

FOCUS REVIEW

Controlled/living polymerization of renewable vinyl monomers into bio-based polymers

Kotaro Satoh^{1,2}

In this focused review, I present an overview of our recent research on bio-based polymers produced by the controlled/living polymerization of naturally occurring or derived renewable monomers, such as terpenes, phenylpropanoids and itaconic derivatives. The judicious choice of initiating system, which was borrowed from conventional petrochemical monomers, not only allowed the polymerization to proceed efficiently but also produced well-defined controlled/living polymers from these renewable monomers. We were able to find several controlled/living systems for renewable monomers that resulted in novel bio-based polymers, including a cycloolefin polymer, an AAB alternating copolymer with an end-to-end sequence, a phenolic and high- T_g alternating styrenic copolymer, and an acrylic thermoplastic elastomer.

Polymer Journal (2015) 47, 527–536; doi:10.1038/pj.2015.31; published online 13 May 2015

INTRODUCTION

Bio-based polymers are attractive materials from the standpoints of being environmentally benign and sustainable. They are usually derived from renewable bio-based feedstocks, such as starches, plant oils and microbiota, as an alternative to traditional polymers from fossil resources.¹ Most of the bio-based polymers produced in the 1990s were polyesters prepared via condensation or ring-opening polymerization, such as poly(lactic acid) or polyhydroxyalkanoate. However, in response to increasing demands for the sustainable development, since the beginning of this century, various attempts have been made to produce novel bio-based polymers that include new polyester or polyamide skeletons and other macromolecules.^{2–17} Although it remains to be determined whether the concept can achieve profitability by lowering the cost or the total emission of carbon dioxide through reducing the use of fossil oil, the use of bio-based polymers is definitely beneficial as a replacement for general-purpose petrochemical monomers for specific applications.

Various polymerization techniques have been developed for vinyl monomers during the past century, the era of the petrochemical industry.¹⁸ The past few decades have witnessed the development of precision polymerization systems based on controlled/living polymerization, in which traditional petrochemical-derived and commodity vinyl monomers can be converted into high-performance polymers with precisely controlled primary structures, such as molecular weight, polydispersity and end-functionality.^{19–38} These tailor-made polymers may also even rival natural macromolecules with their uniform molecular weight, stereoregularity and controllable sequencing. Among the various living polymerization systems, our group has studied cationic and radical polymerizations: the former involves monomers with electron-donating groups, such as vinyl ethers,

aliphatic olefins and styrenes,^{22,23} whereas the latter applies to most unsaturated compounds bearing C=C bonds.^{24–38} Controlled/living radical polymerization can precisely control the molecular weights and the terminal groups of numerous monomers and has opened a new field of precision polymer synthesis that has been applied to the production of a wide variety of functional materials based on controlled polymer structures. The existence of a huge range of vinyl compounds in natural products motivated us to investigate their addition polymerization by using controlled/living polymerization techniques. Although most polymers produced through vinyl polymerization are non-biodegradable, monomers obtained or derived from natural plants can be alternatives to traditional petrochemicals. In addition, the specific structures originating from natural resources, such as chirality, extremely fused rings and multifunctionality, result in high-performance or functional bio-based polymeric materials.

This focused review describes our recent developments in the controlled/living polymerization of naturally occurring or derived vinyl monomers, which may lead to added-value bio-based polymers with well-defined structures (Figure 1). To attain these polymers, judicious initiating systems could be chosen by categorizing the renewable plant-derived monomers according to the inherent structure of the monomers with respect to conventional petrochemical-derived monomers. By developing a polymerization system for each monomer, one may obtain novel bio-based polymers from less-noticed naturally occurring or derived monomers as renewable resources.

CONTROLLED/LIVING POLYMERIZATION

Living polymerization, defined as polymerization free from side reactions such as termination and chain transfer, affords polymers

¹Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, Aichi, Japan and ²Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, Kawaguchi, Saitama, Japan

Correspondence: Dr K Satoh, Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan.

E-mail: satoh@apchem.nagoya-u.ac.jp

Received 11 March 2015; revised 25 March 2015; accepted 26 March 2015; published online 13 May 2015

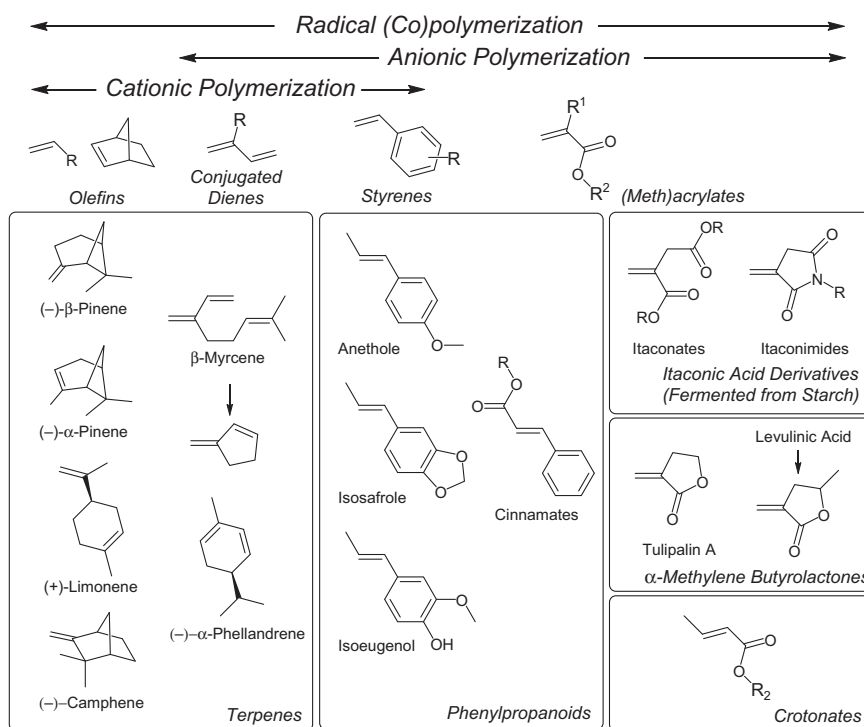


Figure 1 Renewable vinyl monomers, with categories borrowed from petrochemical vinyl compounds.

with well-defined structures and architectures, that is, molecular weight controlled by the initial ratio of the initiator to monomer, narrow molecular weight distribution (MWD), well-defined end-functionality and block copolymerization. Controlled/living polymerizations have remarkably progressed in the field of polymer synthesis, starting from the breakthrough discovery of living anionic polymerization by Szwarc in the 1950s (Scheme 1a).^{19–21} In the 1980s, living cationic polymerization was achieved by the combination of a protonic acid as the initiator and a Lewis acid as the activator, in which the former forms a dormant covalent linkage and the latter reversibly and intermittently activates the dormant bond to suppress the side reactions (Scheme 1b).^{22,23} The extension of the lifetime of the growing carbocation by combination of the initiator and activator is the key to living polymerization. Since the mid-1990s, great progress has been made in controlled/living radical polymerization, which enables the development of numerous types of vinyl monomers, even with polar and functional groups (Scheme 1c). Controlled/living radical polymerization can be categorized into the following three main processes: nitroxide-mediated or stable free-radical polymerization,^{24–26} metal-catalyzed or atom transfer radical polymerization^{27–34} and reversible addition–fragmentation chain transfer polymerization (RAFT).^{35–38} The key to controlled/living radical polymerization lies in the predominant formation of the dormant species at the growing chain end, along with a fast activation–deactivation process relative to the propagation process.

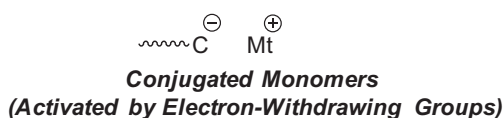
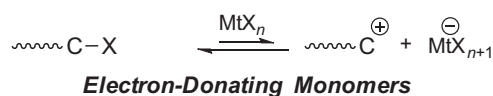
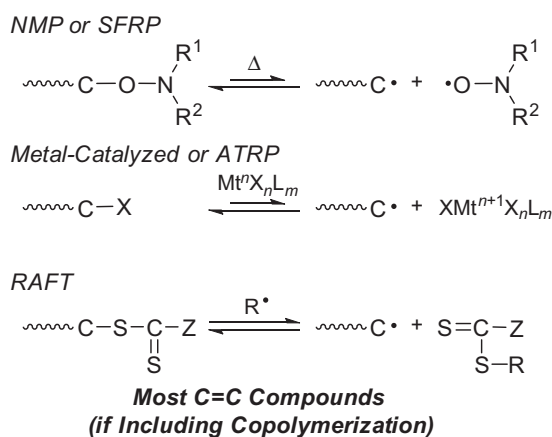
In principle, systems for these controlled/living polymerizations have been implemented depending on the monomer structure. We therefore examined the polymerization of various naturally occurring vinyl compounds by an appropriate choice of the active species as well as the controlled/living system.

