Biobased Cycloolefin Polymers: Carvone-Derived Cyclic Conjugated Diene with Reactive *exo*-Methylene Group for Regioselective and Stereospecific Living Cationic Polymerization

Takenori Nishida,[†] Kotaro Satoh,[†,‡] Shusaku Nagano,[§] Takahiro Seki,[†] Masazumi Tamura,[‖] Yingai Li,[⊥] Keiichi Tomishige,[⊥] and Masami Kamigaito*,[†]

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

[‡]Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-H120 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

[§]Department of Chemistry, College of Science, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo 171-8501, Japan

[‖]Research Center for Artificial Photosynthesis, Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan

[⊥]Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

ABSTRACT: Carvone, a naturally abundant chiral cyclic α,β-unsaturated carbonyl compound, was chemically transformed into cyclic *exo*-methylene conjugated dienes. The *exo*-methylene group had high reactivity in cationic polymerization and was efficiently polymerized in a controlled manner via regioselective 1,4-conjugated additions using initiating systems effective for living cationic polymerization of vinyl ethers. The obtained polymers with 1,3-cyclohexenyl units and tetra-substituted olefins in the main chain showed high glass transition temperatures over 110 °C. The chiral monomer underwent stereospecific polymerization to result in polymers with low solubility and weak packing of the rigid main chain in the lamellar layers. The racemic mixture resulted in soluble amorphous polymers, which were subsequently hydrogenated into cycloolefin polymers with enhanced thermal properties.

In view of sustainable development, renewable resources have received much attention as alternatives for traditional petrochemical raw materials. Recently, various bio-based polymers have been developed using renewable monomers, which can be obtained directly from natural resources or indirectly through their chemical transformation.[1-10] In particular, unique chemical structures originating from natural compounds often give characteristic features to monomers, as well as polymers, in terms of monomer reactivity and polymer properties, which contribute to the development of novel, high-performance and functional polymer materials.

Among various natural compounds, terpenes or terpenoids are most abundant and widely varied in their structures, possessing linear and/or cyclic structures and C=C and/or C=O groups, etc.,[11–13] which are attractive as unique renewable feedstock for novel bio-based polymers.[14-25] Previously, we reported that β-pinene, which is one of the most naturally abundant terpenes, was cationically polymerized into high-molecular-weight polymers using an appropriate initiating system for living cationic polymerization.[17,18] Furthermore, the obtained polymer was converted via subsequent hydrogenation into novel amorphous cycloolefin polymers with excellent properties, such as high transparency, low birefringence, high glass transition temperatures, moisture insensitivity, and low density, which are comparable or superior to those of common cycloolefin (co)polymers (COC or COP) obtained from petroleum-derived cyclic olefins, such as norbornene, dicyclopentadiene, and other derivatives.[26–28] The characteristic structure of β-pinene with an *exo*-methylene group attached to 4- and 6-membered fused rings results in not only its high reactivity in cationic polymerization but also unique polymer properties.
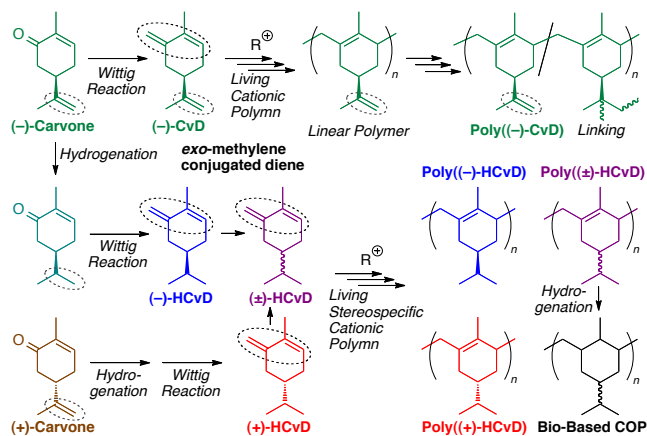
As another abundant terpenoid-based renewable feedstock for novel bio-based polymers with cycloolefin structures, we focused on cyclic α,β-unsaturated carbonyl compound, carvone. Carvone naturally occurs in both enantiomerically pure (*R*)-(−)- and (*S*)-(+)-forms, which are the main constituents of spearmint and caraway or dill oils, respectively, and even in racemic (±)-forms in gingergrass oil.[29–31] They are also readily prepared from (*R*)-(+)- and (*S*)-(−)-limonene and racemic (±)-limonene (dipentene),[32] which are more abundant terpenes obtained from orange and turpentine oils. The annual total production of carvone and limonene can be estimated to be tens of thousands of tons, indicating that carvone is an abun-

