

Valencene as a naturally occurring sesquiterpene monomer for radical copolymerization with maleimide to induce concurrent 1:1 and 1:2 propagation

Hiroaki Hashimoto, Hisaaki Takeshima, Tomonari Nagai, Mineto Uchiyama, Kotaro Satoh,^{*} and Masami Kamigaito^{*}

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

E-mail address: satoh@chembio.nagoya-u.ac.jp (K. Satoh), kamigait@chembio.nagoya-u.ac.jp (M. Kamigaito)

ABSTRACT

Valencene, a naturally occurring sesquiterpene that can be obtained from various citrus fruits, was copolymerized as an unconjugated 1,1-disubstituted bulky vinyl monomer by radical copolymerization with conjugated monomers possessing electron-withdrawing substituents, such as maleimides, acrylates, methacrylates, acrylonitrile, and methacrylonitrile, in toluene and PhC(CF₃)₂OH. The fluorinated alcohol increased the copolymerizability, as in the radical copolymerization of other unconjugated non-polar olefins with those electron-acceptor comonomers. In particular, the copolymerization of valencene and *N*-phenylmaleimide in PhC(CF₃)₂OH proceeded via concurrently occurring 1:1 and 1:2 propagation, in which the monomer reactivity ratio of maleimide and valencene to the maleimide radical with the penultimate valencene unit was close to 1 according to a kinetic analysis of the copolymerization based on the penultimate model. Therefore, the copolymerizability of valencene was higher than that of limonene, which is a similar unconjugated 1,1-disubstituted vinyl monomer with a smaller cyclohexenyl substituent that undergoes selective 1:2 radical copolymerization with maleimide derivatives under the same conditions. Reversible addition-fragmentation chain transfer RAFT copolymerization using a trithiocarbonate resulted in copolymers with controlled molecular weights and chain-end groups. The biobased copolymers of valencene and *N*-phenylmaleimide showed relatively high glass transition temperatures (T_g) of approximately 220–240 °C and relatively high thermal stability with 5% decomposition temperatures (T_{d5}) of approximately 330–340 °C due to their rigid main-chain structures.

Keywords: Terpene; Orange; Radical copolymerization; Alternating copolymerization; Thermal properties

1. Introduction

Biobased polymers have attracted much attention in view of the sustainable development of polymer industries due to the renewability of bioresources and future depletion of fossil resources [1–26]. In addition to such environmental and social demands, the characteristic structures originating from natural products can often provide interesting properties to the resulting polymers such as biodegradability and good thermal, mechanical, and optical properties, which depend on their structures and cannot be easily attained by rather simple petroleum-derived compounds. Various biobased polymers with excellent properties have been produced, and some of them have been commercialized. However, many of them are polyesters and polyamides, which are obtained via the condensation polymerization of naturally occurring or chemically or biologically transformed alcohols, amines, and carboxylic acids. In contrast, there are not many biobased vinyl polymers, which may show high stability due to the stable main-chain carbon-carbon single bond linkage in comparison to ester and amide linkages.

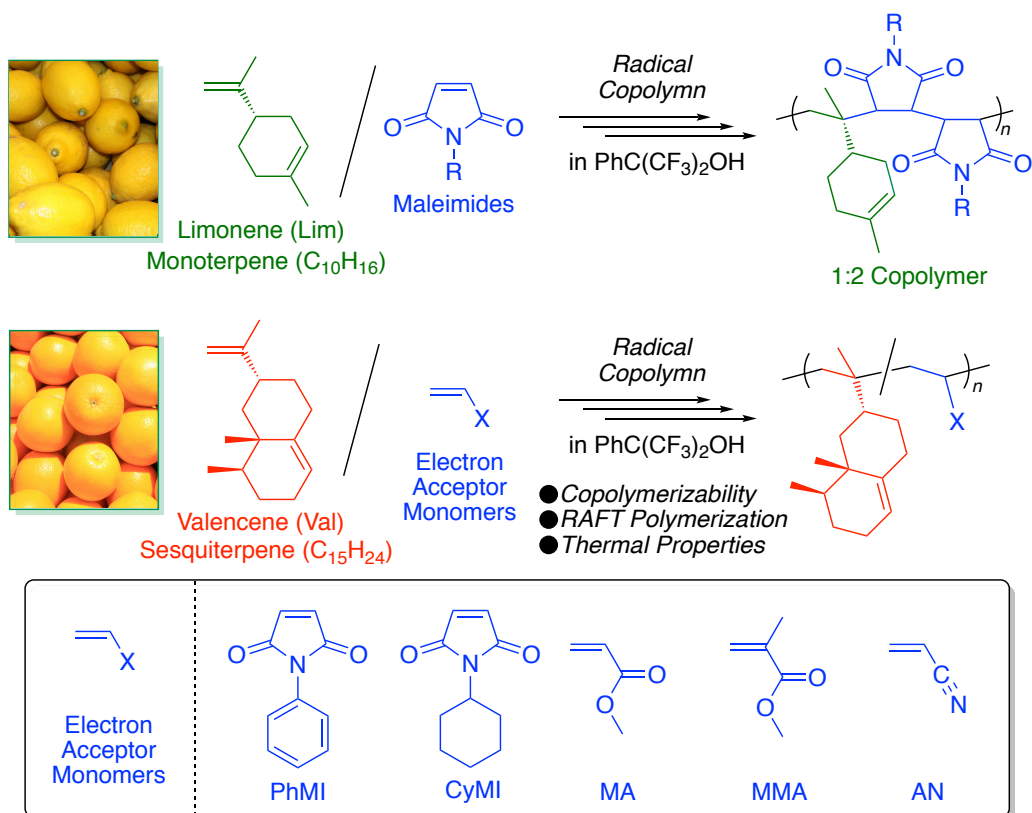
Among the various naturally occurring organic compounds, terpenes are a large and diverse class of abundant compounds produced by a variety of plants [27–30]. Their structures vary with many isomers, though they basically consist of multiples of the C₅-unit according to the biogenetic isoprene rule. Many terpenes have unsaturated carbon-carbon double bonds because they are biologically synthesized from isopentenyl pyrophosphate as the building block. Although the most abundant ones are monoterpenes consisting of two isoprene units with the molecular formula of C₁₀H₁₈, such as limonene and pinene, sesquiterpenes (C₁₅H₂₄), diterpenes (C₂₀H₃₂), and other compounds consisting of a higher number of isoprene units are naturally produced and seen in various plant oils.

Valencene is a sesquiterpene with an *exo*-olefin moiety that occurs in many citrus fruits such as the orange, lemon, and grapefruit [31–39]. Since it is an important aroma component of citrus fruits, it is widely used in the flavor and fragrance industries. Most valencene is obtained from Valencia oranges, but the synthesis has been studied not only via chemical routes [40–42] but also via biotechnological methods using microorganisms [43–45]. Valencene is also used industrially as a starting material for nootkatone, which is another important sesquiterpenoid aroma component of the grapefruit [46–50]. Although the market volume for valencene is not

so large in comparison to monoterpenes such as limonene and pinene, approximately 15 metric tons per year including what is used for the production of nootkatone [45], it is commercially available from chemical companies.

We have been focusing on terpenes and phenylpropanoids as renewable vinyl monomers for novel biobased polymers with characteristic structures and interesting properties [51–70]. We have been mainly investigating the controlled polymerization of the most abundant monoterpenes with unsaturated carbon-carbon double bonds, such as pinene and limonene. Among these, we found that limonene, which has a 1,1-disubstituted unconjugated vinyl group with a bulky cyclohexene substituent and thus cannot be homopolymerized by any propagating species, was efficiently copolymerized with electron-acceptor monomers having conjugated electron-withdrawing substituents using a fluoroalcohol as a solvent for the radical copolymerization [55,59–63]. Especially with a maleimide derivative, which is one of the most electron-deficient vinyl monomers, the selective 1:2-radical copolymerization of limonene (A) and maleimide (B) produces in ABB-sequence regulated copolymers [55,59,61,62]. The selective ABB-propagation is a consequence of the characteristic structure and non-homopolymerizability of limonene, relatively good copolymerizability of maleimide with electron-donor monomers, and hydrogen-bonding interaction of the fluoroalcohol with the carbonyl groups of the maleimide units. Especially, the hydrogen-bonding interaction increased the copolymerizability between limonene and maleimide derivatives by further decreasing electron density of the maleimide radical as well as of the carbon-carbon double bond of maleimide monomer [59,62].