CATIONIC POLYMERIZATION OF NATURALLY OCCURRING TERPENE FOR BIO-BASED CYCLOOLEFIN POLYMERS

Monoterpenes are naturally occurring hydrocarbons with the molecular formula $C_{10}H_{16}$. They include a wide range of alicyclic polymerizable olefins, such as limonene, terpinene, phellandrene and pinene, which generally have non-polar, mono- or bicyclic and chiral structures.^{39,40} The cationic polymerizations of terpenes have been studied since the 1950s or earlier to produce low-molecular-weight polymers with inefficient strength and low glass transition temperatures (T_g).^{41–43} Thus, the commercial utilization of terpene oligomers was limited to tackifiers in adhesives or polymer modifiers in molding compounds.

Cycloolefin polymers or copolymers (COPs or COCs) have attracted attention, especially in the optoelectronic fields because of their low dielectric constant, non-hygroscopicity, good transparency and low density in addition to the high service temperature and mechanical strength provided by their rigid backbone.^{44–47} To obtain COPs or COCs, various approaches have been developed and even applied on an industrial scale for the petroleum fraction monomers, such as the ring-opening metathesis polymerization of polycyclic olefins or coordinated polymerization of cyclic olefins.^{48–52} Among the several methods, the vinyl polymerization of cyclic olefins is promising because it retains the cyclic structures. We hypothesize that the polymerization of naturally occurring terpenes to high-molecular-weight polymers and the subsequent hydrogenation will lead to the development of bio-based COPs with good properties for practical use.

β -Pinene is one of the main components of turpentine, which is an abundant and cheap pine tree oil with a global production of over several hundreds of thousands metric tons per year worldwide.^{53,54} The cationic polymerization of β -pinene was reported via an addition and ring-opening mechanism through β -scission.⁴¹ In general, the polymerization of β -pinene results in low-molecular-weight polymers. The highest T_g value ever reported, by Keszler and Kennedy, was only

a Living Anionic Polymerization**b** Controlled/Living Cationic Polymerization**c** Controlled/Living Radical Polymerization

Scheme 1 Controlled/living polymerization of a vinyl monomer: living anionic polymerization (a), controlled/living cationic polymerization (b), and controlled/living radical polymerization (c).

65 °C.⁵⁵ Higashimura and Deng *et al.*^{56–58} achieved the living cationic polymerization of β -pinene in 1997 with $\text{TiCl}_2(\text{OR})_2$ as the catalyst in conjunction with the HCl adduct of an alkyl vinyl ether as the initiator. Lu *et al.*^{59–62} successfully applied living polymerization to prepare various block and graft COCs of β -pinene. The control over the molecular weight with the Ti-based polymerization system, however, was only for low molecular weights with $M_n < 5000$.

In 2006, we first reported that higher-molecular-weight poly(β -pinene) could be produced by controlling the cationic polymerization, followed by hydrogenation into the bio-based COP.⁶³ The cationic polymerization of β -pinene was examined by thoroughly tuning the reaction conditions, such as the Lewis acid catalyst, monomer concentration and solvent, which resulted in relatively high-molecular-weight poly(β -pinene) ($M_w > 5 \times 10^4$). For further control of the molecular weight, the living cationic polymerization of β -pinene was investigated using EtAlCl_2 as the Lewis acid and the hydrogen chloride adduct of α -methylstyrene as the initiator (Scheme 2).⁶⁴ Although the polymerization with the HCl/ EtAlCl_2 system was instantaneous, upon the addition of Lewis bases such as diethyl ether and ethyl acetate, the β -pinene polymerization was moderately retarded to afford living polymers with relatively narrow MWDs ($M_w/M_n \sim 1.2$) at -78 °C in the solvent mixture of CH_2Cl_2 /cyclohexane. By using the HCl/Al-based system, a much higher molecular weight was achieved, up to tens of thousands, with $T_g \sim 90$ °C.

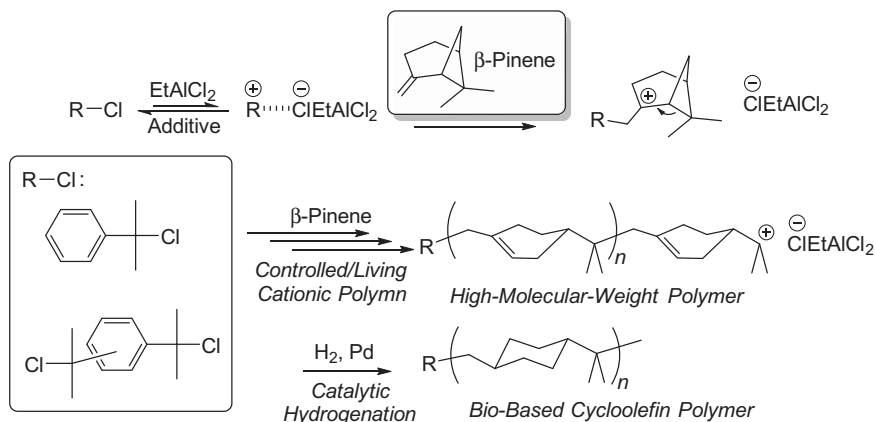
The high-molecular-weight poly(β -pinene) thus obtained was hydrogenated into its saturated form (Figure 2). The hydrogenation

of unsaturated polymers generally leads to higher service temperatures and greater thermal durability. The hydrogenation was then carried out with *p*-toluenesulfonyl hydrazide in *o*-xylene or catalytically with Pd (5 wt%) supported on Al_2O_3 or C in hexane under a 1.0-MPa hydrogen atmosphere. The hydrogenation proceeded quantitatively with the Pd catalyst (>99.9%) to afford a saturated alicyclic hydrocarbon polymer without significant chain scission. The polymerization and hydrogenation could be performed even on a relatively large scale to produce several hundred grams of the polymer, which can be processed through injection molding.⁶⁴ The thermal properties of the bio-based COP were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The T_g was further improved by hydrogenation from 90 to 130 °C, whereas thermal degradation occurred above 400 °C (5% weight loss at 450 °C) for the saturated form. Because the T_g value is responsible for the broad service temperature of such amorphous and transparent polymers without reaching the melting point, the bio-based COP polymer was confirmed to exhibit both a better thermal durability and a higher service temperature than the unsaturated precursor, rivaling the operating parameters of conventional common polymeric materials. In addition to its excellent thermal properties, the bio-based COP showed excellent optical properties as well. The transparency after molding was almost the same as that of poly(methyl methacrylate) (PMMA) (transmittance = 92%), and the birefringence exhibited low values under uniaxial deformation. The bio-based COP possesses excellent physical, thermal and optical properties, rivaling those of conventional optical plastics, and would be applicable for future industrialization. Therefore, we conclude that the abundant terpenes are a promising sustainable resource for the production of COPs not only for their availability but also for their reactivity by cationic polymerization to form high-performance bio-based COPs.

RADICAL (CO)POLYMERIZATION OF TERPENE FOR A SEQUENCE-REGULATED POLYMER

Most monoterpenes are unconjugated olefins and rarely undergo radical homopolymerization. Some examples of radical copolymerization with polar monomers have been reported, such as maleic anhydride and acrylates, in which only a low conversion of terpenes was obtained along with low incorporation into COCs. Attempts have been made to copolymerize β -pinene with various vinyl monomers to produce COCs via β -scission of the growing radical as in cationic polymerization.^{65–67} Lu and colleagues^{68–70} first reported the RAFT copolymerization of β -pinene, which is a typical controlled/living radical polymerization using a thioester compound as the reversible chain transfer agent. Various homopolymerizable monomers, such as acrylonitrile, methylacrylate and *n*-butyl acrylate, were used as comonomers for the combination with β -pinene. As in the copolymerization of petrochemical α -olefins, the copolymerization of β -pinene proceeded to afford COCs with low β -pinene content with acrylonitrile or acrylates (~10%). We found that the use of fluorinated alcohol solvents⁷¹ enhanced the copolymerizability, resulting in the moderate incorporation of β -pinene, up to 34 mol%, in the COC with methylacrylate.⁷² The RAFT copolymerization of β -pinene with *N*-phenylmaleimide exhibited typical features in a controlled manner, with relatively high consumption of β -pinene at a close to 1:2 consumption ratio of β -pinene and *N*-phenylmaleimide, although severe retardation was observed in the copolymerization with *N*-alkylmaleimides.^{73–75}

Among the various terpenes, *d*-limonene (Lim) is one of the most representative and abundant compounds, with an annual production estimated to be over a hundred thousand tons per year.^{39,40,53} However, Lim has less copolymerizability than β -pinene and has



Scheme 2 Synthesis of a high-molecular-weight bio-based cycloolefin polymer by the controlled/living cationic polymerization of β -pinene followed by catalytic hydrogenation.