dant feedstock. In addition, biosynthesis of (*R*)-(+)-carvone from glucose has recently been reported using engineered *Escherichia coli*.[33] Carvone is mainly used in the flavor and food industry and is a useful starting material for pharmaceutical compounds; however, it is not commercially applied in polymer synthesis.

In terms of vinyl monomers, two C=C bonds in carvone are hardly polymerized by any intermediates mainly due to the steric hindrance of the trisubstituted internal cyclic olefin and the pendent bulky 1,1-disubstituted olefin. However, we wondered if the specific, carvone-based cyclic structure could be efficiently built into the main chain of polymers, particularly using cationic polymerization after transformation of the cyclic α,β-unsaturated carbonyl group into a conjugated *transoid* cyclic diene with an *exo*-methylene group (CvD in Scheme 1) via the Wittig reaction because the high reactivity of similar *exo*-methylene groups in the cationic polymerizations was reported for other plant-derived monomers.[34,35] Although the synthesis and radical (co)polymerization of CvD was reported briefly, its reactivity in radical polymerization was very low and resulted in a low polymer yield, for which the polymer properties are unknown.[36] As an alternative pathway to carvone-based polymers, Hillmyer et al reported that carvone and dihydrocarvone were transformed into 7-membered ring lactones via Baeyer-Villiger oxidation and polymerized by ring-opening polymerization into linear polyesters.[37–40] In addition, the carvone moiety was introduced into a side chain in methacrylate after transformation into alcohol via reduction and was subsequently polymerized by radical polymerization.[41] However, there have been no studies on the use of the characteristic cyclic and chiral structures of carvone for high-performance and functional bio-based polymers.

In this study, we synthesized CvD, which possesses an *exo*-methylene conjugated diene and an additional 1,1-disubstituted pendent olefin, and HCvD, in which the pendent olefin is hydrogenated, and then investigated living cationic polymerization for the synthesis of novel bio-based polymers using carvone-based characteristic structures.

Scheme 1. Synthesis and Cationic Polymerization of CvD and HCvD Derived from Naturally Occurring Carvone

(*R*)-(−)-CvD was prepared via the Wittig reaction of (*R*)-(−)-carvone with *in situ*-generated phosphorus ylide in THF at room temperature and was isolated in high yield (71%) by distillation ([α]$_D$ = −175°) (Figures S1A, S2, and S3). (*R*)-(−)-HCvD was synthesized via selective hydrogenation of the

pendent olefin of carvone using PtO$_2$ followed by a Wittig reaction under similar conditions (total yield = 66%) ([α]$_D$ = −143°) (Figure S1B, S4, and S5). In addition, (*S*)-(+)-HCvD ([α]$_D$ = +147°) was similarly prepared from (*S*)-(+)-carvone (Figure S1C). Furthermore, the racemic monomer ((±)-HCvD) was prepared by mixing (*R*)-(−)- and (*S*)-(+)-HCvD in equal amounts ([α]$_D$ = −1.9°) (Figure S1D).

