Density)					
Monomer	C1	C2	C3	C4	C5	C6
MS	−0.327	−0.130	−0.178	−0.155	–	–
Myr	−0.300	0.111	−0.062	−0.298	−0.169	0.079
AA	0.023	−0.212	0.000	−0.209	–	–
T1	−0.489	0.156	−0.207	0.083	–	–
T2	−0.455	0.173	−0.246	−0.115	–	–
T3	−0.386	−0.364	−0.211	−0.361	–	–
T4						–





SCHEME 4 Possible propagation mechanism of T2 accompanying radical isomerization via ring opening reactions.

In order to increase a copolymer yield during the copolymerization of the less-reactive diene monomers, we examined the optimized copolymerization conditions including polymerization temperature, solvent, and an initiator using IP as the diene monomer. The copolymer yield, the Diels–Alder adduct yield, and the PhMI conversion determined for the copolymerization under various reaction conditions are shown in Table 3. Unfortunately, the formation of the Diels–Alder adducts could not be suppressed when the copolymerization was carried out in DMSO-d_6 at 100 °C using ATMP as the high temperature azo initiator ($k_d = 1.3 \times 10^{-5}$ sec^{-1} and half-life time = 15 h at 100 °C).[49] The Diels–Alder reaction rapidly proceeded at the initial stage of polymerization and no effect of the reverse reaction, that is, retro-Diels–Alder addition was observed under the conditions in Table 3. The unsaturated groups in the copolymer produced in 3%–4% yield further reacted and resulted in increasing M_w/M_n values under high temperature conditions. The tailing of the peaks to a high molecular weight region was observed in the SEC elution curves of the copolymers. The trials of the copolymerization under the other conditions at a higher temperature, for example, at 160 °C in 1,2-dichlorobenzene, also provided the Diels–Alder adduct as the major product. Next, the copolymerization at a low temperature was attempted to suppress the Diels–Alder reaction. The copolymerization was carried out in $CDCl_3$ at 0 °C in the presence of AIBN under UV irradiation with a Hg lamp. However, it was failed as shown in Figure 5(a) and Table 3; almost no copolymer was produced. An increase in the AIBN concentration resulted in an increase in the copolymer yield, but a maximum copolymer yield was still less than 10% even after polymerization for 184 h.

It was reported that the copolymerization rate of PhMI increased in a solvent with a large acceptor number.[45,50] In this study, therefore, we examined the copolymerization of PhMI with IP in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), which is one of the highly electron-pair accepting solvents.[51] As a result, the copolymer was obtained in only 7% yield. Thus, the solvent effect was not valid for the control of the reaction pathways in this study, while the copolymerization behavior of the RMIs significantly depended on the Lewis acidity of the solvents, as reported in the literatures.[45,52–54]

Finally, the use of AMVN as the azo initiator baring a high decomposition rate ($k_d = 7.7 \times 10^{-6}$ sec^{-1} and half-life time = 25 h at 30 °C)[55] was confirmed to be valid for the increase in the copolymer yield, as shown in Figure 5(b). The copolymer yield reached 33% after the 21-h polymerization, being better than the yield for the copolymerization at 60 °C using AIBN ($k_d = 9.6 \times 10^{-6}$ sec^{-1} and half-life time = 20 h at 60 °C)[56] in Table 1. However, the main product was still the Diels–Alder adduct, but not the copolymer. We concluded that the reaction pathway was predominantly determined by the diene monomer structure themselves rather than the reaction conditions such as the temperature, solvents, and initiators.

TABLE 3 Yields of Copolymer and Diels–Alder Product During the Copolymerization of PhMI With IP Under Various Conditions