Here, we focused on valencene, which has a 1,1-disubstituted unconjugated vinyl group with a bulky substituent similar to limonene with an additional six-membered ring fused to the cyclohexene substituent of the limonene skeleton as the additional C₅H₆ unit found in the sesquiterpene. Although valencene has a bulkier substituent than limonene, it is expected to show similar reactivity or copolymerizability with maleimide due to the similar environment around the vinyl group. In this paper, we investigated the radical copolymerization and reversible addition-fragmentation chain transfer (RAFT) copolymerization of valencene with those electron-acceptor monomers, especially maleimide derivatives, in fluorinated alcohol, for selective propagation as well as for novel biobased polymers with the characteristic structure of valencene, which will contribute to enhancing the thermal properties of the copolymers (Scheme 1).



Scheme 1. Radical copolymerization of limonene or valencene with electron acceptor monomers

2. Materials and methods

2.1. Materials

(+)-Valencene (Val) (Aldrich, $\geq 70\%$), (+)-*d*-limonene (Lim) (Aldrich, 97%), methyl acrylate (MA) (Tokyo Kasei, $>99\%$), methyl methacrylate (MMA) (Tokyo Kasei, $>98\%$), acrylonitrile (AN) (Aldrich, $\geq 99\%$), and $\text{PhC(CF}_3)_2\text{OH}$ (Wako, $>99\%$) were distilled over calcium hydride under reduced pressure before use. The purity of Val based on the ratio of protons of the *exo*-methylene vinyl group to others by $^1\text{H NMR}$ was 87% after the distillation. *N*-Phenylmaleimide (PhMI) (Aldrich, 97%) and *N*-cyclohexylmaleimide (CyMI) (Aldrich, 97%) were purified by recrystallization from acetone and toluene, respectively. Toluene (KANTO, $>99.5\%$; $\text{H}_2\text{O} < 10$ ppm) was dried and deoxygenized by passage through columns from Glass Contour Solvent Systems before use. α,α -Azobisisobutyronitrile (AIBN) (Kishida, $>99\%$) was purified by recrystallization from methanol. *S*-Cumyl-*S'*-butyl trithiocarbonate (CBTC) was synthesized according to the literature [71].

2.2. Free radical copolymerization

Free radical copolymerization was carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example for Val and PhMI copolymerization with AIBN in PhC(CF₃)₂OH is given below. After PhMI (0.417 g, 2.4 mmol) was placed in a baked 25-mL graduated Schlenk flask, a three-way stopcock was attached. After degassing and filling the flask with dry nitrogen, Val (0.63 mL, 2.4 mmol based on 87% purity) and PhC(CF₃)₂OH were added at room temperature to a total volume of 3.0 mL. Then, a 32 mM PhC(CF₃)₂OH solution of AIBN (1.0 mL, 0.032 mmol) was added, so that the total volume of the reaction mixture was 4.0 mL ([Val]₀/[PhMI]₀/[AIBN]₀ = 600/600/8.0 mM). Immediately after mixing, aliquots (0.6 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C. At predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to -78 °C. The monomer conversion was determined from the concentration of residual monomer measured by ¹H NMR with PhC(CF₃)₂OH as an internal standard (48 h, 38% for Val and 56% for PhMI). The quenched reaction solutions were evaporated to dryness to give the product copolymer ($M_n = 3500$, $M_w/M_n = 1.76$).

2.3. RAFT copolymerization

RAFT copolymerization was carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example for Val and PhMI copolymerization with CBTC/AIBN in PhC(CF₃)₂OH is given below. After PhMI (0.417 g, 2.4 mmol) was placed in a baked 25-mL graduated Schlenk flask, a three-way stopcock was attached. After degassing and filling the flask with dry nitrogen, Val (0.63 mL, 2.4 mmol based on 87% purity), a 510 mM PhC(CF₃)₂OH solution of CBTC (0.47 mL, 0.24 mmol), and PhC(CF₃)₂OH was added at room temperature to a total volume of 3.0 mL. Then, a 32 mM PhC(CF₃)₂OH solution of AIBN (1.0 mL, 0.032 mmol) was added, so that the total volume of the reaction mixture was 4.0 mL ([Val]₀/[PhMI]₀/[CBTC]₀/[AIBN]₀ = 600/600/60/8.0 mM). Immediately after mixing, aliquots (0.6 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under a nitrogen atmosphere. At predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to -78 °C. The monomer conversion was determined from the concentration of residual monomer measured by ¹H NMR with PhC(CF₃)₂OH as an internal standard (48 h, 37% for Val and 58% for PhMI). The

quenched reaction solutions were evaporated to dryness to give the product copolymer ($M_n = 1500$, $M_w/M_n = 1.31$).

2.4. Measurements

The monomer conversion was determined from the concentration of residual monomer measured by ^1H NMR spectroscopy with the reaction solvent as an internal standard. The ^1H NMR spectra for the monomer conversion and product copolymer were recorded in CDCl_3 at $25\text{ }^\circ\text{C}$ and in $(\text{CD}_3)_2\text{CO}$ at $50\text{ }^\circ\text{C}$, respectively, on a JEOL ECS-400 spectrometer operating at 400 MHz. The MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR Plus mass spectrometer (linear mode) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as the ionizing matrix and sodium trifluoroacetate as the ion source. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the product polymers were determined by SEC in THF at $40\text{ }^\circ\text{C}$ on two polystyrene gel columns [Tosoh Multipore H_{XL}-M (7.8 mm i.d. \times 30 cm) \times 2; flow rate 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against standard polystyrene samples (Varian; $M_p = 580\text{-}3053000$, $M_w/M_n = 1.02\text{-}1.23$). The polymer samples for ^1H NMR were purified by preparative SEC (column: Shodex KF-2002) to be free from the unreacted remaining monomers. The glass-transition temperature (T_g : midpoint of the transition) of the polymers was recorded on a Q200 differential scanning calorimeter (DSC) (TA Instruments Inc.). Certified indium and sapphire were used for the temperature and heat flow calibration. The samples were first heated to $300\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$, equilibrated at this temperature for 5 min, and then cooled to $40\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$. After being held at this temperature for 5 min, the sample was then reheated to $350\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$. All T_g values were obtained from the second scan, after removing the thermal history. Thermogravimetric analyses (TGA) were performed on a Q500 system (TA Instruments Inc.) at $5\text{ }^\circ\text{C}/\text{min}$ under a N_2 gas flow.

3. Results and discussion

3.1. Radical copolymerization of valencene with various electron-acceptor monomers

The radical copolymerizations of Val with various electron-acceptor monomers such as PhMI, CyMI, MA, MMA, and AN were investigated at a 1:1 molar feed ratio in $\text{PhC}(\text{CF}_3)_2\text{OH}$ at $60\text{ }^\circ\text{C}$ using AIBN as a radical initiator (Table 1). Although the radical homopolymerization of

Val did not occur, Val was copolymerized with those electron-acceptor monomers. In all cases, the conversion of Val was lower than that of its comonomers, and the incorporation (mol%) in the copolymers was thus consistently below 50% due to the non-homopolymerizability of Val. However, the incorporation of Val was high in spite of the bulkier substituent as a sesquiterpene when compared with Lim as a monoterpene, which has a similar 1,1-disubstituted unconjugated vinyl group attached to a less bulky cyclohexenyl substituent [55,59,61,62]. In addition, the incorporation of Val in the copolymerization with maleimide derivatives such as PhMI and CyMI was approximately 40% (entries 1 and 3), higher than the 33% theoretical value for 1:2 radical copolymerization observed for Lim and maleimide derivatives in our previous paper (entries 2 and 4).