The cationic polymerization of these dienes was examined with a typical initiating system for living cationic polymerization of vinyl monomers with a relatively high reactivity, such as vinyl ethers and *p*-methoxystyrene. Figure 1 shows the cationic polymerization using the hydrogen chloride adduct (**1**) of 2-chloroethyl vinyl ether (CEVE) as an initiator in conjunction with SnCl$_4$ as a Lewis acid catalyst in the presence of *n*Bu$_4$NCl as an additive ([M]$_0$/[**1**]$_0$/[SnCl$_4$]$_0$/[*n*Bu$_4$NCl]$_0$ = 100/1.0/5.0/4.0 mM) in a 1:1 mixture of toluene and CH$_2$Cl$_2$ at −78 °C.[42]

In the cationic polymerization of (−)-CvD, the *exo*-methylene group was consumed relatively fast and quantitatively, whereas the pendent olefin was consumed slowly to finally result in an insoluble gel via a crosslinking reaction, in which the monomer worked as a heterobifunctional divinyl monomer with different reactivities (Figure 1A). The polymers obtained at the initial stage showed controlled molecular weight and narrow molecular weight distributions (MWDs) (Figure 1B), indicating that controlled/living cationic polymerization proceeded via chemoselective reaction of the more reactive *exo*-methylene conjugated diene when the pendent olefin consumption was low. At the later stage, however, the less reactive pendent olefin gradually participated in the cationic polymerization to result in very broad MWDs for the soluble fraction and then resulted in an insoluble gel via the crosslinking reaction. These results indicate that the *exo*-methylene conjugated *transoid* cyclic diene structure possesses unique reactivities, *i.e.*, high reactivity in cationic polymerization and low reactivity in radical homopolymerization and that cationic polymerization is suitable for this structure.
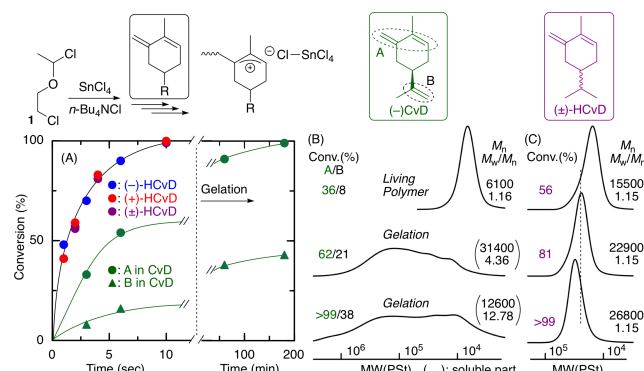

Figure 1. Time-conversion (A) and SEC curves (B and C) obtained in cationic polymerization of (−)-CvD, (−)-HCvD, (+)-HCvD, and (±)-HCvD: [M]$_0$/[**1**]$_0$/[SnCl$_4$]$_0$/[*n*Bu$_4$NCl]$_0$ = 100/1.0/5.0/4.0 mM in toluene/CH$_2$Cl$_2$ (50/50 vol%) at −78 °C.

For the monomer without the pendent olefin, *i.e.*, (−)-HCvD and (+)-HCvD, its *exo*-methylene was consumed very rapidly within 10 sec (Figures 1A and S6). However, irrespective of the absence of the pendent olefin, the obtained polymers were insoluble in common organic solvents, such as toluene, CH$_2$Cl$_2$, CHCl$_3$, and THF, which can be ascribed to the formation of stereoregular polymers via stereospecific polymerization induced by the chirality of the monomer.

Then, the racemic monomer (±)-HCvD was polymerized with the same initiating system under the same conditions. The cationic polymerization was similarly completed in 10 sec and resulted in a soluble polymer quantitatively. The number average molecular weight (M_n) increased in direct proportion to the monomer conversion, and the MWDs remained narrow throughout the polymerization ($M_w/M_n = 1.15$) (Figure 1C). These results show that (±)-HCvD or exo-methylene possess high reactivity in cationic polymerization and can be polymerized in a controlled or living fashion using the same initiating system for living cationic polymerization as that of vinyl ethers.