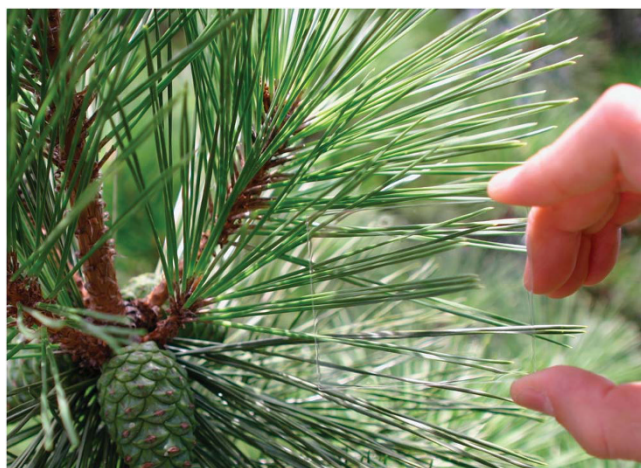


Figure 2 Photograph of a specimen of high-molecular-weight hydrogenated poly(β -pinene) produced through hot-pressed molding at 200 °C.

rarely copolymerized with vinyl monomers such as acrylate, even in fluoroalcohol,⁷² although there have been some reports on its free-radical copolymerization.^{76–78} In 2010, we reported the quantitative radical copolymerization of Lim with *N*-arylmaleimide or *N*-alkylmaleimide derivatives, such as *N*-phenylmaleimide and *N*-cyclohexylmaleimide, in fluoroalcohol to produce near-perfect 1:2 alternating COCs.⁷⁹ Lim could be replaced by other limonene-like terpenes such as β -pinene (Figure 3).^{73,74,80,81} In $\text{PhC}(\text{CF}_3)_2\text{OH}$, the terpene and maleimides were smoothly consumed at an almost 1:2 ratio to COCs with moderate molecular weights irrespective of the feed ratio, and the 1:2 cross propagation was confirmed using a monomer reactivity ratio with a penultimate model. Similar features were subsequently reported for various combinations of vinyl monomers with maleimides, although Lim gave the highest tendency for the 1:2 copolymerization.^{75,82,83} The selective propagation is assumed to be owing to the interaction of the fluorinated alcohol solvent with the carbonyl groups in the maleimide unit and the bulkiness of the penultimate alicyclic structure of Lim. The COCs obtained from the terpenes and maleimides exhibited a higher T_g (220–250 °C) and chirality ($[\alpha]_D \sim 8$ for *d*-limonene and ~ 77 for β -pinene).^{75,79}

When coupled with RAFT copolymerization using *n*-butyl cumyl trithiocarbonate as the RAFT agent in $\text{PhC}(\text{CF}_3)_2\text{OH}$, not only control

over the molecular weight but also a well-defined initiating and end-capping sequence was achieved, along with selective 1:2 alternating propagation.⁷⁹ As also shown in Figure 3, the obtained COC showed a simple matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrum with the highest series of peaks separated by the total molecular weights of one terpene and two maleimide units, which is totally different from the simulated spectrum of statistical random COCs with multiple sequences.

This 1:2 sequence-regulated propagation is applicable to the specific functionalization of the polymer main chain by using a hydroxyl-functionalized monoterpene, such as perillyl alcohol and carveol, to produce periodically functionalized bio-based copolymer possessing one hydroxyl group in every three-monomer unit.⁸⁰ On the other hand, a hydroxyl-functionalized maleimide afforded two hydroxyl groups in every three-monomer unit. The functionality was further converted into periodic graft or comb-like polymer chains^{84,85} in every three-monomer units in combination with the ruthenium-catalyzed living radical polymerization of methyl methacrylate initiated from the backbone COCs (Scheme 3).

NATURALLY OCCURRING CONJUGATED DIENES

Monoterpene and sesquiterpene both possess naturally occurring conjugated 1,3-dienes (Scheme 4). Some acyclic conjugated dienes such as β -myrcene and β -farnesene can be polymerized into living polymers similar to isoprene or butadiene via anionic polymerization.⁸⁶ Quirk *et al.*^{87,88} reported a poly(styrene-*b*-myrcene-*b*-styrene) triblock copolymer, which could be used as a thermoplastic elastomer. Hoye and Hillmyer⁸⁹ reported a similar polymer combined with bio-based styrene prepared by the dehydrogenation of limonene. They also reported that the acyclic monoterpene of myrcene can be converted into a cyclic diene, 3-methylenecyclopentene by ring-closing metathesis.⁹⁰ The cyclic diene monomer could be polymerized into a COP by both anionic and cationic polymerization systems, in which the living cationic polymerization is attained in a 1,4-regioselective manner, although the polymers are semicrystalline even after hydrogenation. A similar cyclic monoterpene with a conjugated diene skeleton from plant-derived oil was also cationically polymerized into a COP. We also examined the Lewis acid-catalyzed cationic polymerization of α -phellandrene, which has a conjugated diene structure along with an alicyclic skeleton. Although the molecular weight was low ($M_w \sim 1 \times 10^4$), the polymer from α -phellandrene exhibited a relatively high T_g (> 130 °C), even in the unsaturated form.⁶³

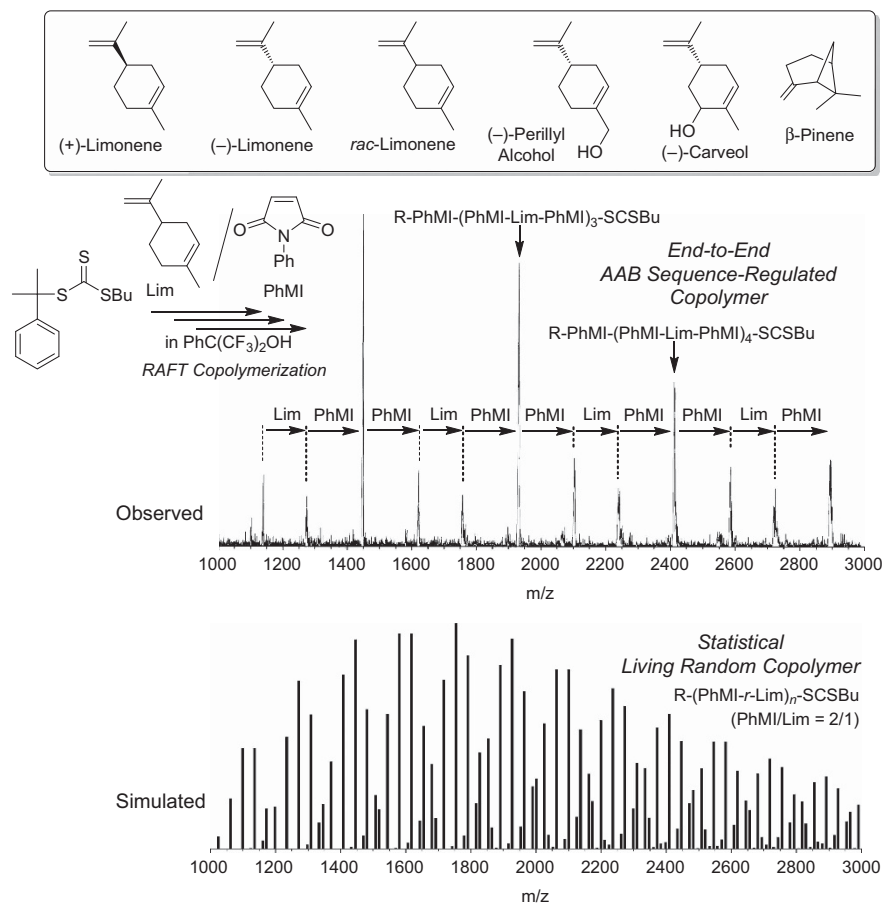
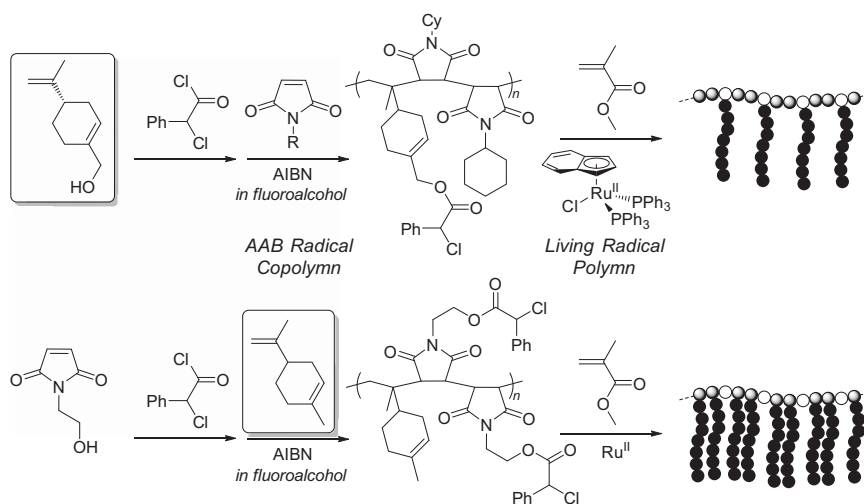


Figure 3 Monoterpenes for 1:2 alternating copolymerization with maleimide derivatives and MALDI-TOF mass spectrum of the end-to-end AAB sequence-regulated copolymer of *d*-limonene (Lim) with *N*-phenylmaleimide (PhMI) obtained by reversible addition-fragmentation chain transfer polymerization (RAFT) copolymerization compared with a simulated spectrum of a statistical living random copolymer.



Scheme 3 AAB sequence-regulated radical copolymerization of functional limonene and maleimide and ruthenium-catalyzed polymerization of MMA for periodically grafted copolymers.