Table 1

Free radical copolymerization of valencene or limonene with various electron-acceptor monomers in PhC(CF₃)₂OH at 60 °C.^a

entry	M ₁	M ₂	Time (h)	Conv. (M ₁ /M ₂) ^f (%)	M _n ^g	M _w /M _n ^g	M ₁ /M ₂ ^h (Calcd)	M ₁ /M ₂ ⁱ (NMR)
1	Val	PhMI	48	39/56	3500	1.76	41/59	41/59
2	Lim	PhMI	113	50/99	9400	2.16	34/66	38/62
3	Val	CyMI	48	34/54	3300	1.54	39/61	40/60
4	Lim	CyMI	106	45/99	7700	2.00	31/69	34/66
5	Val	MA	48	14/30	3100	1.71	32/68	30/70
6 ^{b,c}	Lim	MA	490	20/55	8500	1.96	27/73	20/80
7	Val	MMA	28	9/68	8400	1.95	12/88	0.2/99.8
8 ^{c,d}	Lim	MMA	27	1/95	25600	3.12	1/99	0.01/99
9	Val	AN	24	4/7	1300	1.54	37/63	24/76
10 ^e	Lim	AN	144	23/51	4100	2.64	31/69	33/67

^a[M₁]₀/[M₂]₀/[AIBN]₀ = 600/600/8.0 mM. ^b[M₁]₀/[M₂]₀/[AIBN]₀ = 1000/1000/10 mM.

^cReference 61. ^d[M₁]₀/[M₂]₀/[AIBN]₀ = 1000/2000/20 mM. ^e[M₁]₀/[M₂]₀/[AIBN]₀ = 1000/1000/20 mM. ^fDetermined by ¹H NMR analysis of reaction mixtures. ^gDetermined by size-exclusion chromatography. ^hDetermined by the monomer feed ratio and monomer conversion. ⁱDetermined by ¹H NMR analysis of the obtained polymers.

3.2. Monomer reactivity in radical copolymerization of valencene and *N*-phenylmaleimide or methyl acrylate

The radical copolymerization of Val and PhMI was then investigated at a 1:2 feed ratio in PhC(CF₃)₂OH at 60 °C using AIBN and was compared with that of Lim and PhMI under the same conditions (Fig. 1). The consumption of both Val and PhMI was slower than that for Lim and PhMI under the same conditions (Fig. 1). The conversion of Val was higher than that of PhMI, unlike the same conversions that were achieved for Lim and PhMI at the 1:2 feed ratio. In addition, the nearly constant conversions after approximately 100 h can be ascribed to almost complete consumption of the radical initiator. The molecular weight of the polymers was lower than that of the Lim and PhMI reaction, most likely due to the slower propagation rate and/or higher chain transfer constant of Val.

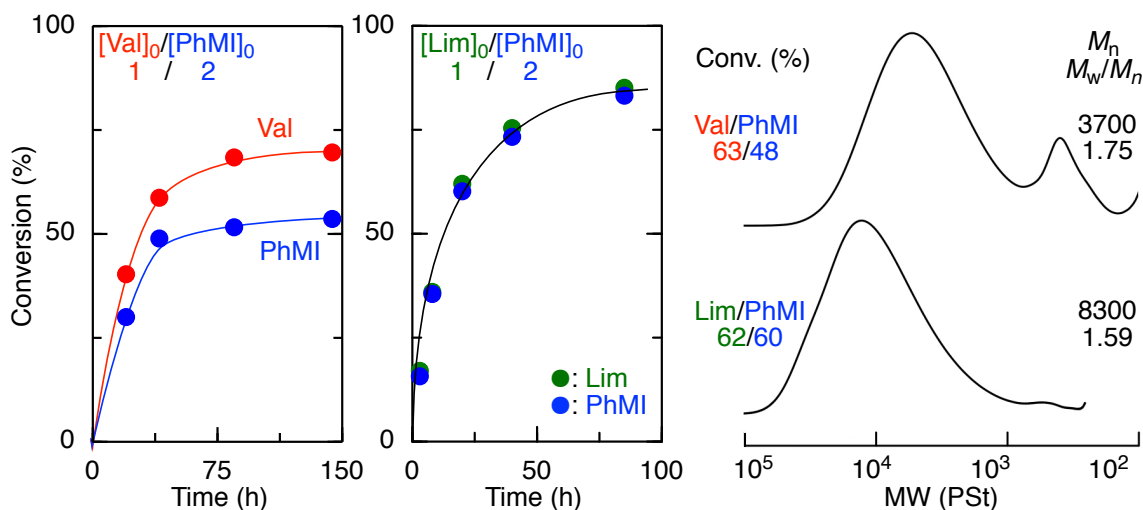


Fig. 1. Time-conversion curves for radical copolymerization of valencene (Val) or limonene (Lim) with *N*-phenylmaleimide (PhMI) at 1:2 monomer feed ratio in PhC(CF₃)₂OH at 60 °C and size-exclusion chromatography (SEC) curves of the obtained copolymers: [Val]₀ = [Lim]₀ = 400 mM, [PhMI]₀ = 800 mM, [AIBN]₀ = 8.0 mM.

The ¹H NMR spectrum (Fig. 2B) of the obtained polymers shows broad signals in the aliphatic regions from 0.5 to 4.0 ppm, which are due to the pendent protons of the Val unit (Fig. 2A) and main-chain methylene and methine protons of the Val and PhMI units generated via the vinyl copolymerization, and phenyl protons (*p*) of the PhMI unit in the aromatic regions (7.0–7.5 ppm). The remaining internal olefin proton (*f*) at 5.1–5.4 ppm and disappearance of the *exo*-olefin (*a*) at 4.7 ppm suggest that Val was incorporated into the copolymers via an addition

reaction of the 1,1-disubstituted vinyl group. The unit ratio of Val and PhMI calculated from peaks *f* and *p* was 37/63 mol%, which is close to the calculated value (40/60 mol%) from the initial feed ratio and conversions of the monomers, indicating that the incorporation of Val measured by ¹H NMR of the resulting copolymers was also higher than 33 mol%. These results demonstrate that Val was radically copolymerized via a reaction of the *exo*-olefin and that its copolymerizability with PhMI was higher than that of Lim with PhMI.

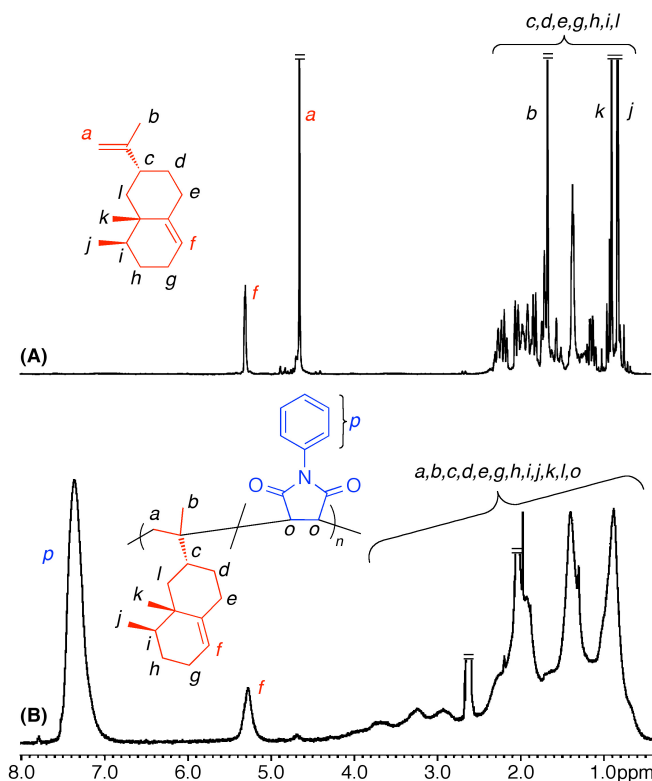


Fig. 2. ¹H NMR spectra ((A): CDCl₃, 25 °C, (B): (CD₃)₂CO, 50 °C) of valencene (Val) (A) and copolymers (B) of Val and *N*-phenylmaleimide (PhMI) obtained in the radical copolymerization at 1:2 monomer feed ratio in PhC(CF₃)₂OH at 60 °C: [Val]₀ = 400 mM, [PhMI]₀ = 800 mM, [AIBN]₀ = 8.0 mM

