Polymerization

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Bio-Based Polyketones by Selective Ring-Opening Radical Polymerization of α-Pinene-Derived Pinocarvone

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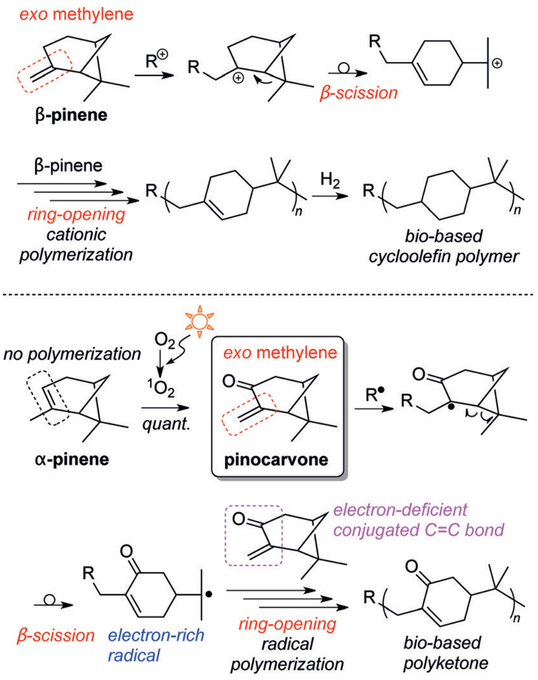
Abstract: *The most abundant naturally occurring terpene, α-pinene, which cannot be directly polymerized into high polymers by any polymerization method, was quantitatively converted under visible-light irradiation into pinocarvone, which possesses a reactive exo methylene group. The bicyclic vinyl ketone was quantitatively polymerized in fluoroalcohols by selective (99 %) ring-opening radical polymerization of the four-membered ring, which results in unique polymers containing chiral six-membered rings with conjugated ketone units in the main chain. These polymers display good thermal properties, optical activities, and contain reactive conjugated ketone units. Reversible addition fragmentation chain transfer (RAFT) polymerization was successfully accomplished by using appropriate trithiocarbonate RAFT agents, enabling the synthesis of thermoplastic elastomers based on controlled macromolecular architectures.*

Currently, naturally occurring compounds are receiving much attention as renewable resources for sustainable developments in science, industry, and society owing to serious environmental issues, such as dwindling fossil resources and global warming.[1–12] Among various natural resources, abundant products, especially those obtained from the non-edible parts of plants, are preferred from the viewpoint of another serious global issue, food shortage.

Turpentine is one of the most abundant plant oils and primarily obtained from pine trees. Its annual production has been roughly estimated to be 300000 metric tons worldwide.[13–16] Turpentine is widely used in industry as a solvent for paints and varnishes as well as a cleaning solvent and a starting material for pharmaceuticals and other organic compounds, fragrances, and aromas in perfumes and food flavorings. The oil is composed of various terpenes, and α- and β-pinene are the major components. The constituents and their amounts depend on the type of pine tree, the geographical location of the tree, and the harvest season. α-Pinene is more predominant than the β-form in the main turpentine oil though they can isomerize into each other. Therefore, α-pinene is regarded as one of the most abundant naturally occurring terpenes that can be obtained from non-edible plants.

Structurally, α-pinene is a bicyclic monoterpene hydrocarbon consisting of four- and six-membered rings with an internal trisubstituted carbon–carbon double bond in the six-membered ring (Scheme 1). As a vinyl monomer for addition polymerization, α-pinene is difficult to polymerize into high polymers owing to the large steric hindrance around the trisubstituted C=C bond.[17] In contrast, its isomer, β-pinene, which consists of similarly fused rings but contains a reactive *exo* methylene group, exhibits very high reactivity in cationic polymerization; β-scission of the four-membered ring into stable tertiary carbocations results in unique polymer structures containing an unsaturated six-membered ring in the main chain.[18–22] Although the molecular weight was low owing to frequent chain-transfer reactions, we have succeeded in synthesizing high-molecular-weight poly(β-pinene) by living cationic polymerization and its fully saturated cycloolefin polymer by subsequent hydrogenation.[23] Interestingly, the obtained bio-based cycloolefin polymer exhibits excellent thermal, optical, and physical properties owing to its



Scheme 1. Structures of α- and β-pinene and pinocarvone and their polymerizations.