To confirm the molecular weight control, the feed ratio of the monomer to initiator ($[M]_0/[1]_0$) was varied by changing the concentration of initiator while keeping that of the monomer constant. For (±)-HCvD, the polymerization smoothly proceeded in all cases ($[M]_0/[1]_0 = 50, 100, 200$) to yield polymers with narrow MWDs ($M_w/M_n \leq 1.15$) and controlled molecular weights, although the M_n values based on the calibration by polystyrene standards in SEC were higher than the calculated values due to differences in the hydrodynamic volumes (Figure 2). Indeed, the absolute molecular weights measured by a multiangle laser light scattering (MALLS) detector coupled to SEC were closer to the calculated values, assuming that one initiator generates one polymer chain. Furthermore, monomer addition experiments were successful as shown in Figure S7.
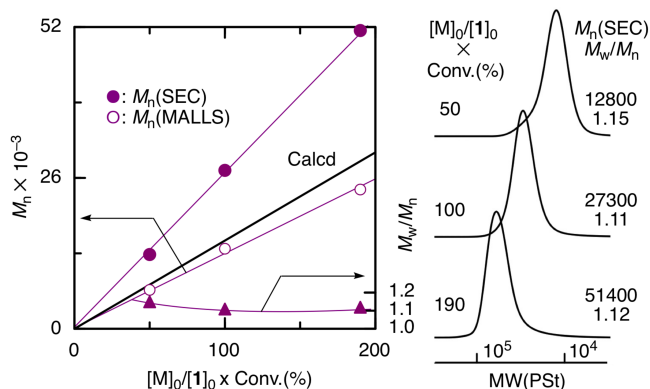

Figure 2. M_n, M_w/M_n, and SEC curves of poly((±)-HCvD) obtained in living cationic polymerization: $[(\pm)$-HCvD$]_0/[1]_0/[SnCl_4]_0/[nBu_4NCl]_0 = 100/0.5–2.0/5.0/4.0$ mM in toluene/CH_2Cl_2 (50/50 or 75/25 vol%) at −78 °C.

For (−)-CvD, the polymer obtained at varying feed ratios also had a controlled molecular weight at the initial stage and suffered gradual broadening of MWDs to finally result in an insoluble gel, particularly at a relatively high feed ratio ($[M]_0/[1]_0 = 50$ and 100) (Figure S8). However, the final products obtained at a lower feed ratio ($[M]_0/[1]_0 = 25$) were soluble because a shorter polymer chain had a lower number of crosslinking points in the polymer chain.

The structures of the polymers obtained from (−)-CvD and (±)-HCvD were analyzed by NMR in CDCl$_3$, whereas the polymers obtained from (−)-HCvD and (+)-HCvD were successfully analyzed in C$_2$D$_2$Cl$_4$, which is generally effective for solubilizing many crystalline polyolefins (Figure 3). All of the large peaks observed in the ^{1}H and ^{13}C NMR spectra could be assigned to the polymers with tetra-substituted olefins and main-chain 1,3-cyclohexenyl rings, which formed via regioselective 1,4-conjugated addition of the exo-methylene conjugated diene, using DEPT, COSY, and HMQC techniques (Figures S9–S13). In addition, the M_n(NMR) values, which were obtained from the peak intensity ratios of the main chain (a, c, and f for poly(CvD) and h for poly(HCvD)) to the CEVE unit (α_2-α_4) originating from the initiator, were close to the calculated values (M_n(Calcd)), assuming that one initiator generates one polymer chain (Figure 3). These results indicate that **1** efficiently initiated regioselective living cationic polymerization of these exo-methylene conjugated dienes.
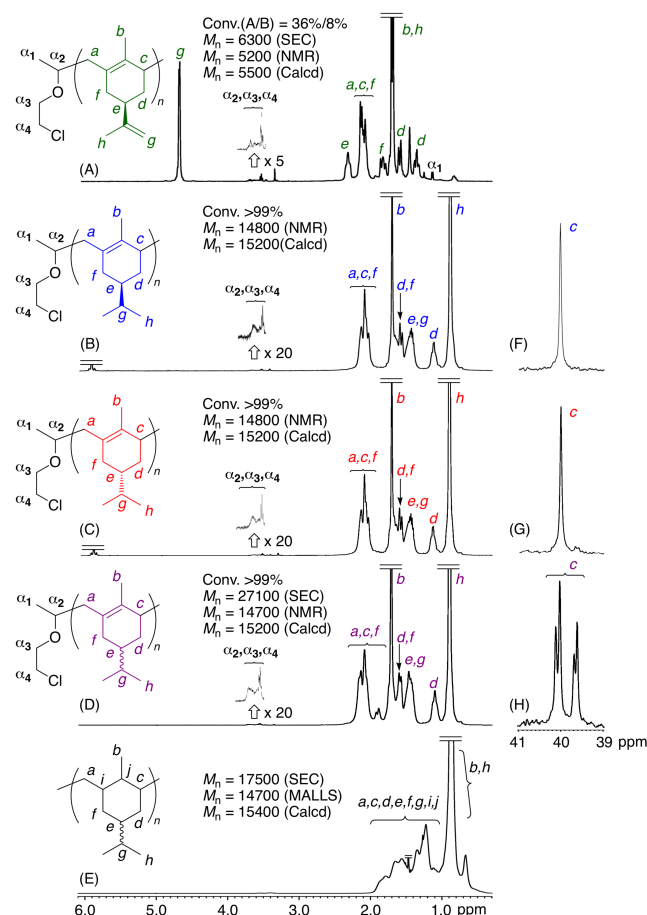