To further evaluate the copolymerizability of Val with PhMI, Val (M₁) was copolymerized with PhMI (M₂) under varying feed ratios in PhC(CF₃)₂OH as well as toluene at 60 °C. The incorporation of Val units obtained at the initial stages (total conversion ≤ 15%) in the radical copolymerization was plotted against the initial feed ratio of the monomers (Fig. 3). The plots obtained in PhC(CF₃)₂OH (red-filled circles) were consistently higher than those obtained in toluene (red-filled triangles), suggesting that the copolymerizability of Val is higher in the

fluorinated alcohol than in toluene. The plots for Val in $\text{PhC}(\text{CF}_3)_2\text{OH}$ were also higher than those for Lim in the same fluoroalcohol (green-filled circles), namely, the line for 1:2 copolymerization (0.33). Furthermore, almost all the plots for Val in $\text{PhC}(\text{CF}_3)_2\text{OH}$ were located below the dotted line (0.5) for 1:1 alternating copolymerization and above that (0.33) for 1:2 copolymerization. These results indicate again that no homopolymerization of Val occurs and further suggest that the 1:1 and 1:2 copolymerizations of Val and PhMI concurrently occur in $\text{PhC}(\text{CF}_3)_2\text{OH}$.

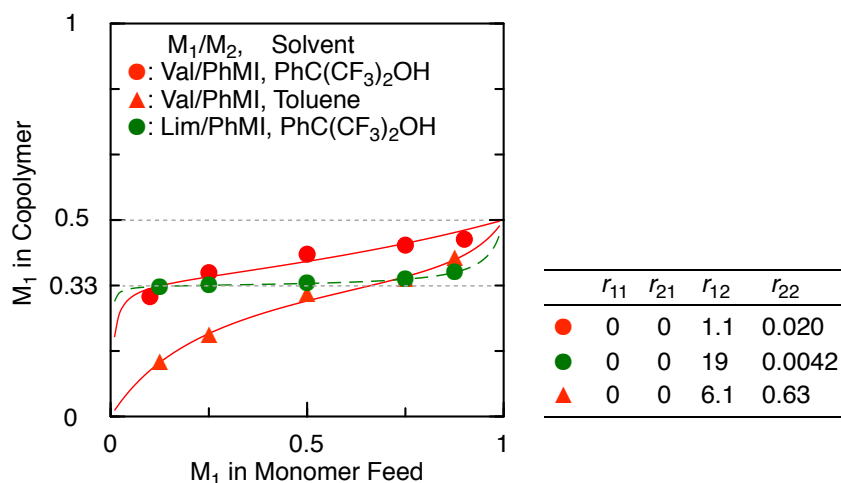
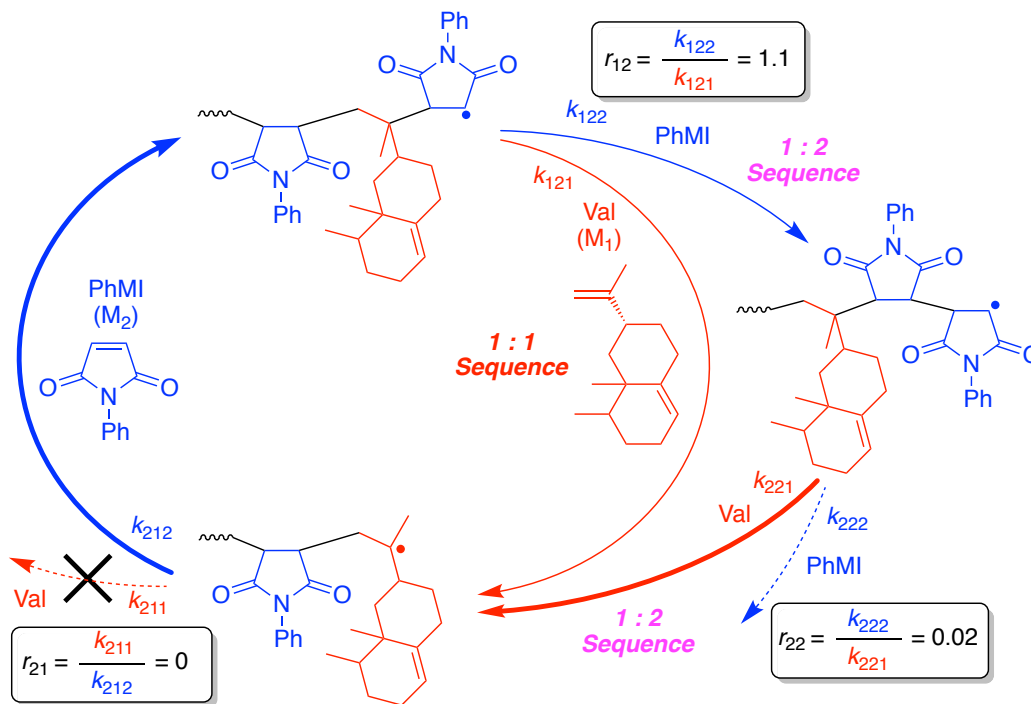


Fig. 3. Copolymer composition curves for radical copolymerization of valencene (Val) or limonene (Lim) as M_1 and N -phenylmaleimide (PhMI) as M_2 in $\text{PhC}(\text{CF}_3)_2\text{OH}$ or toluene at 60 °C obtained at varying the monomer feed ratios: $[M_1]_0 + [M_2]_0 = 1.2 \text{ M}$, $[\text{AIBN}]_0 = 8.0 \text{ mM}$. The curved lines were fitted by the Kelen-Tüdös method for the penultimate model assuming that no homopropagation of Val or Lim occurs ($r_{11} = r_{21} = 0$).

These data were analyzed using the penultimate model and assuming that the homopropagation of Val does not occur ($r_{11} = r_{21} = 0$) [72,73]. They were fitted well with the solid red line, which was obtained by the monomer reactivity ratios using the Kelen-Tüdös method [55,59,62]. The r_{12} value in $\text{PhC}(\text{CF}_3)_2\text{OH}$ was 1.1, which means that the PhMI radical with a penultimate Val unit has almost no preference for Val or PhMI monomers, resulting in a Val radical with a penultimate PhMI unit (path a) and a PhMI radical with a penultimate PhMI unit (path b) at almost the same probability, particularly under the same concentrations of both monomers (Scheme 2). In addition, the r_{22} value was 0.020, nearly zero, which indicates that the PhMI radical with a penultimate PhMI unit highly selectively reacts with Val to complete the

1:2 sequence. These results demonstrate that both the 1:1 and 1:2 copolymerizations concurrently proceed in PhC(CF₃)₂OH and occur at almost the same probability, particularly with similar monomer feed ratios. Therefore, the copolymerizability of Val was proven to be higher than that of Lim, which only results in the 1:2 monomer sequence and a lower incorporation of the terpene unit.



Scheme 2. Radical copolymerization of valencene (val) with *N*-phenylmaleimide (PhMI) via 1:1 and 1:2 concurrent propagation

On the other hand, the highly selective 1:2 monomer sequence for Lim can be ascribed to the presence and location of the internal olefin in the penultimate Lim unit because similar selective 1:2 monomer propagation occurs for β -pinene and 4-isopropenylcyclohexene that can both result in similar endocyclic olefins at the same position in the cyclohexenyl ring of the penultimate unit relative to the terminal maleimide radical [62]. However, in the case of Val, the endocyclic olefin is located slightly far from the terminal PhMI radical. The endocyclic olefin at the specific position in the penultimate olefin unit may interact with the terminal PhMI radical intramolecularly to enhance the selective reaction with the electron-deficient PhMI to form the ABB sequence selectively in the case of Lim, β -pinene, and 4-isopropenylcyclohexene.