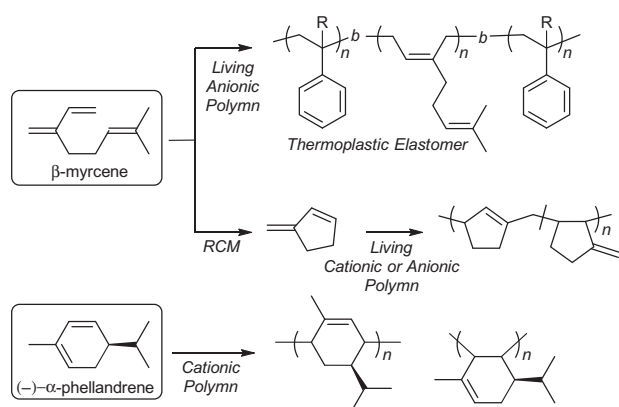
CATIONIC POLYMERIZATION OF NATURALLY OCCURRING STYRENES

β -Substituted styrenes are also abundantly produced in natural plants as phenylpropanoids, which contain a phenyl ring with a C_3 side chain derived from phenylalanine and/or tyrosine. The most abundant poly

(phenylpropanoid) in nature is lignin, which is the main constituent of the cell walls of plants for antioxidant and sunburn protection, and is biosynthesized via oxidative coupling rather than vinyl polymerization.⁹¹ The naturally occurring cinnamic derivatives can be converted into styrenic monomers via decarboxylation, which

polymerizes easily in the same manner as petrochemical styrenes.^{92–94} β -Substituted styrene derivatives have rarely been used directly as monomers to attain β -substituents because the steric effect inhibits the propagation, although we can obtain various β -methylstyrenes from nature, such as *trans*-anethole (4-methoxy derivative) from anise or fennel oil and isoeugenol (4-hydroxy-3-methoxy derivative) or its precursor of eugenol from clove or ylang-ylang oil, of which thousands of tons are annually put to practical use in the flavor and fragrance industry.^{18,95} Although there are reports of their conventional cationic (co)polymerizations, they resulted in only ill-defined polymers or low-molecular-weight oligomers in low yields.^{96–101} Among them, isoeugenol is one of the most promising monomers as the model for the lignin components due to its coniferyl [(4-hydroxy-3-methoxyphenyl)propenyl] structure, availability and expected reactivity.

We investigated the controlled/living cationic polymerization and copolymerization of isoeugenol, as well as *trans*-anethole



Scheme 4 Controlled/living polymerization of naturally occurring conjugated 1,3-dienes.

(Figure 4).^{102,103} For this, we used a unique system based on borontrifluoride etherate (BF_3OEt_2) as the catalyst coupled with the water adduct of the monomer as the initiator, which efficiently induces the direct controlled/living cationic polymerization of *p*-hydroxystyrene without any protection of its phenolic group.^{104–106} This system requires water in an amount approximately equal to the monomer concentration and a large excess over BF_3OEt_2 , in sharp contrast to the usual living cationic polymerizations in rigorously dried reaction media.^{22,23} The copolymerization of isoeugenol or anethole with *p*-methoxystyrene proceeds in a controlled fashion by the alcohol/ BF_3OEt_2 system to afford copolymers with controlled molecular weights and distributions ($M_w/M_n = 1.2–1.4$), although the homopolymerization of isoeugenol did not proceed.¹⁰² In addition, the copolymerization of isoeugenol proceeds in an almost alternating fashion, in which isoeugenol is simultaneously consumed with *p*-methoxystyrene at almost the same rate. The unprecedented alternating cationic copolymerization exhibited a typical alternating line in the composition curve, similar to that of the conventional alternating radical copolymerization, which is also confirmed by MALDI-TOF-MS (mass spectrometry) analysis. This alternating propagation probably results from the highly bulky and electron-rich IEu. Because phenol-based vinyl polymers have been applicable as photoresists, epoxy-curing agents and antioxidants, isoeugenol-based polymers might also be useful as an alternative to conventional petrochemical polymers.

RADICAL COPOLYMERIZATION OF *B*-METHYLSTYRENE AND OTHER PHENYLPROPANOIDS

The 1,2-disubstituted phenylpropanoid has also been used as a non-homopolymerizable monomer in copolymerizations with petrochemical-derived monomers.^{107–109} Although radical polymerization is highly tolerant of functional groups, the phenolic moiety, as in isoeugenol, is fatal to radical polymerization due to its antioxidative properties.

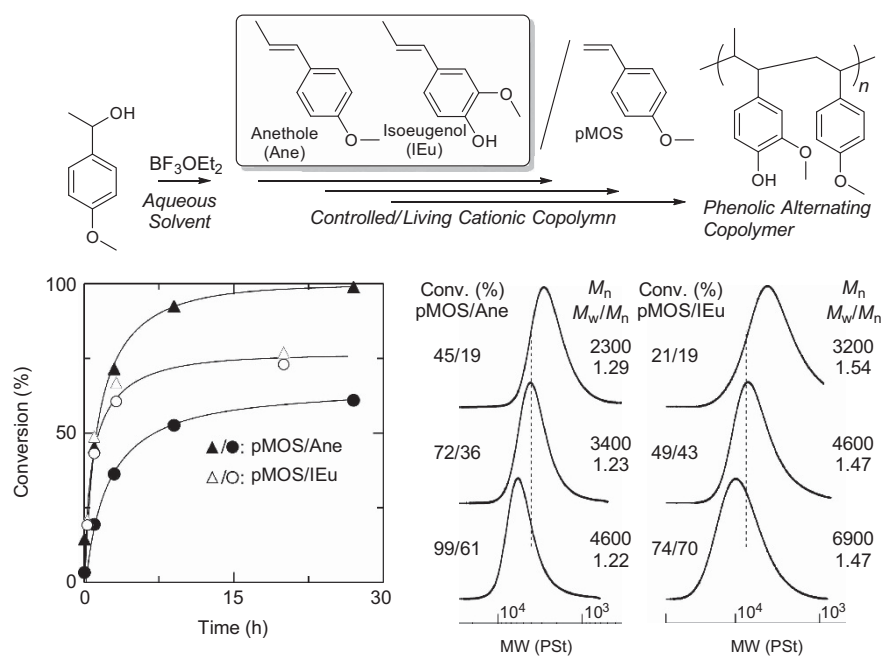
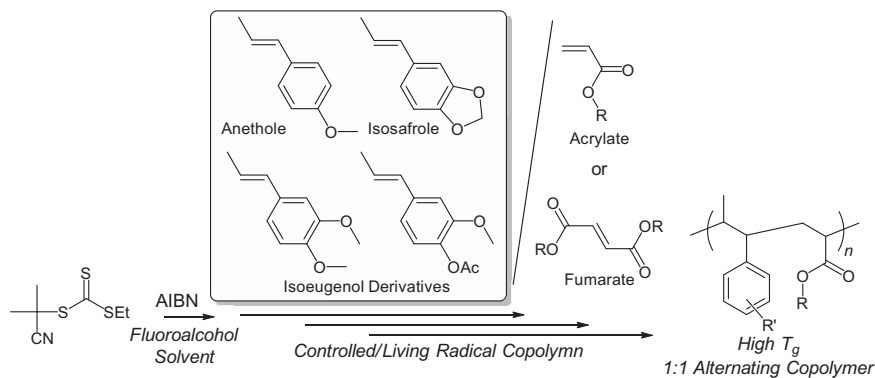


Figure 4 Controlled/cationic copolymerization of *p*-methoxystyrene/anethole (pMOS/Ane) and *p*-methoxystyrene/isoeugenol (pMOS/IEu) to produce a phenolic alternating copolymer: $\text{R-OH}/\text{BF}_3\text{OEt}_2/\text{H}_2\text{O}$ (4.0/10/200 mM for Ane and 4.0/10/100 mM for IEu) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (8/2) at 0 (Ane) or -15°C (IEu), $[\text{pMOS}]_0 = [\beta\text{-methylstyrene}]_0$, $[\text{Ane}]_0 = 100\text{ mM}$ and $[\text{IEu}]_0 = 200\text{ mM}$.



Scheme 5 1:1 Alternating reversible addition–fragmentation chain transfer (RAFT) polymerization of naturally occurring β -methylstyrenes in fluoroalcohol.