Solvent	Initiator (mol/L)	Temp (°C)	Time (h)	Copolymer Yield (%)	$M_n \times 10^{-3}$	M_w/M_n	Diels–Alder Adduct Yield (%)	PhMI Conversion (%)
DMSO-d_6	ATMP (0.01)	100	0.5	3.4	7.0	4.47	84.0	97.9
			1	3.9	6.0	5.69	87.7	99.1
$CDCl_3$	AIBN (0.01)	0 (UV)	15	0.17	5.3	1.17	66.7	71.8
			31	0.22	4.8	1.18	81.3	85.7
			93	1.2	4.0	1.26	87.8	96.7
$CDCl_3$	AIBN (0.5)	0 (UV)	6	0.17	5.8	1.54	45.0	51.2
			22	0.21	6.9	1.37	74.4	81.8
			78	7.5	6.0	1.58	78.1	92.8
HFIP	AIBN (0.01)	60	3	7.0	23.7	3.61	86.4	92.5
			10	7.4	23.7	2.93	85.5	93.0
			15	7.2	21.0	2.98	85.4	93.3
$CDCl_3$	MAIB (0.01)	30	1	12.5	23.1	1.59	38.9	56.4
			3	21.3	18.6	1.60	52.6	77.4
			21	33.2	13.0	1.74	60.7	94.1

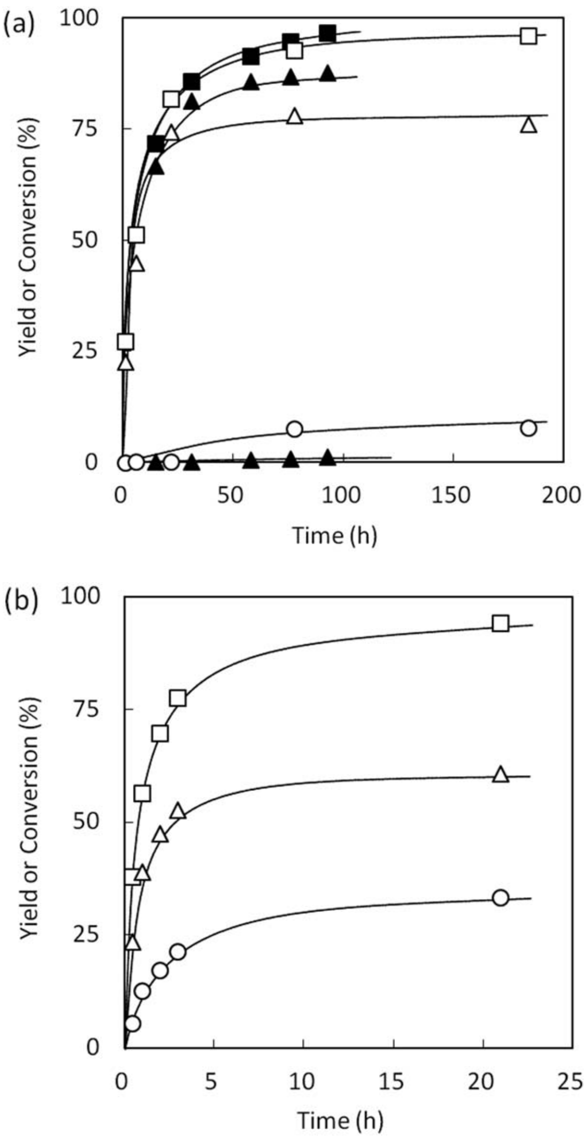


FIGURE 5 Relationship between polymerization time and the copolymer yield (○), the yield of Diels–Alder adduct (△), and the conversion of PhMI (□) during the radical copolymerization of PhMI with IP. (a) Photopolymerization in CDCl$_3$ at 0 °C, [AIBN] = 0.01 (closed symbols) and 0.5 (open symbols) mol/L and (b) in CDCl$_3$ at 30 °C, [AMVN] = 0.01 mol/L.

CONCLUSIONS

We have demonstrated that the radical copolymerization of diene monomers with PhMI predominantly proceeded as a result of the suppression of Diels–Alder addition by the molecular design of the monomers. The diene monomers with an exomethylene moiety and a fixed s-trans diene structure exhibited the highest copolymerization reactivity and the noncyclic diene monomers with hindered substituents also resulted in the formation of a high-molecular-weight copolymer. In contrast, it has been revealed that the control of the reaction pathway of the copolymerization and Diels–Alder addition was difficult by the tuning of the reaction conditions, such as temperature and solvents. The copolymerization at a relatively low temperature in the presence of an azo initiator with a large decomposition rate constant was valid for the synthesis of the copolymers in a higher yield. The obtained copolymers showed high onset temperatures of decomposition and high T_g values. The copolymers of the RMIs with diene monomers would be useful for various application fields related to optics and optoelectronics materials, similar to the copolymers of the RMIs and olefins.

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