In toluene, the r_{12} value was 6.1, indicating that the PhMI radical with a penultimate Val

unit reacts with PhMI at a rate approximately six times greater than that with Val to preferentially form the PhMI radical with the penultimate PhMI unit. Furthermore, the r_{22} ($= k_{222}/k_{221}$) value of 0.63, i.e., $\sim 4/6$, means that the resulting PhMI radical with a penultimate PhMI unit will statistically react with PhMI approximately 4 times out of 10 ($= 4 + 6$) propagations with both PhMI and Val, particularly with similar monomer concentrations. This indicates that a PhMI sequence of more than three units can occur due to the low copolymerizability of Val in toluene. Thus, $\text{PhC}(\text{CF}_3)_2\text{OH}$ enhances the copolymerizability of Val with PhMI via hydrogen bonding interactions with the carbonyl groups in PhMI as well as in the terminal and penultimate PhMI units as in the copolymerization of Lim and PhMI [55,59,62].

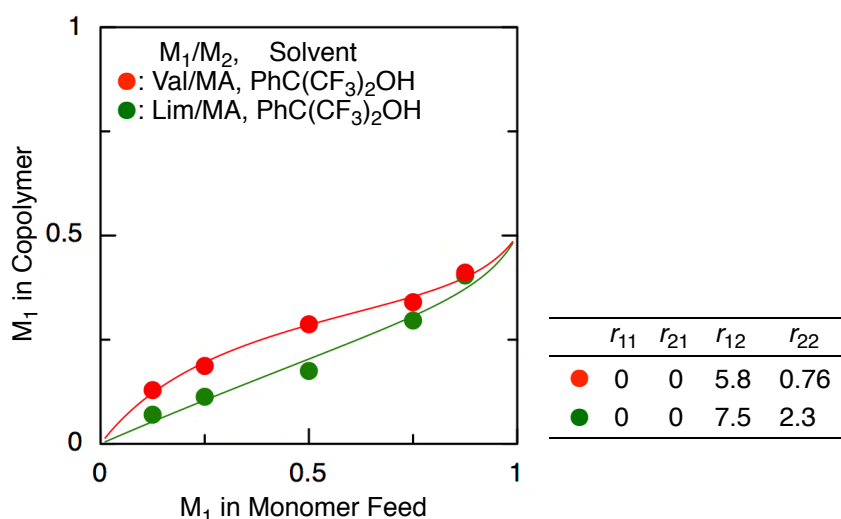


Fig. 4. Copolymer composition curves for radical copolymerization of valencene (Val) as M_1 and methyl acrylate (MA) as M_2 in $\text{PhC}(\text{CF}_3)_2\text{OH}$ at 60 °C obtained at varying the monomer feed ratios: $[M_1]_0 + [M_2]_0 = 1.2 \text{ M}$, $[\text{AIBN}]_0 = 8.0 \text{ mM}$. The curved lines were fitted by the Kelen-Tüdös method for the penultimate model assuming that no homopropagation of Val occurs ($r_{11} = r_{21} = 0$).

A higher copolymerizability of Val than Lim was also observed for radical copolymerization with acrylate in $\text{PhC}(\text{CF}_3)_2\text{OH}$. As shown in Fig. 4, the incorporation of Val (red-filled circles) was consistently higher than that of Lim (green-filled circles) in the copolymers with MA as a comonomer. The copolymer composition curves, which were similarly obtained by using the Kelen-Tüdös method for the penultimate model, were fitted well with these plots. Both the r_{12} and r_{22} values for Val were smaller than those for Lim (r_{12} : 5.8 (Val) $<$ 7.5 (Lim), r_{22} : 0.76 (Val) $<$ 2.3 (Lim)), indicating again the relatively high reactivity of Val in comparison to Lim, even in

the radical copolymerization of MA. Interestingly, the copolymer composition curve as well as the monomer reactivity ratios for Val/MA in PhC(CF₃)₂OH were similar to those for Val/PhMI in toluene.

3.3. RAFT copolymerization of valencene and *N*-phenylmaleimide

To obtain copolymers with controlled molecular weights and chain-end groups, which will lead to clarifying the formed monomer sequences and developing functional polymers, the RAFT copolymerization of Val and PhMI was investigated using CBTC as the RAFT agent, which is effective in controlling the radical copolymerization of Lim and PhMI [59,62], in PhC(CF₃)₂OH at 60 °C. Fig. 5 shows the SEC curves and M_n of the copolymers obtained in the RAFT copolymerization while varying the initial feed ratios of the monomers and RAFT agent ($([Val]_0 + [PhMI]_0)/[CBTC]_0 = 80, 40, \text{ and } 20$; $[Val]_0 = [PhMI]_0 = 600 \text{ mM}$) and at various conversions. Although the molecular weight distributions (MWDs) were slightly broad ($M_w/M_n = 1.3\text{--}1.5$), the SEC curves shifted to high molecular weights as the feed ratios and conversions became larger. The M_n values increased with the feed ratios and the total monomer conversions, aligning in almost a single line, whereas they were lower than the calculated values, assuming that one RAFT agent generates one polymer chain, partially due to the difference in hydrodynamic volumes between the obtained copolymers and standard polystyrenes.

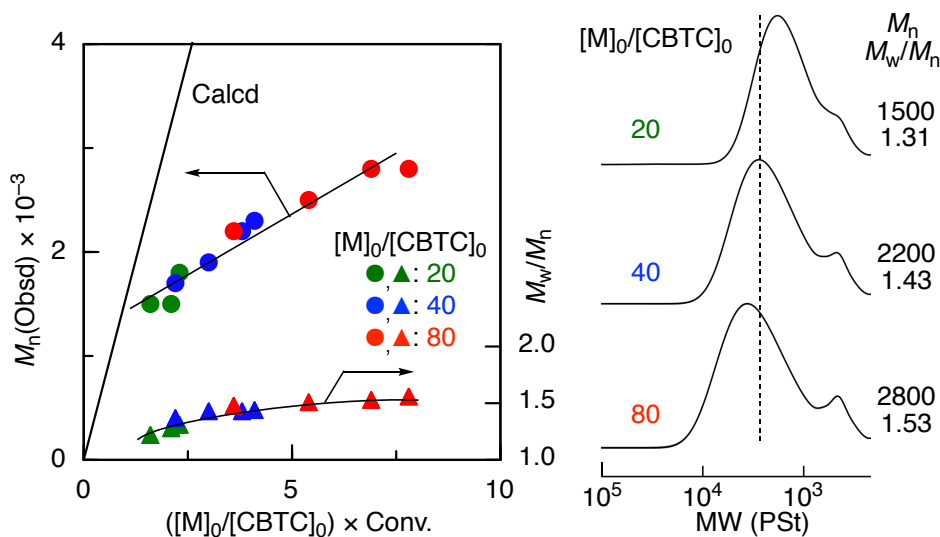


Fig. 5. RAFT copolymerization of valencene (Val) and *N*-phenylmaleimide (PhMI) with *S*-cumyl-*S'*-butyl trithiocarbonate (CBTC) and AIBN in PhC(CF₃)₂OH at 60 °C by varying [CBTC]₀: [Val]₀ = [PhMI]₀ = 600 mM, [CBTC]₀ = 60, 30, and 15 mM, [AIBN]₀ = 8.0 mM.

To clarify the monomer sequences, the copolymers obtained in the RAFT copolymerization were subjected to MALDI-TOF-MS analysis (Fig. 6). The spectrum is relatively simple and consists of several series of peaks. Almost all the relatively large peaks marked by pink-filled circles can be assigned to the copolymers consisting of the 1:1 and 1:2 monomer sequences of Val and PhMI units and capped with cumyl and trithiocarbonate groups at the α - and ω -ends, respectively, whereas the peaks marked by pink-filled triangles are those generated via the loss of the trithiocarbonate moiety at the ω -end, most likely during the laser irradiation for the analysis. Furthermore, the peaks marked by red-filled symbols are ascribed those of the copolymers mainly consisting of the 1:1 monomer sequence. The MALDI-TOF-MS analysis also indicates the coexistence of 1:1 and 1:2-sequenced propagations during the radical copolymerization of Val and PhMI in $\text{PhC}(\text{CF}_3)_2\text{OH}$, which is different from what was observed for the 1:2-selective radical copolymerization of Lim and PhMI in the same solvent [55,59,62].