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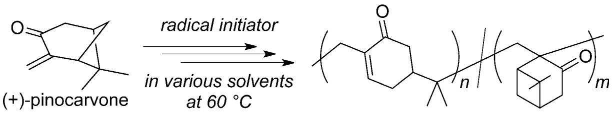
unique polymer structure, which originates from natural products.[24] This result suggests the potential of preparing novel high-performance polymers from natural resources by developing controlled polymerizations that can efficiently polymerize bio-based monomers while preserving their unique structures.[25–27]

Table 1: Radical polymerization of (+)-pinocarvone in various solvents.[a]



Entry	Solvent	t [h]	Conv. [%][d]	M_n[e]	M_w/M_n[e]	n:m[d]
1	–	358	55	17100	2.15	68:32
2	toluene	480	37	15100	2.56	77:23
3	DMF	480	40	20200	3.24	80:20
4	HFIP	98	92	45200	1.91	97:3
5[b]	HFIP	18	100	26300	1.77	99:1
6[c]	HFIP	250	63	47500	2.96	89:11
7	$C_6H_5C(CF_3)_2OH$	312	97	53900	2.13	92:8
8	m-$[C(CF_3)_2OH]_2C_6H_4$	190	100	48200	2.01	93:7
9	$C(CF_3)_3OH$	60	95	30200	2.32	96:4

[a] Polymerization conditions: $[(+)\text{-pinocarvone}]_0 = 2.0$ M (in solvents) or 6.1 M (bulk), $[\text{AIBN}]_0 = 10$ mM (in solvents) or 61 mM (bulk) at 60 °C. [b] $[(+)\text{-pinocarvone}]_0 = 0.50$ M. [c] Under visible-light irradiation with a mixture of camphorquinone/dimethylaniline as the photoinitiator at 40 °C; $[\text{camphorquinone}]_0 = [\text{dimethylaniline}]_0 = 10$ mM. [d] Determined by ^1H NMR analysis. [e] Determined by SEC in HFIP.

A judicious route for utilizing α-pinene as a feedstock for novel bio-based polymers is to convert it into a polymerizable compound by preferably simple, quantitative, robust, and environmentally friendly transformations and then to develop an appropriate polymerization system for the derived bio-based monomer. Therefore, in this study, α-pinene was quantitatively converted into pinocarvone (> 99 %) by a simple visible-light photooxidation with singlet oxygen, which was produced in the presence of tetraphenylporphyrin as a photosensitizer under mild conditions at room temperature according to a literature method (Figure S1).[28] Pinocarvone, which is also contained in several eucalyptus plant oils,[15,16,29] features an *exo* methylene group that is similar to that of β-pinene. However, the *exo* methylene group is a C=C bond in conjugation with a carbonyl moiety, and therefore, this compound can be regarded as a vinyl ketone. Pinocarvone may be polymerizable by homolytic β-scission of the four-membered ring into a nucleophilic alkyl radical, which can react with the electron-deficient C=C bond of pinocarvone to yield a unique polymer structure with a six-membered ring with a conjugated ketone group in the main chain.

Pinocarvone, which was obtained from α-pinene, was polymerized by using 4,4′-azobis(isobutyronitrile) (AIBN) at 60 °C under bulk conditions and in various solvents, such as toluene, dimethylformamide (DMF), fluorinated cumyl alcohol ($PhC(CF_3)_2OH$), hexafluoroisopropanol (HFIP), m-$[C(CF_3)_2OH]_2C_6H_4$, and $C(CF_3)_3OH$. The polymers formed irrespective of the solvent, but the polymerization rates and polymer molecular weights were dependent on the solvents (Supporting Information, Figure S2 and Tables 1 and S1). In particular, in fluorinated alcohols (Table 1, entries 4–9), the reaction proceeded relatively fast and quantitatively, resulting in the production of high-molecular-weight polymers ($M_n > 45000$). Furthermore, under visible-light irradiation, a photo-radical initiator was also employed to polymerize pinocarvone, which had been prepared by visible-light photooxidation (Table 1, entry 6). These results demonstrate that pinocarvone is a promising renewable vinyl monomer that can be easily derived from the most abundant terpene, α-pinene.[30] No reactions occurred under anionic polymerization conditions even with the use of *tert*-butyllithium in the absence and presence of aluminum additives ($AlEt_3$ and $MeAl(ODBP)_2$) or diethyl zinc.