Figure 3. ^{1}H (A–E) and ^{13}C (F–H) NMR spectra (A, D, E: in CDCl$_3$ at 55 °C; B, C, F–H: in C$_2$D$_2$Cl$_4$ at 100 °C) of poly((−)-CvD), poly((−)-HCvD), poly((+)-HCvD), poly((±)-HCvD) obtained in cationic polymerization ($[M]_0/[1]_0/[SnCl_4]_0/[nBu_4NCl]_0 = 100/1.0/5.0/4.0$ mM in toluene/CH_2Cl_2 (50/50 vol%) at −78 °C), and hydrogenated poly((±)-HCvD)

The well-defined terminal structures were also confirmed by the MALDI-TOF-MS of poly((±)-HCvD) as well as poly((−)-HCvD), in which a single series of peaks were mainly observed by a 150 Da interval, i.e., the molar mass of HCvD and were assigned to the polymers possessing one CEVE unit at the initiating terminal, although the ω-termini were different from each other (Figure S16). The molar masses of each peak for poly((±)-HCvD) agreed well with those for the polymer possessing the CEVE moiety at the α-end and the methoxy group at the ω-end, which originated from methanol as the quencher for the living cationic polymerization. However, the peaks for poly((−)-HCvD) can be assigned to those of the polymers with an olefin at the ω-terminus most likely due to the loss of chlorine at the living chain end during the workup. Since the resulting poly((−)-HCvD) was precipitated during

3

the polymerization due to the insolubility, substitution of the terminal chloride with methoxide during quenching was very difficult.

Furthermore, the pendent olefin peaks of poly((−)-CvD) became smaller as the polymerization proceeded (Figure S9), indicating that the crosslinking reaction gradually occurred. In contrast, ^{1}H NMR of poly((−)-HCvD) and poly((+)-HCvD)) showed relatively sharp peaks (Figures 3B and 3C). In addition, all the ^{13}C MNR peaks of poly((−)-HCvD) and poly((+)-HCvD)) were much simpler than those of poly((±)-HCvD) (Figure S12). In particular, only one peak was observed for carbon c at the 4-position (Figures 3F and 3G), unlike four peaks, which were observed for poly((±)-HCvD) obtained from the racemic monomer (Figure 3H). These results suggest that the isopropyl group attached to the chiral center (e) strongly influences conformation of the 6-membered ring via 1,3-diaxial interactions and then dictates the absolute configuration of c during the cationic propagation. The four diastereomeric carbons of poly((±)-HCvD) can be attributed to the different triads of the racemic monomers, *i.e.*, *RRR*, *RRS*, *SRR*, and *SRS* (and their enantiomeric forms, *SSS*, *SSR*, *RSS*, and *RSR*) with the regular relative configuration between the isopropyl group and the polymer chain in the 1,3-*cis* form (Figure S14). The only one carbon (c) for poly((−)-HCvD) or poly((+)-HCvD)) indicates the same triad *RRR* or *SSS* of the enantiomeric monomer with the regular relative configuration.[43] A stereoregular polymer was thus obtained in the living cationic polymerization of enantiomeric pure (−)-HCvD or (+)-HCvD via stereospecific polymerization.