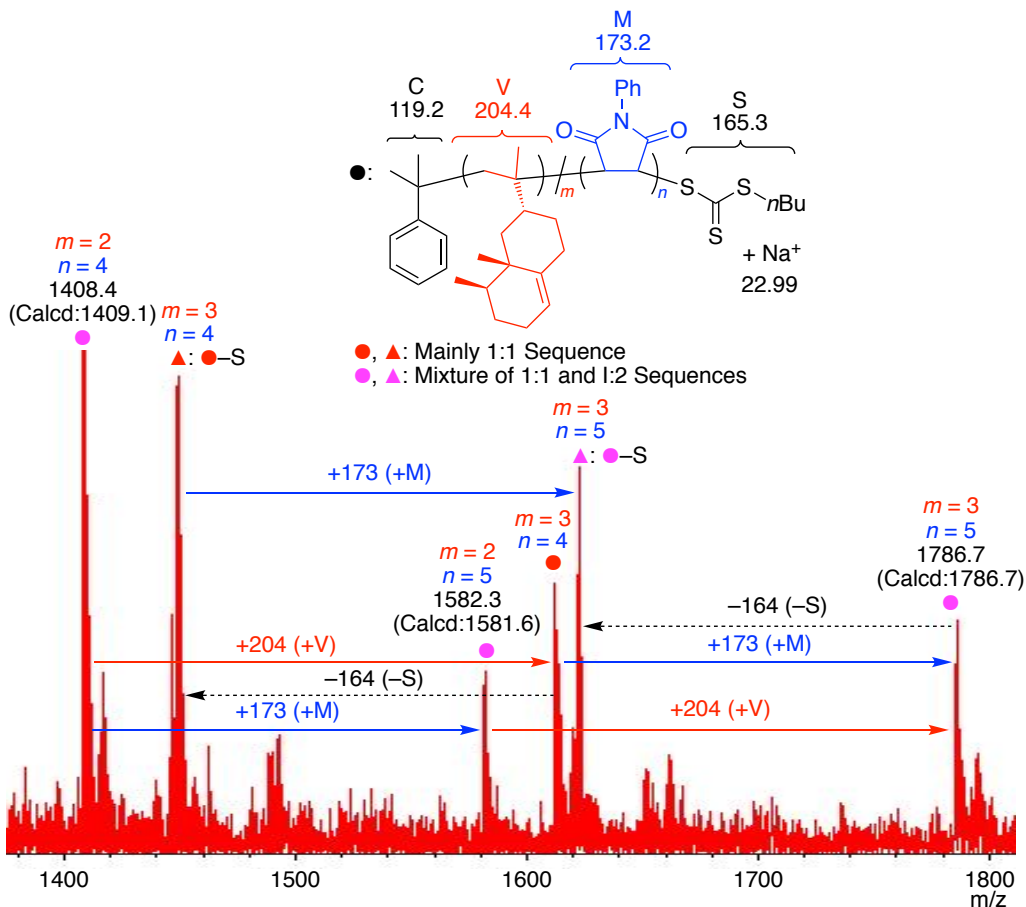


Fig. 6. MALDI-TOF-MS spectrum of copolymers of valencene (Val) and *N*-phenylmaleimide (PhMI) ($M_n = 1300$, $M_w/M_n = 1.27$) obtained at conversion of Val/PhMI = 28%/44% in RAFT copolymerization with *S*-cumyl-*S'*-butyl trithiocarbonate (CBTC) and AIBN.

3.4. Thermal properties of copolymers of valencene and phenylmaleimide

The thermal properties of the copolymers of Val and PhMI with different incorporation ratios, which were obtained by the free radical copolymerization in $\text{PhC}(\text{CF}_3)_2\text{OH}$ at $60\text{ }^\circ\text{C}$ by changing the monomer feed ratios, were analyzed using DSC and TGA (Fig. 7). The glass transition temperatures (T_g) of the copolymers were above $220\text{ }^\circ\text{C}$ due to the two rigid vinyl monomer units and slightly increased from 220 to $242\text{ }^\circ\text{C}$ with an increase in the PhMI incorporation from 59 to $68\text{ mol}\%$. The T_g of the copolymers with Val/PhMI = $32/68\text{ mol}\%$ was almost the same as that ($T_g = 243\text{ }^\circ\text{C}$) of the copolymers of Lim and PhMI with a similar incorporation ratio (Lim/PhMI = $33/67\text{ mol}\%$), despite the bulkier sesquiterpene unit of Val [59,62]. The 5% decomposition temperatures (T_{d5}) were approximately $330\text{--}340\text{ }^\circ\text{C}$ and almost independent of the incorporation ratio, suggesting the relatively high thermal stability of the copolymers.

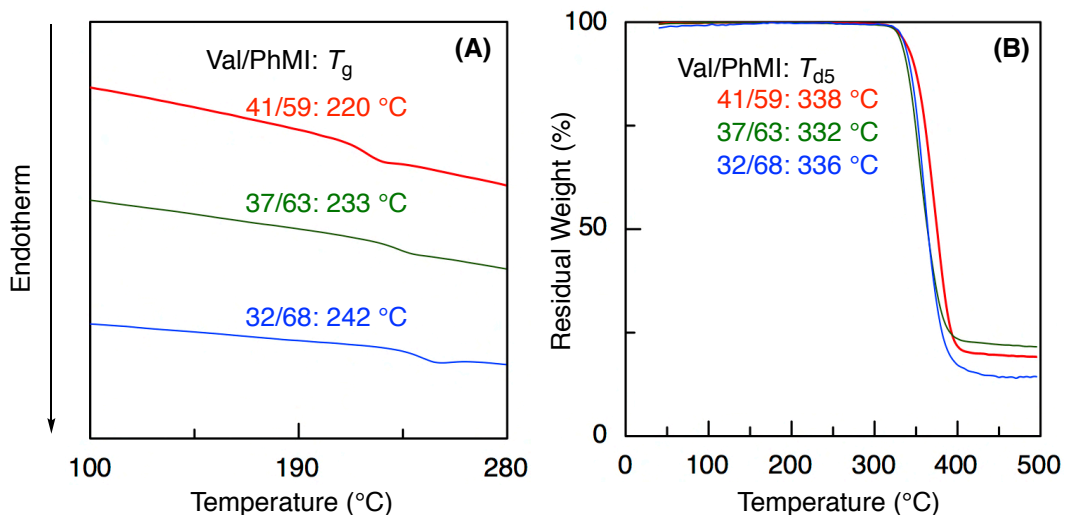


Fig. 7. (A) Differential scanning calorimetry (DSC) and (B) thermogravimetric analysis (TGA) of valencene (Val) and *N*-phenylmaleimide (PhMI) copolymers with different incorporation ratios (Val/PhMI in mol%) and almost the same molecular weights (M_n) obtained in the radical copolymerization in $\text{PhC}(\text{CF}_3)_2\text{OH}$ at $60\text{ }^\circ\text{C}$: $[\text{Val}]_0 + [\text{PhMI}]_0 = 1.2\text{ M}$, $[\text{AIBN}]_0 = 8.0\text{ mM}$: Val/PhMI, M_n : 41/59, 4300 (red lines); 37/63, 4400 (green lines); 32/68, 4900 (blue lines).

4. Conclusion

In conclusion, valencene, which is a naturally occurring sesquiterpene having an unconjugated 1,1-disubstituted vinyl group attached to a fused ring consisting of two C6-rings

and an internal olefin, was radically copolymerized with maleimides, acrylates, and other (meth)acrylic monomers. Valencene showed a higher copolymerizability than limonene, which has a similar unconjugated 1,1-disubstituted vinyl group attached to a single C6-ring with an internal olefin, in spite of the bulkier substituent and underwent concurrent 1:1 and 1:2-radical copolymerization with *N*-phenylmaleimide in PhC(CF₃)₂OH. The obtained copolymers had relatively high glass transition temperatures and high thermal stabilities. The characteristic chemical structures of the biobased products thus enable radical copolymerization with specific monomer sequences to produce novel biobased polymers with unique properties.

Acknowledgments

This work was supported in part by JSPS KAKENHI Grant Number JP18H04647 for M.K. in Hybrid Catalysis for Enabling Molecular Synthesis on Demand.