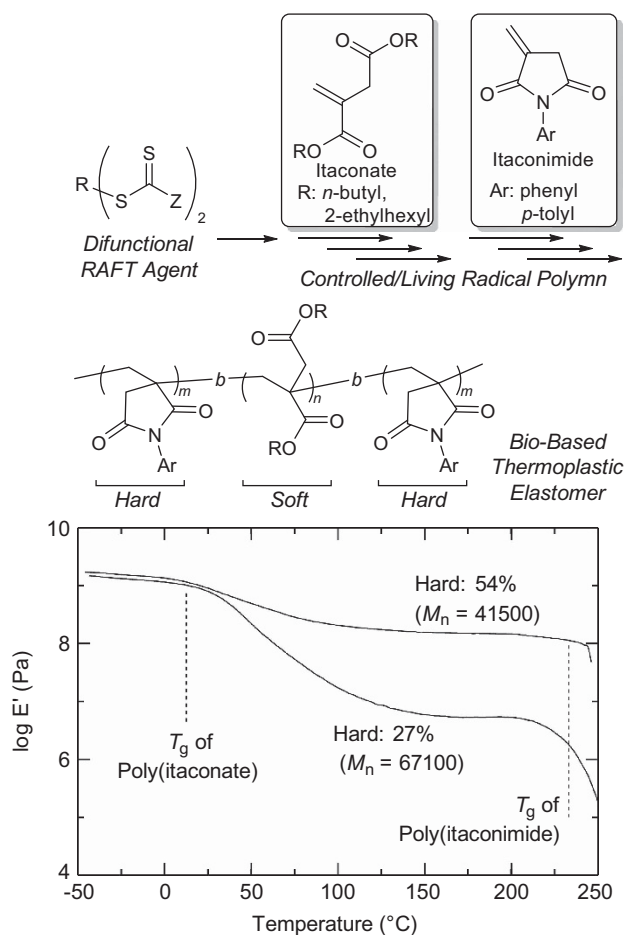


Figure 5 Bio-based triblock copolymer as an acrylic thermoplastic elastomer prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization of dialkyl itaconate and itaconimide and its dynamic tensile storage (E') as a function of temperature (heating rate: $10\text{ }^{\circ}\text{C min}^{-1}$; frequency: 11 Hz) of; $M_n=67,100$, $M_w/M_n=1.20$, dibutyl itaconate/diphenyl itaconimide = 73/27 (wt%); $M_n=41,500$, $M_w/M_n=1.20$, dibutyl itaconate/diphenyl itaconimide = 46/54 (wt%).

We examined the radical copolymerization of β -methylstyrenes, such as anethole, isosafrole, methyl isoeugenol and acetyl isoeugenol, as electron-donating monomers in conjunction with electron-withdrawing monomers, such as maleic anhydride, acrylonitrile

and alkyl acrylates (Scheme 5).¹¹⁰ The controlled/living radical copolymerization of those monomers was examined with 2-cyanoprop-2-yl ethyl trithiocarbonate, which was used as a RAFT agent in conjunction with α , α -azobisisobutyronitrile (AIBN) as the radical source to afford copolymers with controlled molecular weight and distribution ($M_w/M_n \sim 1.2$). Furthermore, the incorporation of β -methylstyrenes into the COCs depends on the reaction solvents, with fluorinated alcohol $m\text{-C}_6\text{H}_4[\text{C}(\text{CF}_3)_2\text{OH}]_2$ giving the highest content ($\sim 50\text{ mol}\%$), which indicates the formation of 1:1 alternating copolymers.⁷¹ The living nature and alternating pattern was confirmed by MALDI-TOF-MS to determine the terminal and sequence structures of the copolymers. The alternating copolymers with relatively narrow MWDs also exhibited a high T_g , up to $\sim 130\text{ }^{\circ}\text{C}$ due to their rigid 1,2-substituted structure. Other phenylpropanoids, such as cinnamic acid derivatives, were also copolymerized with petrochemical monomers in a controlled fashion with RAFT agents or transition metal catalysts.

NATURALLY DERIVED ACRYLIC MONOMERS

(Meth)acrylic compounds are also important monomers in the polymer industry. α -Methylene butyrolactone is a cyclic acrylate analog with an exo-methylene moiety adjacent to a carbonyl group, which is a natural product found in tulips called as tulipalin A.³ This monomer and its derivatives were homopolymerized via radical, anionic, group transfer and coordination polymerizations in a similar manner to methacrylates, although they were originally derived from petrochemical products.^{111–114} The free-radical polymerization of tulipalin A produced polymers with a higher service temperature ($T_g > 190\text{ }^{\circ}\text{C}$) than those from methyl methacrylate ($\sim 110\text{ }^{\circ}\text{C}$) due to the rigid lactone ring, which also provides the polymer with a good durability and a good refractive index. The controlled radical polymerization of tulipalin A with Cu(I)-catalyzed atom transfer radical polymerization was first reported by Matyjaszewski and colleagues^{115,116} to produce polymers with relatively narrow MWDs ($M_w/M_n < 1.2$). The block copolymerization with butyl acrylates could produce a thermoplastic elastomer, with the poly(tulipalin A) segment acting as the hard binding phase. From the biomass-derived levulinic acid, the similar α -methylene- γ -methyl- γ -butyrolactone can be prepared,¹¹⁷ which was also homopolymerized via using the RAFT system in a heterogeneous miniemulsion system to give high T_g polymers.¹¹⁸ Chen and colleagues¹¹⁹ reported a fast and living group transfer polymerization system for these methylene butyrolactones to produce relatively high-molecular-weight polymers with very narrow MWDs ($M_n > 500\text{ K}$, $M_w/M_n = 1.01$). They also reported a living

coordination polymerization system with early transition metal catalysts.¹¹⁴

Itaconic acid and its derivatives are another candidate for bio-based acrylic monomers, which are produced via the fermentation of carbohydrates such as lactic acid or the pyrolysis of natural citric acid. The polymerization of itaconic acid and its diester derivatives has been reported since the 1870s via radical and anionic polymerization to produce relatively high-molecular-weight polymers, and they have been widely used for vinyl copolymerization even in industry.^{120–126} Furthermore, itaconamide and itacoimide were also polymerized via anionic and radical intermediates, with the latter exhibiting excellent thermal properties due to their cyclic structures ($T_g > 220\text{ }^\circ\text{C}$).^{127,128} The RAFT polymerization of alkyl itaconates, an itaconic acid derivative, gave polymers with controlled molecular weights, although the MWDs broadened,^{129,130} and Cu(I)-catalyzed atom transfer radical polymerization was used for the block copolymerization of *N*-aryl itaconimide with methyl methacrylate (MMA).¹³¹ We also examined the controlled/living radical polymerization of itaconic acid derivatives to produce bio-based acrylic thermoplastic elastomer (Figure 5).¹³² The combination of itaconic acid imides, such as *N*-phenylitaconimide and *N*-(*p*-tolyl)itaconimide, and itaconic acid diesters, such as di-*n*-butyl itaconate and bis(2-ethylhexyl) itaconate, succeeded in achieving the sequential block RAFT copolymerization. The RAFT polymerization of both itaconic derivatives proceeded to give polymers with controlled molecular weights with relatively narrow MWDs using both mono- and di-functional RAFT agents. The triblock copolymers were then prepared by the sequential block copolymerization of itaconate and itaconimide, in that order, from di-functional RAFT, which produce chains with inner soft poly(itaconate) and outer hard poly(itaconimide) segments. The obtained triblock copolymer exhibited the characteristic properties of thermoplastic elastomers along with the microphase-separated morphology observed by AFM.

CONCLUSIONS

New bio-based polymers can be synthesized from naturally occurring or derived vinyl monomers by controlled/living polymerization, as has been developed for conventional petrochemicals. To create environmentally benign materials that meet social needs and to establish a new industry, they must satisfy the market needs without losing any performance as materials or costing more. The combination of controlled/living polymerization and renewable vinyl monomers with characteristic skeletons would contribute to further progress in bio-based polymeric materials with high performance and/or functions that will enable their commercialization in the near future.

ACKNOWLEDGEMENTS

I thank all of the colleagues and collaborators involved in this project. I especially express my sincere thanks to Professor Masami Kamigaito who completed this work with me, Professor M Sawamoto at Kyoto University and Distinguished Invited University Professor Y Okamoto at Nagoya University for their helpful discussions.

- Klass, D. L. *Fuels, and Chemicals* (Academic Press, San Diego, CA, USA, 1998).
- Sudesh, K., Abe, H. & Doi, Y. Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters. *Prog. Polym. Sci.* **25**, 1503–1555 (2000).
- Mullin, R. Sustainable specialties. *Chem. Eng. News* **82**, 29–37 (2004).
- Wool, R. P. & Sun, X. S. *Bio-Based Polymers and Composites* (Elsevier, Oxford, UK, 2005).
- Belgacem, N. N. & Gandini, A. *Monomers, Polymers and Composites from Renewable Resources* (Elsevier, Oxford, UK, 2008).