The thermal properties of the polymers were evaluated by differential scanning calorimetry (DSC). The DSC curves of soluble poly((−)-CvD) (M_n(SEC) = 4000) and poly((±)-HCvD) (M_n(MALLS) = 13700) showed glass transition temperatures (T_g) of 86 °C and 113 °C, respectively (Figure 4A). The lower T_g of poly((−)-CvD) was due to the lower molecular weight of the soluble polymer before gelation. In particular, poly((±)-HCvD), which is derived from carvone, had a higher T_g than that of poly(β-pinene) or poly(β-phellandrene) ($T_g \sim 90$ °C), which are derived from other naturally occurring terpenes, β-pinene and β-phellandrene, respectively.[17,18,35] Poly((−)-HCvD) (M_n(Calcd) = 15200) and poly((+)-HCvD)) (M_n(Calcd) = 15200) showed similar T_gs around 110 °C and another endotherm around 240 °C, which can be attributed to the melting point, just before the decomposition started (T_{d5} = 280 °C in Figure S17).

The structure of poly((−)-HCvD) was further evaluated by powder X-ray diffraction (XRD) (Figure 4B). In the small-angle region, a series of broad scatterings were observed at 2θ angles of 3.4° (2.6 nm), 6.8° (1.3 nm), and 10.3° (0.86 nm). These equal interval peaks were ascribed to a periodic lamellar structure with weak regularity. A broad peak at 17.4° (0.51 nm) in the wide angle corresponded to the weak packing of the main chain in the lamellar layers. This structure resulted in low solubility of the rigid polymer backbone and could be attributed to the stereoregular structure formed via stereospecific polymerization. Although the optical activity of poly((−)-HCvD) could not be measured due to the insolubility in common organic solvents at room temperature, the soluble poly((−)-CvD) (M_n(SEC) = 4000) showed optical rotation (($[\alpha]_D$ = −102°) in THF at 25 °C due to the pendent chiral group and, possibly, the resulting new asymmetric carbon in the main chain (Table S1). In contrast, almost no optical ac-

tivity was observed for poly((±)-HCvD) ($[\alpha]_D$ = +0.65°) obtained from the racemic monomer. These results indicate that the unique structure originating from naturally occurring chiral carvone enables the synthesis of novel bio-based cycloolefin polymers with stereoregularity, chirality, a lamella-like periodic structure, and good thermal properties.
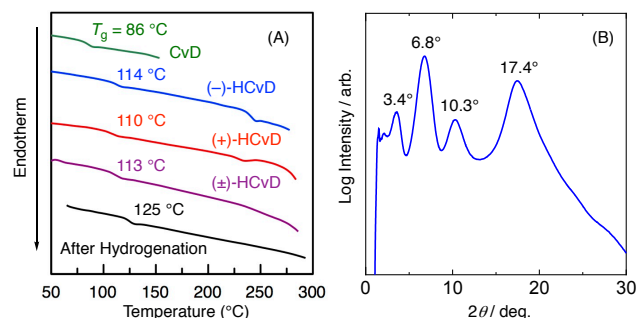

Figure 4. Differential scanning calorimetry (DSC) curves of poly((−)-CvD) (green), poly((−)-HCvD) (blue), poly((+)-HCvD) (red), poly((±)-HCvD) (purple), and hydrogenated poly((±)-HCvD) (black) (A) and powder X-ray diffraction (XRD) profile of poly((−)-HCvD).