References

- [1] P.R. Wool, X.S. Sun, *Bio-based polymers and composites*, Elsevier, Oxford, 2005.
- [2] A. Gandini, M.N. Belgacem, *Monomers, polymers and composites from renewable resource*, Elsevier, Oxford, 2005.
- [3] *Sustainable polymers from biomass*, C. Tang, C.Y. Ryu, Eds., Wiley-VCH, Weinheim, 2017.
- [4] M.A.R. Meier, J.O. Metzger, U.S. Schubert, *Plant oil renewable resources as green alternatives in polymer science*, *Chem. Soc. Rev.* 36 (2007)1788–1802.
- [5] A. Gandini, *Polymers from renewable resources: a challenge for the future of macromolecular materials*, *Macromolecules* 41 (2008) 9491–9504.
- [6] G.W. Coates, M.A. Hillmyer, *A virtual issue of Macromolecules: “Polymers from renewable resources”*, *Macromolecules* 42 (2009) 7987–7989.
- [7] Y. Kimura, *Molecular, structural, and material design of bio-based polymers*, *Polym. J.* 41 (2009) 797–807.
- [8] G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, *Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art*, *Biomacromolecules* 11 (2010) 2825–2835.
- [9] U. Biermann, U. Bornsheuer, M.A.R. Meier, J.O. Metzger, H.J. Schäfer, *Oils and fats as renewable raw materials in chemistry*, *Angew. Chem. Int. Ed.* 50 (2011) 3854–3871.
- [10] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.-P. Pascault, *Biobased thermosetting epoxy; present and future*. *Chem. Rev.* 114 (2014) 1082–1115.
- [11] K. Yao, C. Tang, *Controlled polymerization of next-generation renewable monomers and beyond*, *Macromolecules* 46 (2013) 1689–1712.
- [12] R. Müllhaupt, *Green polymer chemistry and bio-based plastics: dreams and reality*, *Macromol. Chem. Phys.* 214 (2013) 159–174.
- [13] S.A. Miller, *Sustainable polymers: opportunities for the next decade*, *ACS Macro Lett.* 2 (2013) 550–554.
- [14] M.A. Hillmyer, W.B. Tolman, *Aliphatic polyester block polymers: renewable, degradable*,

- and sustainable, *Acc. Chem. Res.* 47 (2014) 2390–2396.
- [15] A.L. Holmberg, K.H. Reno, R.P. Wool, T.H. Epps, III, Biobased building blocks for the rational design of renewable block polymers, *Soft Matter* 10 (2014) 7405–7424.
- [16] C. Vilela, A.F. Sousa, A.C. Fonseca, A.C. Serra, J.F.J. Coelho, C.S.R. Freire, A.J.D. Silvestre, The quest for sustainable polyesters – insights into the future, *Polym. Chem.* 5 (2014) 3119–3141.
- [17] C. Voirin, S. Caillol, N.V. Sadavarte, B.V. Tawade, B. Boutevin, P.P. Wadgaonkar, Funcitonalization of cardanol: towards biobased polymers and additives, *Polym. Chem.* 5 (2014) 3142–3162.
- [18] T. Iwata, Biodegradable and bio-based polymers: future prospects of eco-friendly plastics, *Angew. Chem. Int. Ed.* 54 (2015) 3210–3215.
- [19] A.F. Sousa, C. Vilela, A.C. Fonseca, M. Matos, C.S.R. Freire, G.-J.M. Gruter, J.F.J. Coelho, A.J.D. Silvestre, Biobased polyesters and other polymers from 2,5-furandicarboxylic acid: a tribute to furan excellency, *Polym. Chem.* 6 (2015) 5961–5983.
- [20] Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, *Nature* 540 (2016) 354–362.
- [21] V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, B. Boutevin, Biobased amines: from synthesis to polymers; present and future, *Chem. Rev.* 116 (2016) 14181–14224.
- [22] A. Llevot, P.-K. Dannecker, M. von Czapiewski, L.C. Over, Z. Söyer, M.A.R. Meier, Renewability is not enough: recent advances in the sustainable synthesis of biomass-derived monomers and polymers, *Chem. Eur. J.* 22 (2016) 11510–11521.
- [23] M.R. Thomsett, T.E. Storr, O.R. Monaghan, R.A. Stockman, S.M. Howdle, Progress in the sustainable polymers from terpenes and terpenoids, *Green Mater.* 4 (2016) 115–134.
- [24] A. Llevot, E. Grau, S. Carlotti, S. Grelier, H. Cramail, From lignin-derived aromatic compounds to novel biobased polymers, *Macromol. Rapid Commun.* 37 (2016) 9–28.
- [25] D.K. Schneiderman, M.A. Hillmyer, There is a great future in sustainable polymers, *Macromolecules* 50 (2017) 3733–3749.
- [26] H.T.H. Nguyen, P. Qi, M. Rostagno, A. Feteha, S.A. Miller, The quest for high glass transition temperature bioplastics, *J. Mater. Chem. A* 6 (2018) 9298–9331.
- [27] E. Breitmaier, *Terpenes: flavors, fragrances, pharmaca, pheromones*, Wiley-VCH, Weinheim, 2006.
- [28] W.F. Erman, *Chemistry of the monoterpenes: an encyclopedia handbook*, Marcel Dekker, Inc., New York, 1985.
- [29] J.D. Connolly, R.A. Hill, *Dictionary of terpenoids*, Chapman & Hall, London, 1991.
- [30] *Handbook of essential oils: science, technology, and applications*, K.H.C. Başer, G. Buchbauer, Eds., CRC Press, Boca Baton, 2016.
- [31] G.L.K. Hunter, W.B. Brogden, Jr., Terpenes and sesquiterpenes in cold-pressed orange oil, *J. Food Sci.* 30 (1965) 1–4.
- [32] G.L.K. Hunter, W.B. Brogden, Jr., Analysis of the terpene and sesquiterpene hydrocarbons in some citrus oils, *J. Food Sci.* 30 (1965) 383–387.
- [33] M.M. Bomgardner, The sweet smell of microbes, *Chem. Eng. News* 90(29) (2012) 25–29.
- [34] H. Bovill, Natural aroma chemicals from oranges and other botanical sources, *Perfumer & Flavorist* 21 May/June (1996) 9–11.
- [35] E. Maccarone, S. Campisi, B. Fallico, P. Rapisarda, R. Sgarlata, Flavor components of Italian orange juice, *J. Agric. Food Chem.* 46 (1998) 2293–2298.
- [36] A. Högnadóttir, R.L. Rouseff, Identification of aroma active compounds in orange essence oil using gas chromatography–olfactometry and gas chromatography–mass spectrometry, *J.*