^1H NMR analysis of the obtained polymers indicated the presence of two repeating units; whereas the first one is based on the bicyclic framework of pinocarvone and generated by normal radical addition polymerization, the second unit is formed by radical addition followed by ring opening of the four-membered ring and thus contains an unsaturated six-membered ring in the main chain (Figure 1). The ring-opened structure was predominantly formed under bulk conditions and in all of the solvents and accounted for more than 90 % of the products formed in the fluoroalcohols. As the amount of ring-opened polymer increased, the polymers became insoluble in typical organic solvents, such as toluene, chloroform, THF, and DMF, and were only soluble in fluorinated alcohols, such as HFIP. The content became higher as the temperature was increased or the monomer concentration decreased and finally reached 99 % at 60 °C in HFIP under dilute conditions ($[\text{monomer}]_0 = 0.50$ M; Table 1, entry 5). The ^1H NMR spectrum was very simple, and all of the peaks were sharp (Figure 1 B) compared to those obtained under bulk (Figure 1 A) and other conditions (Figure S3). These peaks were fully assigned by ^1H and ^{13}C NMR as well as DEPT, ^1H–^1H COSY, and HMQC spectroscopy (Figures S4 and S5). These results indicate that highly selective radical ring-opening polymerization of pinocarvone occurred under the optimized conditions. The high selectivity was due to hydrogen-bonding interactions of the fluoroalcohol with the carbonyl groups of the monomer as well as the propagating terminal radicals, as they decrease the electron density of the conjugated vinyl group of the monomer and enhance their reactivity with the nucleophilic or electron-rich alkyl radicals obtained by ring opening. A similar effect was observed for fluorinated alcohols in the radical copolymerization of a conjugated electron-deficient vinyl monomer, acrylate, and β-pinene, which generates a similar tertiary alkyl radical by β-scission.[31] Furthermore, the hydrogen-bonding interactions with the carbonyl group of the ring-unopened radical species may enhance β-scission, resulting in the ring-opened structure.

The higher ring-opening selectivity improved the thermal properties of the polymers (Figure 2). The glass transition temperature (T_g) of the polymers increased nearly linearly with the percentage of ring-opened units. Finally, at 96 %, T_g reached 162 °C, which is higher than that of hydrogenated