- Gandini, A. Polymers from renewable resources: a challenge for the future of macromolecular materials. *Macromolecules* **41**, 9491–9504 (2008).
- Gandini, A. The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **13**, 1061–1083 (2011).
- Williams, C. K. & Hillmyer, M. A. Polymers from renewable resources: a perspective for a special issue of polymer reviews. *Polymer Rev.* **48**, 1–10 (2008).
- Kimura, Y. Molecular, structural, and material design of bio-based polymers. *Polym. J.* **41**, 797–807 (2009).
- Coates, G. W. & Hillmyer, M. A. Polymers from renewable resources. *Macromolecules* **42**, 7987–7989 (2009).
- Hillmyer, M. A. & Tolman, W. B. Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Acc. Chem. Res.* **47**, 2390–2396 (2014).
- Mathers, R. T. How well can renewable resources mimic commodity monomers and polymers? *J. Polym. Sci. A Polym. Chem.* **50**, 1–15 (2012).
- Yao, K. & Tang, C. Controlled polymerization of next-generation renewable monomers and beyond. *Macromolecules* **46**, 1689–1712 (2013).
- Wilbon, P. A., Chu, F. & Tang, C. Progress in renewable polymers from natural terpenes, terpenoids, and rosin. *Macromol. Rapid Commun.* **34**, 8–37 (2013).
- Miller, S. A. Sustainable polymers: opportunities for the next decade. *ACS Macro Lett.* **2**, 550–554 (2013).
- Holmberg, A. L., Reno, K. H., Wool, R. P. & Epps, T. H. III Biobased building blocks for the rational design of renewable block polymers. *Soft Matter*. **10**, 7405–7424 (2014).
- Iwata, T. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. *Angew. Chem. Int. Ed. Engl.* **54**, 3210–3215 (2015).
- Odian, G. *Principles of Polymerization* 4th edn (John Wiley and Sons, Inc., Hoboken, NJ, USA, 2004).
- Szwarc, M. Living polymers. *Nature* **178**, 1168–1169 (1956).
- Hatada, K. & Kitayama, T. Structurally controlled polymerizations of methacrylates and acrylates. *Polym. Int.* **49**, 11–47 (2000).
- Hirao, A., Hayashi, M., Loykulnant, S., Sugiyama, K., Ryu, S. W., Woog, S., Haraguchi, N., Matsuo, A. & Higashihara, T. Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives. *Prog. Polym. Sci.* **30**, 111–182 (2005).
- Sawamoto, M. Modern cationic vinyl polymerization. *Prog. Polym. Sci.* **16**, 111–172 (1991).
- Aoshima, S. & Kanaoka, S. A renaissance in living cationic polymerization. *Chem. Rev.* **109**, 5245–5287 (2009).
- Georges, M. K., Veregin, R. P. N., Kazmaier, P. M. & Hamer, G. K. Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules* **26**, 2987–2988 (1993).
- Hawker, C. J. Molecular weight control by a "living" free-radical polymerization process. *J. Am. Chem. Soc.* **116**, 11185–11186 (1994).
- Hawker, C. J., Bosman, A. W. & Harth, E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.* **101**, 3661–3688 (2001).
- Kato, M., Kamigaito, M., Sawamoto, M. & Higashimura, T. Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris(triphenylphosphine)ruthenium (II)/methylaluminum bis(2,6-di-*tert*-butylphenoxide) initiating system: possibility of living radical polymerization. *Macromolecules* **28**, 1721–1723 (1995).
- Wang, J. S. & Matyjaszewski, K. Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes. *J. Am. Chem. Soc.* **117**, 5614–5615 (1995).
- Percec, V. & Barboiu, B. "Living" radical polymerization of styrene initiated by arenesulfonil chlorides and Cu(I)Cl. *Macromolecules* **28**, 7970–7972 (1995).
- Granel, C., Dubois, P., Jerome, R. & Teyssie, P. Controlled radical polymerization of methacrylic monomers in the presence of a bis(ortho-chelated) arylnickel(II) complex and different activated alkyl halides. *Macromolecules* **29**, 8576–8582 (1996).
- Haddleton, D. M., Jasieczek, C. B., Hannon, M. J. & Shooter, A. J. Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper(I) complexes. *Macromolecules* **30**, 2190–2193 (1997).
- Matyjaszewski, K. & Xia, J. H. Atom transfer radical polymerization. *Chem. Rev.* **101**, 2921–2990 (2001).
- Kamigaito, M., Ando, T. & Sawamoto, M. Metal-catalyzed living radical polymerization. *Chem. Rev.* **101**, 3689–3745 (2001).
- Kamigaito, M. Recent developments in metal-catalyzed living radical polymerization. *Polym. J.* **43**, 105–120 (2011).
- Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., Mayadunne, R. T. A., Meijs, G. F., Moad, C. L., Moad, G., Rizzardo, E. & Thang, S. H. Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process. *Macromolecules* **31**, 5559–5562 (1998).
- Charmot, D., Corpart, P., Adam, H., Zard, S. Z., Biadatti, T. & Bouhadir, G. Controlled radical polymerization in dispersed media. *Macromol. Symp.* **150**, 23–32 (2000).
- Destarac, M., Charmot, D., Franck, X. & Zard, S. Z. Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents. *Macromol. Rapid Commun.* **21**, 1035–1039 (2000).
- Moad, G., Rizzardo, E. & Thang, S. H. Living radical polymerization by the RAFT process. *Aust. J. Chem.* **58**, 379–410 (2005).
- Braddock, R. J. *Handbook of Citrus By-Products and Processing Technology* (John Wiley & Sons, New York, USA, 1999).
- Breitmaier, E. *Terpenes* (Wiley-VCH, Weinheim, Germany, 2006).