- Chromatogr. A 998 (2003) 201–211.
- [37] G. Flamini, P.L. Cioni, I. Morelli, Volatiles from leaves, fruits, and virgin oil from *Olea europaea* cv. Olivastra Seggianese from Italy, *J. Agric. Food Chem.* 51 (2003) 1382–1386.
- [38] X. Wei, M. Song, C. Chen, H. Tong, G. Liang, F.G. Gmitter, Jr., Juice volatile composition differences between Valencia orange and its mutant Rohde Red Valencia are associated with carotenoid profile differences, *Food Chem.* 245 (2018) 223–232.
- [39] C.S. Letizia, J. Cocchiara, G.A. Wellington, C. Funk, A.M. Api, Valencene, *Food Chem. Toxicol.* 38 (2000) S235–S236.
- [40] F. Näf, R. Decorzant, W. Thommen, A stereocontrolled entry to racemic eremophilane and valencene sesquiterpenes via an intramolecular Diels-Alder reaction, *Helv. Chim. Acta*, 65 (1982) 2212–2223.
- [41] M. McGuira, H.C. Odom, A.R. Pinder, Further synthetic studies in the nootkatane sesquiterpene group. a new total synthesis of (±)-valencene and (±)-nootkatone, *J. Chem. Soc. Perkin I* (1974) 1879–1883.
- [42] S. Torii, T. Inokuchi, K. Handa, Functionalization of trans-decalin. V. A synthesis of (±)-nootkatone and (±)-valencene from 4β,4αβ-dimethyl-Δ^{6,7}-octalin-1-one ethylene acetal, *Bull. Chem. Soc. Jpn.* 55 (1982) 887–890.
- [43] P.K. Ajikumar, K. Tyo, A. Carlsen, O. Mucha, T.H. Phon, G. Stephanopoulos, Terpenoids: opportunities for biosynthesis of natural product drugs using engineered organisms, *Mol. Pharm.* 5 (2008) 167–190.
- [44] M. Farhi, E. Marhevka, T. Masci, E. Marcos, Y. Eyal, M. Ovadis, H. Abeliovich, A. Vainstein, Harnessing yeast subcellular compartments for the production of plant terpenoids, *Metab. Eng.* 13 (2001) 474–481.
- [45] J. Beekwilder, A. van Houwelingen, K. Cankar, A.D.J. van Dijk, R.M.de Jong, G. Stoopen, H. Bouwmeester, J. Achkar, T. Sonke, D. Bosch, Valencene synthase from the heartwood of Nootka cypress (*Callitropsis nootkatensis*) for biotechnological production of valencene, *Pant Biotechnol. J.* 12 (2014) 174–182.
- [46] W.D. MacLeod, Jr., N. M. Buigues, Sesquiterpenes. I. Nootkatone, a new grapefruit constituent, *J. Food. Sci.* 29 (1964) 565–568.
- [47] W.D. MacLeod, Jr., The constitution of nootkatone, nootkatene and valencene, *Tetrahedron Lett.* 52 (1965) 4779–4783.
- [48] G.L.K. Hunter, W.B. Brogden, Jr., Conversion of valencene to nootkatone, *J. Food Sci.* 30 (1965) 876–878.
- [49] C.W. Wilson, III, P.E. Shaw, Synthesis of nootkatone from valencene, *J. Agric. Food Chem.*, 26 (1978) 1430–1432.
- [50] M. Furusawa, T. Hashimoto, Y. Noma, Y. Asakawa, Highly efficient production of nootkatone, the grapefruit aroma from valencene, by biotransformation, *Chem. Pharm. Bull.* 53 (2005) 1513–1514.
- [51] K. Satoh, M. Kamigaito, New polymerization methods for biobased polymers, In *Bio-based polymers*, Y. Kimura, Ed., CMC, Tokyo, 2013, pp 95–111.
- [52] M. Kamigaito, K. Satoh, K. Bio-based hydrocarbon polymers, In *Encyclopedia of polymeric nanomaterials*, S. Kobayashi, K. Müllen, Eds, Springer, Heidelberg, 2015, Vol. 1, pp 109–118.
- [53] M. Kamigaito, K. Satoh, Sustainable vinyl polymers via controlled polymerization of terpenes, In *Sustainable polymers from biomass*, C. Tang, C.Y. Ryu, Eds., Wiley-VCH, Weinheim, 2017, pp 55–90.
- [54] K. Satoh, Controlled/living polymerization of renewable vinyl monomers into bio-based

- polymers, *Polym. J.* 47 (2015) 527–536.
- [55] K. Satoh, M. Kamigaito, Controlled/living polymerization of naturally occurring terpenes, *Kobunshi Ronbunshu* 72 (2015) 421–432.
- [56] K. Satoh, H. Sugiyama, M. Kamigaito, Biomass-derived heat-resistant hydrogenated alicyclic hydrocarbon polymers: poly(terpenes) and their derivatives, *Green Chem.* 8 (2006) 878–882.
- [57] K. Satoh, A. Nakahara, K. Mukunoki, H. Sugiyama, H. Saito, M. Kamigaito, Sustainable cycloolefin polymer from pine tree oil for poly(β -pinene). Optoelectronics material and catalytic hydrogenation for high-molecular-weight hydrogenated: living cationic polymerization of β -pinene, *Polym. Chem.* 5 (2014) 3222–3230.
- [58] H. Miyaji, K. Satoh, M. Kamigaito, Bio-based polyketones by selective ring-opening radical polymerization of α -pinene-derived pinocarvone, *Angew. Chem. Int. Ed.* 55 (2016) 1372–1376.
- [59] K. Satoh, M. Matsuda, K. Nagai, M. Kamigaito, AAB-sequence living radical chain copolymerization of naturally-occurring limonene with maleimide: an end-to-end sequence-regulated copolymer, *J. Am. Chem. Soc.* 132 (2010) 10003–10005.
- [60] M. Matsuda, K. Satoh, M. Kamigaito, Periodically functionalized and grafted copolymers via 1:2-sequence-regulated radical copolymerization of naturally occurring functional limonene and maleimide derivatives, *Macromolecules* 46 (2013) 5473–5482.
- [61] M. Matsuda, K. Satoh, M. Kamigaito, Controlled radical copolymerization of naturally-occurring terpenes with acrylic monomers in fluorinated alcohol, *KGK Kaut. Gummi Kunstst.* 66 (5) (2013) 51–56.
- [62] M. Matsuda, K. Satoh, M. Kamigaito, 1:2-Sequence-regulated radical copolymerization of naturally occurring terpenes with maleimide derivatives in fluorinated alcohol, *J. Polym. Sci., Part A: Polym. Chem.* 51 (2013) 1774–1785.
- [63] M. Ojika, K. Satoh, M. Kamigaito, BAB-*random-C* monomer sequence via radical terpolymerization of limonene (A), maleimide (B), and methacrylate (C): terpene polymers with randomly distributed periodic sequences, *Angew. Chem. Int. Ed.* 56 (2017) 1789–1793.
- [64] K. Satoh, S. Saitoh, M. Kamigaito, A linear lignin analogue: phenolic alternating copolymers from naturally occurring β -methylstyrene via aqueous-controlled cationic copolymerization, *J. Am. Chem. Soc.* 129 (2007) 9586–9587.
- [65] Y. Nonoyama, K. Satoh, M. Kamigaito, Renewable β -methylstyrenes for bio-based heat-resistant styrenic copolymers: radical copolymerization enhanced by fluoroalcohol and controlled/living copolymerization by RAFT, *Polym. Chem.* 5 (2014) 3182–3189.
- [66] K. Satoh, D.-H. Lee, K. Nagai, M. Kamigaito, Precision synthesis of bio-based acrylic thermoplastic elastomer by RAFT polymerization of itaconic acid derivatives, *Macromol. Rapid Commun.* 35 (2014) 161–167.
- [67] H. Takeshima, K. Satoh, M. Kamigaito, Bio-based functional styrene monomers derived from naturally occurring ferulic acid for poly(vinylcatechol) and poly(vinylguaicol) via controlled radical polymerization, *Macromolecules* 50 (2017) 4206–4216.
- [68] H. Takeshima, K. Satoh, M. Kamigaito, Scalable synthesis of bio-based functional styrene: protected vinyl catechol from caffeic acid and controlled radical and anionic polymerizations thereof, *ACS Sustainable Chem. End.* 6 (2018) 13681–13686.
- [69] H. Takeshima, K. Satoh, M. Kamigaito, Naturally-derived amphiphilic polystyrenes prepared by aqueous controlled/living cationic polymerization and copolymerization of

- vinylguaiacol with R–OH/BF₃·OEt₂, *Polymers* 10 (2018) 1404.
- [70] Y. Terao, K. Satoh, M. Kamigaito, Controlled radical copolymerization of cinnamic derivatives as renewable vinyl monomers with both acrylic and styrenic substituents: reactivity, regioselectivity, properties, and functions, *Biomacromolecules* 20 (2019) 192–203.
- [71] S.H. Thang, Y.K. Chong, R.T.A. Mayadunne, G. Moad, E. Rizzardo, A novel synthesis of functional dithioesters, dithiocarbamates, xanthates, and trithiocarbonates, *Tetrahedron Lett.* 40 (1999) 2435–2438.
- [72] J.M.G. Cowie, *Alternating copolymers*, Plenum Press, New York, 1985.
- [73] C. Hagiopol, *Copolymerization: toward a systematic approach*, Kluwer Academic/Plenum Publishers, New York, 1999.