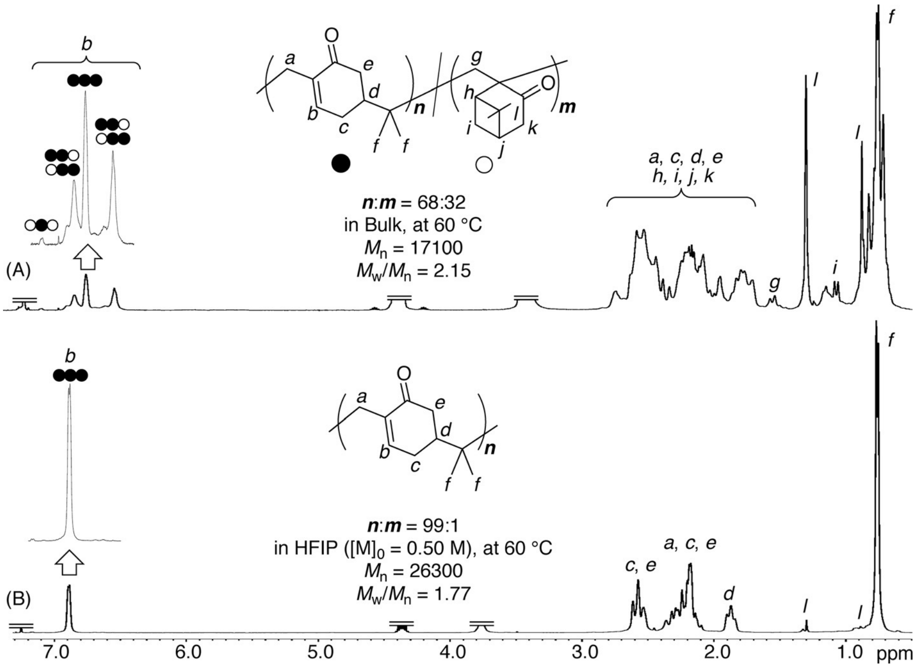


Figure 1. ^{1}H NMR spectra (in $CDCl_3$/HFIP-d_2, 1:1 at 55 °C) of a poly(pinocarvone) sample obtained by radical polymerization of (+)-pinocarvone with AIBN under bulk conditions at 60 °C ([monomer]$_0$ = 6100 mм, [AIBN]$_0$ = 61 mм; A) and in HFIP at 60 °C ([monomer]$_0$ = 500 mм, [AIBN]$_0$ = 10 mм; B).

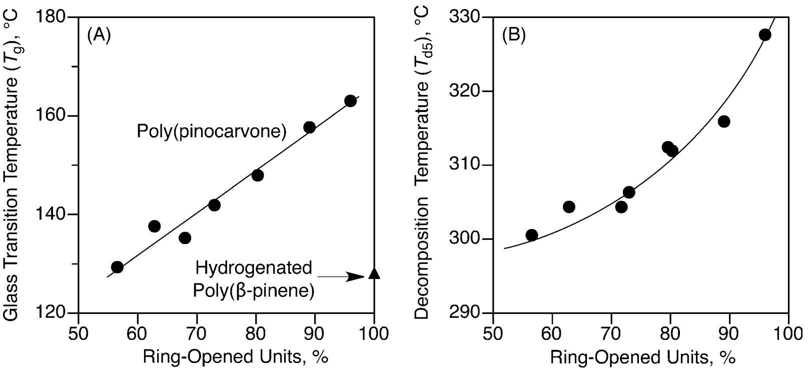


Figure 2. Dependence of T_g (A) and T_{d5} (B) on the percentage of ring-opened units in poly(pinocarvone) samples obtained by free radical polymerization of (+)-pinocarvone under various conditions.

poly(β-pinene) (130 °C).[23,24] The thermal stability also increased, and the 5% decomposition temperature (T_{d5}) increased to 327 °C. These results indicate that novel heat-resistant bio-based polymers can be obtained from pinocarvone, which can be produced from the most abundant terpene by a simple transformation, by selective ring-opening radical polymerization.

A notable feature of the bio-based terpenoids is their chirality. The polymer obtained from (+)-pinocarvone, which originates from (−)-α-pinene, exhibited optical activity. The specific optical rotation (365 nm, HFIP, 20 °C) further changed from +100° to −30° depending on the amount of ring-opened units (from 68% to 99%). Along with this change, the CD spectrum also changed (Figure 3). Furthermore, its enantiomer, (−)-pinocarvone, which was obtained from naturally occurring (+)-α-pinene, was similarly polymerized to afford polymers with opposite optical activities and mirror-image CD spectra.

Radical copolymerizations of these enantiomers were also investigated by changing the feed ratio. Both co-monomers polymerized at the same rate to yield copolymers with nearly the same molecular weights. The optical activity linearly changed from those of the homopolymers of each enantiomer along with the feed ratio (Figure S6). In particular, at a feed ratio of 50:50, copolymerization of the racemic mixture resulted in products with barely any optical activity. Therefore, the optical activity of poly(pinocarvone) can be arbitrarily tuned by varying the feed ratio of the enantiomers.

Another feature of the polymers that were obtained by selective ring-opening polymerization of pinocarvone is the presence of potentially reactive α,β-unsaturated ketones in the repeating units, which are available for further functionalization by various transformations. We investigated the thiol-ene reaction with *para*-toluenethiol by both radical and Michael addition pathways by using AIBN and triethylamine, respectively (Table S2). Although the transformations were not quantitative and stopped at approximately 30%, the resulting polymers exhibited T_g values higher than 200 °C. The reduction of the conjugated ketone by lithium aluminum hydride proceeded nearly quantitatively to afford hydroxy moieties in the repeating units.