- 41 Roberts, W. J. & Day, A. R. A study of the polymerization of α - and β -pinene with Friedel-Crafts type catalysts. *J. Am. Chem. Soc.* **72**, 1226–1230 (1950).
- 42 Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory* (Wiley-Interscience, New York, USA, 1975).
- 43 Kennedy, J. P. & Maréchal, E. *Carbocationic Polymerization* (John Wiley and Sons, Inc., Hoboken, NJ, USA, 1982).
- 44 Dragutan, V. & Streck, R. *Studies in Surface Science and Catalysis* vol 131 (Elsevier Science, Amsterdam, The Netherlands, 2000).
- 45 Coates, G. W. Precise control of polyolefin stereochemistry using single-site metal catalysts. *Chem. Rev.* **100**, 1223–1252 (2000).
- 46 Trnka, T. M. & Grubbs, R. H. The development of L2X2Ru=CHR olefin metathesis catalysts: an organometallic success story. *Acc. Chem. Res.* **34**, 18–29 (2001).
- 47 Tritto, I., Boggioni, L. & Ferro, D. R. Metallocene catalyzed ethene- and propene co-norbornene polymerization: Mechanisms from a detailed microstructural analysis. *Coord. Chem. Rev.* **250**, 212–241 (2006).
- 48 Cherdron, H., Brekner, M. J. & Osan, F. Cycloolefin-copolymers: eine neue klasse transparenter thermoplaste. *Angew. Makromol. Chem.* **223**, 121–133 (1994).
- 49 Inoue, T., Takiguchi, O., Osaki, K., Kohara, T. & Natsuume, T. Dynamic birefringence of amorphous polyolefins I. measurements on poly[1-ethyl-5-methyl-octahydro-4,7-methano-1H-indene-12,3-diy]. *Polym. J.* **26**, 133–139 (1994).
- 50 Inoue, T., Okamoto, H., Osaki, K., Kohara, T. & Natsuume, T. Dynamic birefringence of amorphous polyolefins II. Measurements on polymers containing five-membered ring in main chain. *Polym. J.* **27**, 943–950 (1995).
- 51 Kodemura, J. & Natsuume, T. Synthesis and properties of hydrogenated ring-opening polymers of endo/exo-dicyclopentadiene. *Polym. J.* **27**, 1167–1172 (1995).
- 52 Otsuki, T., Goto, K. & Komiya, Z. Development of hydrogenated ring-opening metathesis polymers. *J. Polym. Sci. A Polym. Chem.* **38**, 4661–4668 (2000).
- 53 Coppen, J. J. W. & Hone, G. A. *Gum Naval Stores: Turpentine and Rosin from Pine Resin* (Natural Resource Institute, Food and Agriculture Organization of the United Nations, Rome, Italy, 1995).
- 54 Langenheim, J. H. *Plant Resins* (Timber Press Inc., Portland, OR, USA, 2003).
- 55 Keszier, B. & Kennedy, J. P. Synthesis of high molecular weight poly(β -pinene). *Adv. Polym. Sci.* **100**, 1–9 (1992).
- 56 Lu, J., Kamigaito, M., Sawamoto, M., Higashimura, T. & Deng, Y. X. Living cationic isomerization polymerization of beta-pinene. Initiation with HCl-2-chloroethyl vinyl ether adduct TiCl₃(Oi-Pr) in conjunction with n-Bu₄NCl. *Macromolecules* **30**, 22–26 (1997).
- 57 Lu, J., Kamigaito, M., Sawamoto, M., Higashimura, T. & Deng, Y. X. Living cationic isomerization polymerization of β -pinene. 2. Synthesis of block and random copolymers with styrene or p-methylstyrene. *Macromolecules* **30**, 27–31 (1997).
- 58 Lu, J., Kamigaito, M., Sawamoto, M., Higashimura, T. & Deng, Y. X. Living cationic isomerization polymerization of β -pinene. 3. Synthesis of end-functionalized polymers and graft copolymers. *J. Polym. Sci. A Polym. Chem.* **35**, 1423–1430 (1997).
- 59 Hui, L. & Jiang, L. Synthesis of poly(β -pinene)-g-polystyrene from allylic brominated poly(β -pinene). *J. Appl. Polym. Sci.* **75**, 599–603 (2000).
- 60 Lu, J., Liang, H., Zhang, R. F. & Li, B. Synthesis of poly(β -pinene)-b-polytetrahydrofuran from β -pinene-based macroinitiator. *Polymer* **42**, 4549–4553 (2001).
- 61 Lu, J., Liang, H., Zhang, W. & Cheng, Q. Synthesis of poly(β -pinene)-g-poly(meth)acrylate by the combination of living cationic polymerization and atom transfer radical polymerization. *J. Polym. Sci. A Polym. Chem.* **41**, 1237–1242 (2003).
- 62 Lu, J., Liang, H., Li, A. L. & Cheng, Q. Synthesis of block and graft copolymers of β -pinene and styrene by transformation of living cationic polymerization to atom transfer radical polymerization. *Eur. Polym. J.* **40**, 397–402 (2004).
- 63 Satoh, K., Sugiyama, H. & Kamigaito, M. Biomass-derived heat-resistant alicyclic hydrocarbon polymers: poly(terpenes) and their hydrogenated derivatives. *Green Chem.* **8**, 878–882 (2006).
- 64 Satoh, K., Nakahara, A., Mukunoki, K., Sugiyama, H., Saito, H. & Kamigaito, M. Sustainable cycloolefin polymer from pine tree oil for optoelectronics material: Living cationic polymerization of β -pinene and catalytic hydrogenation for high-molecular-weight hydrogenated poly(β -pinene). *Polym. Chem.* **5**, 3222–3230 (2014).
- 65 Maslinskasolich, J. & Rudnicka, I. Optically active polymers I. Copolymerization of β -pinene with maleic anhydride. *Eur. Polym. J.* **24**, 453–456 (1988).
- 66 Ramos, A. M. & Lobo, L. S. Polymers from pine gum components: radical and coordination homo and copolymerization of pinenes. *Macromol. Symp.* **127**, 43–50 (1998).
- 67 Paz-Pazos, M. & Pugh, C. Synthesis of optically active copolymers of 2,3,4,5,6-pentafluorostyrene and β -pinene with low surface energies. *J. Polym. Sci. A Polym. Chem.* **44**, 3114–3124 (2006).
- 68 Li, A. L., Wang, Y., Liang, H. & Lu, J. Controlled radical copolymerization of β -pinene and acrylonitrile. *J. Polym. Sci. Part A Polym. Chem.* **44**, 2376–2387 (2006).
- 69 Wang, Y., Li, A. L., Liang, H. & Lu, J. Reversible addition-fragmentation chain transfer radical copolymerization of β -pinene and methyl acrylate. *Eur. Polym. J.* **42**, 2695–2702 (2006).
- 70 Li, A. L., Wang, X. Y., Liang, H. & Lu, J. Controlled radical copolymerization of β -pinene and n-butyl acrylate. *React. Funct. Polym.* **67**, 481–488 (2007).
- 71 Koumura, K., Satoh, K. & Kamigaito, M. Mn₂(CO)₁₀-induced controlled/living radical copolymerization of methyl acrylate and 1-hexene in fluoroalcohol: High α -olefin content copolymers with controlled molecular weights. *Macromolecules* **42**, 2497–2504 (2009).
- 72 Matsuda, M., Satoh, K. & Kamigaito, M. Controlled radical copolymerization of naturally-occurring terpenes with acrylic monomers in fluorinated alcohol. *KGK Kaut. Gummi Kunstst.* **66**, 51–56 (2013).
- 73 Wang, Y., Chen, Q., Liang, H. & Lu, J. Conventional and RAFT radical copolymerizations of β -pinene with N-substituted maleimides. *Polym. Int.* **56**, 1514–1520 (2007).
- 74 Matsuda, M., Satoh, K. & Kamigaito, M. Sequence-controlled radical copolymerization of alicyclic terpenes with maleimide derivatives. *Polym. Prepr. Jpn.* **58**, 518 (2009).
- 75 Matsuda, M., Satoh, K. & Kamigaito, M. 1:2-Sequence-regulated radical copolymerization of naturally occurring terpenes with maleimide derivatives in fluorinated alcohol. *J. Polym. Sci. A Polym. Chem.* **51**, 1774–1785 (2013).
- 76 Doiuchi, T., Yamaguchi, H. & Minoura, Y. Cycloolefin polymerization of d-limonene with maleic anhydride. *Eur. Polym. J.* **17**, 961–968 (1981).
- 77 Maslinskasolich, J., Kupka, T., Kluczká, M. & Solich, A. Optically active polymers. 2. Copolymerization of limonene with maleic anhydride. *Macromol. Chem. Phys.* **195**, 1843–1850 (1994).
- 78 Sharma, S. & Srivastava, A. K. Synthesis and characterization of copolymers of limonene with styrene initiated by azobisisobutyronitrile. *Eur. Polym. J.* **40**, 2235–2240 (2004).
- 79 Satoh, K., Matsuda, M., Nagai, K. & Kamigaito, M. AAB-sequence living radical chain copolymerization of naturally occurring limonene with maleimide: An end-to-end sequence-regulated copolymer. *J. Am. Chem. Soc.* **132**, 10003–10005 (2010).
- 80 Matsuda, M., Satoh, K. & Kamigaito, M. Periodically functionalized and grafted copolymers via 1:2-sequence-regulated radical copolymerization of naturally occurring functional limonene and maleimide derivatives. *Macromolecules* **46**, 5473–5482 (2013).
- 81 Yamamoto, D. & Matsumoto, A. Penultimate unit and solvent effects on 2:1 sequence control during radical copolymerization of N-phenylmaleimide with β -pinene. *Macromol. Chem. Phys.* **213**, 2479–2485 (2012).
- 82 Hisan, M., Takeda, K., Takashima, T., Jin, Z., Shiibashi, A. & Matsumoto, A. Sequence-controlled radical polymerization of N-substituted maleimides with 1-methylenebenzocycloalkanes and the characterization of the obtained copolymers with excellent thermal resistance and transparency. *Macromolecules* **46**, 3314–3323 (2013).
- 83 Hisan, M., Takeda, K., Takashima, T., Jin, Z., Shiibashi, A. & Matsumoto, A. Sequence-controlled radical copolymerization of N-substituted maleimides with olefins and polyisobutene macromonomers to fabricate thermally stable and transparent maleimide copolymers with tunable glass transition temperatures and viscoelastic properties. *Macromolecules* **46**, 7733–7744 (2013).
- 84 Miura, Y., Satoh, K., Kamigaito, M. & Okamoto, Y. Well-defined graft copolymers of methacrylate, acrylate, and styrene via ruthenium-catalyzed living radical polymerization. *Polym. J.* **38**, 930–939 (2006).
- 85 Miura, Y., Satoh, K., Kamigaito, M., Okamoto, Y., Kaneko, T., Jinnai, H. & Kobukata, S. AxBAx-type block-graft polymers with middle soft segments and outer hard graft chains by ruthenium-catalyzed living radical polymerization: synthesis and characterization. *Macromolecules* **40**, 465–473 (2007).
- 86 Sivola, A. n-Butyllithium-initiated polymerization of myrcene and its copolymerization with styrene. *Acta Polytech. Scand. Chem. Technol. Ser.* **134**, 7–65 (1977).
- 87 Quirk, R. P. & Huang, T.-L. *New Monomers and Polymers* (Plenum Press, New York, USA, 1984).
- 88 Quirk, R. P. *Thermoplastic Elastomers* 3rd edn (Holden, G., Kricheldorf, H. R. & Quirk, R. P.) Ch 4, 69–91 (Hanser, Munich, Germany, 2004).
- 89 Bolton, J. M., Hillmyer, M. A. & Hoyer, T. R. Sustainable thermoplastic elastomers from terpene-derived monomers. *ACS Macro Lett.* **3**, 717–720 (2014).
- 90 Kobayashi, S., Lu, C., Hoyer, T. R. & Hillmyer, M. A. Controlled polymerization of a cyclic diene prepared from the ring-closing metathesis of a naturally occurring monoterpene. *J. Am. Chem. Soc.* **131**, 7960–7963 (2009).
- 91 Lewis, N. G. & Sarkanen, S. *Lignin and Lignan Biosynthesis* (ACS Symposium Series 697) (American Chemical Society, Washington, D.C., 1998).
- 92 Wiley, R. H. & Hobson, P. H. Decarboxylation of p- and o-formylcinnamic acids to p-formylstyrene and 1-indanone. *J. Am. Chem. Soc.* **71**, 2429–2431 (1949).
- 93 Sovish, R. C. Preparation and polymerization of p-vinylphenol. *J. Org. Chem.* **24**, 1345–1347 (1959).
- 94 Hatakeyama, H., Hayashi, E. & Haraguchi, T. Biodegradation of poly(3-methoxy-4-hydroxystyrene). *Polymer* **18**, 759–763 (1977).
- 95 Salvin, S. M. B. & Byrne, T. (eds). *The New Crop Industries Handbook* (Rural Industries Research and Development Corporation, Canberra, ACT, Australia, 2004).
- 96 Alfrey, T., Arond, L. & Overberger, C. G. Acid-catalyzed copolymerization behavior of anethole. *J. Polym. Sci.* **4**, 539–541 (1949).
- 97 Overberger, C. G., Tanner, D. & Pearce, E. M. Ionic polymerization. Copolymerization of nuclear and side-chain alkyl-substituted styrene monomers. *J. Am. Chem. Soc.* **80**, 4566–4568 (1958).
- 98 Mizote, A., Tanaka, T., Higashimura, T. & Okamura, S. Cationic polymerization of α,β -disubstituted olefins. Part I. Cationic copolymerization of β -methylstyrenes. *J. Polym. Sci. A* **3**, 2567–2578 (1965).
- 99 Higashimura, T., Masuda, T. & Kawamura, K. Cationic copolymerization of anethole: reactivity of geometric isomers of α,β -disubstituted ethylenes. *J. Polym. Sci. A-1 Polym. Chem.* **10**, 85–93 (1972).
- 100 Alexander, R., Jefferon, A. & Lester, P. D. Cationic oligomerization and polymerization of some propenylbenzene derivatives. *J. Polym. Sci. A Polym. Chem.* **19**, 695–706 (1981).
- 101 Trumbo, D. L. Attempted cationic polymerization of isosafrole. *Polym. Bull.* **33**, 643–649 (1994).
- 102 Satoh, K., Saitoh, S. & Kamigaito, M. A linear lignin analogue: phenolic alternating copolymers from naturally occurring β -methylstyrene via aqueous-controlled cationic copolymerization. *J. Am. Chem. Soc.* **129**, 9586–9587 (2007).