To control the molecular weights, terminal groups, and macromolecular architectures of the bio-based polymers, various reversible addition-fragmentation chain transfer (RAFT) agents (R−SC(S)Z) with different R and Z groups were employed[32] because it was difficult to predict which groups would be most suitable for this special monomer that generates both conjugated and unconjugated radical species depending on whether the associated β-scission of the four-membered ring occurs or not.

For RAFT agents with R = cyanoisopropyl, among the employed Z groups, namely dithiobenzoate, trithiocarbonate, and dithiocarbamate, trithiocarbonate enabled the fastest quantitative polymerization in $PhC(CF_3)_2OH$ at 80 °C in the presence of AIBN and yielded the most controlled molecular weights with the narrowest molecular weight distribution (MWD; Figure S7). Then, trithiocarbonates with different

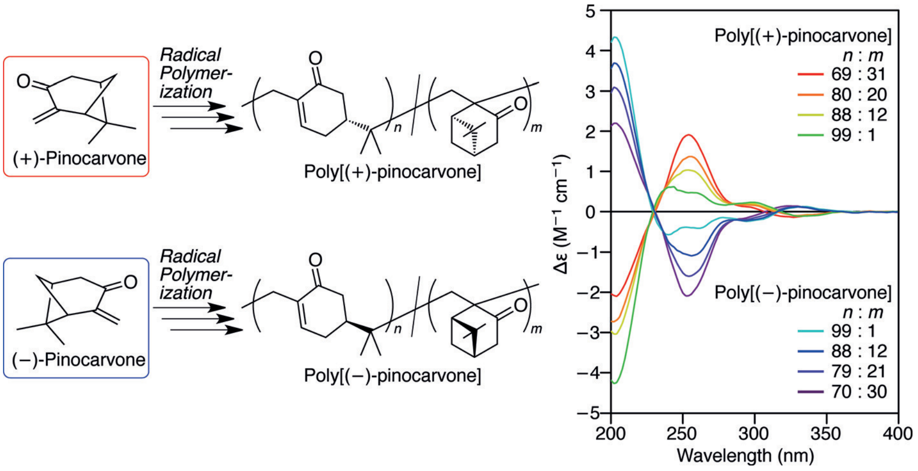


Figure 3. CD spectra (in HFIP, RT) of a series of poly(pinocarvone) samples with different amounts of ring-opened units obtained by free radical polymerization of (+)- or (−)-pinocarvone under different conditions.

R groups (R = PhCH(CO_2Me), cyanoisopropyl, and cumyl) were tested under the same conditions (Figure S8). With R = PhCH(CO_2Me), which generates the most stable radical, the narrowest MWD was achieved ($M_w/M_n = 1.35$) even though no large differences were observed. The relatively broad MWDs compared to those obtained after RAFT polymerization of other vinyl monomers are due to the slow chain transfer, which was affected by the bulky monomer and the two different propagating radical species. The observed molecular weights, which were higher than the calculated values, are due to differences in the hydrodynamic volumes compared to those of the poly(methyl methacrylate) standard used for calibration of the size-exclusion chromatography (SEC). Indeed, the molecular weight determined by ^{1}H NMR spectroscopy using the peaks of the terminal RAFT groups and the main-chain units was much closer to the calculated value (Figure S9), indicating that the molecular weight and the chain-end groups of poly(pinocarvone) can be finely controlled by the trithiocarbonate RAFT agents. Furthermore, the selectivity of the ring-opening polymerization was similarly high (95 %), even for RAFT polymerization in PhC(CF_3)$_2$OH.

To utilize the high T_g value of the poly(pinocarvone) units for novel bio-based functionalized polymers, block copolymers with polyacrylate, which has a low T_g, were synthesized by block RAFT copolymerization between pinocarvone and methyl (MA) or *n*-butyl acrylate (BA). The trithiocarbonate-based macro-RAFT agents were prepared by RAFT polymerization of the acrylates in toluene and then used for block copolymerization with pinocarvone in PhC(CF_3)$_2$OH. The narrow SEC curves of the macro-RAFT agents shifted to high molecular weights while unimodal MWDs were maintained (Figure S10). ^{1}H NMR analysis of the products indicated that the measured unit ratios of acrylate and pinocarvone are nearly the same as the calculated ones (Figure S11), indicating the successful formation of diblock copolymers.

Next, a bifunctional trithiocarbonate-type RAFT agent was synthesized and employed for the triblock copolymerization of BA and pinocarvone. The narrow SEC curves of the bifunctional macro-RAFT agents of BA were similarly shifted to high molecular weights along with the consumption of pinocarvone (Figure S12). A series of the obtained triblock copolymers with different unit ratios were characterized by atomic force microscopy (AFM) of the spin-coated films after annealing. As shown in Figure 4, the images show distinct microphase separations that gradually change from spherical or cylindrical to lamellae-like structures as the chain length of the poly(pinocarvone) segments increased. Furthermore, the dynamic viscoelasticity curve indicated two glass transition temperatures ($T_\alpha = -30$ and 140 °C), which correspond to the poly(BA) and poly(pinocarvone) segments (Figure S13), respectively. This result indicates that novel bio-based ther-

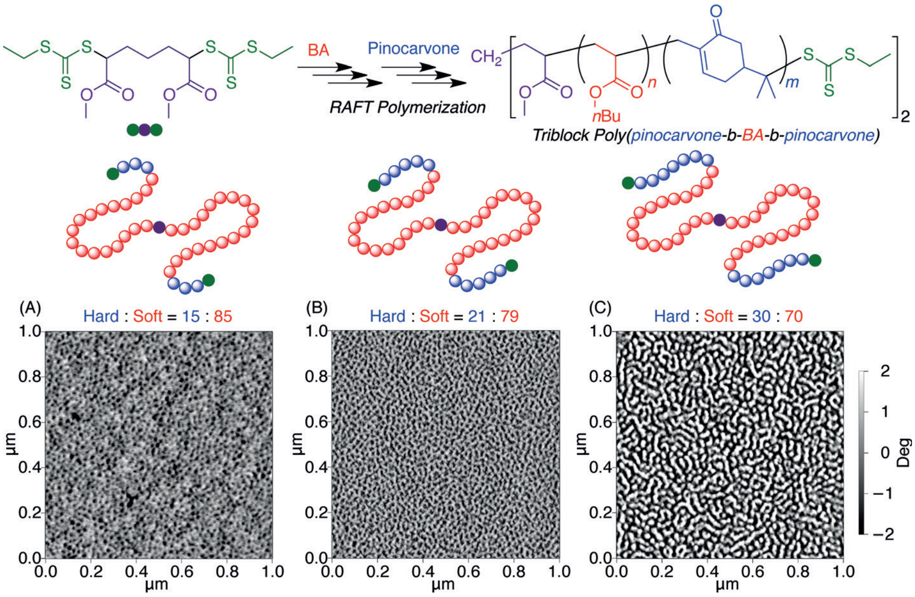


Figure 4. Phase AFM images showing the morphologies of triblock poly(pinocarvone-*b*-BA-*b*-pinocarvone) polymers with poly(pinocarvone) segments with different block lengths obtained at various conversions of pinocarvone in the RAFT polymerization. Pinocarvone/BA (w/w) and M_n: 15:85 and 39 600 (A), 21:79 and 42 800 (B), 30:70 and 48 700 (C).

moplastic elastomers with a high service temperature (approximately 140 °C) can be obtained from pinocarvone, which is derived from α-pinene, an abundant renewable resource, by selective ring-opening-controlled radical polymerization.

In conclusion, α-pinene, which is abundantly produced by a metabolic photo-biosynthetic process in plants using visible light, can be directly and quantitatively transformed into pinocarvone, which bears a reactive *exo* methylene group, by chemical photooxidation under visible-light irradiation. The easily accessible renewable compound undergoes radical homopolymerization and can be quantitatively polymerized in a selective ring-opening process under optimized conditions to afford novel bio-based polymers with good thermal properties, optical activities, and reactive groups. These unique features of a polymer derived from renewable natural resources should promote the development of novel functional materials that cannot be easily prepared from petroleum-derived compounds.

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