- 103 Satoh, S., Satoh, K. & Kamigaito, M. Living cationic polymerization of plant-derived β -methylstyrenes with electron-donating groups. *Polym. Prepr. Jpn* **57**, 2965–2966 (2008).
- 104 Satoh, K., Kamigaito, M. & Sawamoto, M. Direct living cationic polymerization of p-hydroxystyrene with boron trifluoride etherate in the presence of water. *Macromolecules* **33**, 5405–5410 (2000).
- 105 Satoh, K., Kamigaito, M. & Sawamoto, M. Direct synthesis of amphiphilic random and block copolymers of p-hydroxystyrene and p-methoxystyrene via living cationic polymerization with BF₃OEt₂/ROH systems. *Macromolecules* **33**, 5830–5835 (2000).
- 106 Satoh, K., Nakashima, J., Kamigaito, M. & Sawamoto, M. Novel BF₃OEt₂/R-OH initiating system for controlled cationic polymerization of styrene in the presence of water. *Macromolecules* **34**, 396–401 (2001).
- 107 Braun, D., Schacht, M., Elsasser, H. & Tudos, F. Alternating terpolymerization of three non-homopolymerizable monomers. *Macromol. Rapid Commun.* **18**, 335–342 (1997).
- 108 Braun, D. & Hu, F. C. Polymers from non-homopolymerizable monomers by free radical processes. *Prog. Polym. Sci.* **31**, 239–276 (2006).
- 109 Kokubo, T., Iwatsuki, S. & Yamashita, Y. Studies on charge-transfer complex and polymerization. XX. Terpolymerizations with the anethole-maleic anhydride alternating copolymerization system. *Macromolecules* **3**, 518–523 (1970).
- 110 Nonoyama, Y., Satoh, K. & Kamigaito, M. Renewable β -methylstyrenes for bio-based heat-resistant styrenic copolymers: radical copolymerization enhanced by fluorooalcohol and controlled/living copolymerization by RAFT. *Polym. Chem.* **5**, 3182–3189 (2014).
- 111 Akkapeddi, M. K. Poly (α -methylene- γ -butyrolactone) synthesis, configurational structure, and properties. *Macromolecules* **12**, 546–551 (1979).
- 112 Akkapeddi, M. K. The free radical copolymerization characteristics of α -methylene γ -butyrolactone. *Polymer* **20**, 1215–1216 (1979).
- 113 Suenaga, J., Sutherland, D. M. & Stille, J. K. Polymerization of (RS)- and (R)- α -methylene- γ -methyl- γ -butyrolactone. *Macromolecules* **17**, 2913–2916 (1984).
- 114 Miyake, G. M., Newton, S. E., Mariott, W. R. & Chen, E. Y. X. Coordination polymerization of renewable butyrolactone-based vinyl monomers by lanthanide and early metal catalysts. *Dalton Trans.* **39**, 6710–6718 (2010).
- 115 Mosnacek, J. & Matyjaszewski, K. Atom transfer radical polymerization of tulipalin A: a naturally renewable monomer. *Macromolecules* **41**, 5509–5511 (2008).
- 116 Mosnacek, J., Yoon, J. A., Juhari, A., Koynov, K. & Matyjaszewski, K. Synthesis, morphology and mechanical properties of linear triblock copolymers based on poly(α -methylene- γ -butyrolactone). *Polymer* **50**, 2087–2094 (2009).
- 117 Manzer, L. E. Biomass derivatives: a sustainable source of chemicals. *ACS Symp. Ser.* **921**, 40–51 (2006).
- 118 Qi, G. G., Nolan, M., Schork, F. J. & Jones, C. W. Emulsion and controlled miniemulsion polymerization of the renewable monomer γ -methyl- α -methylene- γ -butyrolactone. *J. Polym. Sci. A Polym. Chem.* **46**, 5929–5944 (2008).
- 119 Miyake, G. M., Zhang, Y. T. & Chen, E. Y. X. Living polymerization of naturally renewable butyrolactone-based vinylidene monomers by amphiphilic silicon propagators. *Macromolecules* **43**, 4902–4908 (2010).
- 120 Tate, B. E. Polymerization of itaconic acid derivatives. *Adv. Polym. Sci.* **5**, 214–232 (1967).
- 121 Marvel, C. S. & Shepherd, T. H. Polymerization reactions of itaconic acid and some of its derivatives. *J. Org. Chem.* **24**, 599–605 (1959).
- 122 Nagai, S. Polymerization and polymers of itaconic acid derivatives. V. The copolymerization reactivity of itaconic acid in an aqueous solution. *Bull. Chem. Soc. Jpn.* **36**, 1459–1463 (1963).
- 123 Ishida, S. & Saito, S. Polymerization of itaconic acid derivatives. *J. Polym. Sci. A-1 Polym. Chem.* **5**, 689–68 (1967).
- 124 Sato, T., Inui, S., Tanaka, H., Ota, T., Kamachi, M. & Tanaka, K. Kinetic and ESR studies on the radical polymerization of di-n-butyl itaconate in benzene. *J. Polym. Sci. A Polym. Chem.* **25**, 637–652 (1987).
- 125 Otsu, T. & Yang, J. Z. Radical polymerization of itaconic anhydride and reactions of the resulting polymers with amines and alcohols. *Polym. Int.* **25**, 245–251 (1991).
- 126 Hirano, T., Tateiwa, S., Seno, M. & Sato, T. Temperature dependence of stereospecificity in the radical polymerization of di-n-butyl itaconate in bulk. *J. Polym. Sci. A Polym. Chem.* **38**, 2487–2491 (2000).
- 127 Watanabe, H., Matsumoto, A. & Otsu, T. Polymerization of N-alkyl-substituted itaconimides and N-(alkyl-substituted phenyl) itaconimides and characterization of the resulting polymers. *J. Polym. Sci. A Polym. Chem.* **32**, 2073–2083 (1994).
- 128 Watanabe, H., Matsumoto, A. & Otsu, T. Radical polymerization of N-substituted itaconamic esters and itaconamides. *J. Polym. Sci. A Polym. Chem.* **32**, 2085–2091 (1994).
- 129 Szablan, Z., Toy, A. A., Davis, T. P., Hao, X., Stenzel, M. H. & Barner-Kowollik, C. Reversible addition fragmentation chain transfer polymerization of sterically hindered monomers: toward well-defined rod/coil architectures. *J. Polym. Sci. A Polym. Chem.* **42**, 2432–2443 (2004).
- 130 Szablan, Z., Toy, A. A., Terrenoire, A., Davis, T. P., Stenzel, M. H., Müller, A. H. E. & Barner-Kowollik, C. Living free-radical polymerization of sterically hindered monomers: Improving the understanding of 1,1-disubstituted monomer systems. *J. Polym. Sci. A Polym. Chem.* **44**, 3692–3710 (2006).
- 131 Anand, V., Agarwal, S., Greiner, A. & Choudhary, V. Synthesis of methyl methacrylate and N-aryl itaconimide block copolymers via atom-transfer radical polymerization. *Polym. Int.* **54**, 823–828 (2005).
- 132 Satoh, K., Lee, D.-H., Nagai, K. & Kamigaito, M. Precision synthesis of bio-based acrylic thermoplastic elastomer by RAFT polymerization of itaconic acid derivatives. *Macromol. Rapid Commun.* **35**, 161–167 (2014).



Kotaro Satoh received his PhD degrees from Kyoto University under supervision of Professor Mitsuo Sawamoto in 2000. During 2000–2004, he worked for Kuraray Co Ltd as a researcher. In 2004, he moved to Nagoya University as an Assistant Professor working with Professor Masami Kamigaito and then promoted to an Associate Professor (current position) in 2010. In 2009–2010, he was a visiting scientist at University of California, Santa Barbara, working with Professor Craig J. Hawker. Since 2014, he concurrently serves as a PRESTO researcher of Japan Science and Technology Agency. He received the Awards for the Encouragement of Research in Polymer Science SPSJ (2008), The Young Scientists' Prize by the Minister of Education, Culture, Sports, Science and Technology, Japan (2012), and the SPSJ Asahi Kasei Award (2012). His research interest includes exploring new precision polymerization systems, as well as developments of bio-based polymers by means of precision polymerizations of renewable vinyl monomers.