Furthermore, hydrogenation of poly((±)-HCvD) was investigated to obtain the cycloolefin polymer structure. Although the hydrogenation was unsuccessful with *p*-toluenesulfonyl hydrazide unlike poly(β-pinene),[17] Pd/Al$_2$O$_3$ catalyst enabled the hydrogenation. As shown in Figure 3E and Figure S18, allylic protons and olefinic carbons completely disappeared. Whereas the SEC curve shifted to lower molecular weights (Figure S18), the M_n(MALLS) was almost unchanged. The hydrogenation resulted in increased thermal properties, *i.e.*, a slight increase of T_g from 113 to 125 °C (Figure 4) and a significant increase of T_{d5} from 288 to 372 °C (Figure S17). The novel bio-based cycloolefin polymers with good thermal properties were thus obtained.

Another interesting carvone-derived structure of (−)-CvD is the less reactive pendent olefin, which participates in the cationic polymerization at the later stage and induces the crosslinking reaction. The unique heterobifunctional monomer with different reactivities is often to be used for the synthesis of core-crosslinked star polymers in living cationic block copolymerization.[44,45] CEVE was thus first polymerized with the same initiating system consisting of **1**, SnCl$_4$, and *n*Bu$_4$NCl under the same conditions to give living linear poly(CEVE), to which (−)-CvD was added after complete consumption of CEVE (Figure 5). The SEC curve shifted to a high molecular weight while maintaining a narrow MWD at the initial stage, indicating the formation of the block copolymer via living cationic polymerization of the more reactive *exo*-methylene moiety of (−)-CvD, and finally shifted to a much higher molecular weight region over 10^5 Da with broadening. The absolute weight-average molecular weight of the final product (M_w(MALLS)) was slightly higher than M_w(SEC) obtained using a refractive index (RI) detector (Table S2), indicating the formation of star polymers with loosely crosslinked cores due to the less reactive pendent olefin. The average number of arm chains per star polymer (N_{arm}) was calculated to be 21. Thus, (−)-CvD works as the unique heterobifunctional monomer for the synthesis of characteristic star polymers in living cationic polymerization.
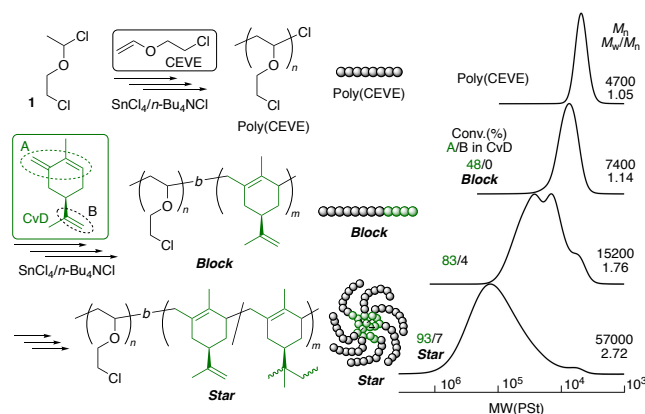
Figure 5. SEC curves of the polymers obtained in block copolymerization of CEVE and (−)-CvD: $[CEVE]_0/[(-)-CvD]_{add}/[1]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 200/100/4.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at −78 °C.

In conclusion, a naturally occurring carvone was successfully transformed via simple chemical reactions into *exo*-methylene cyclic *transoid* conjugated dienes that possess high reactivity in cationic polymerization and can be efficiently polymerized in a controlled manner via regioselective conjugated additions by initiating systems for living cationic polymerization vinyl ethers. The obtained polymers with the substituted 1,3-cyclohexenyl unit and tetra-substituted olefin in the main chain exhibit relatively high T_g values over 110 °C. The subsequent hydrogenation resulted in novel bio-based cycloolefin polymers with enhanced thermal properties. In addition, the chiral monomer undergoes stereospecific polymerization to result in optically active polymers with low solubility and a weakly periodic lamella structure due to stereoregularity. Furthermore, an additional pendent olefin originating from carvone could be used for the synthesis of loosely core-crosslinked star polymers. The unique structures derived from natural compounds enable the synthesis of novel vinyl polymers and further contribute to the development of bio-based polymers as high-performance materials that are unable to be obtained from petroleum-derived compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental and characterization details (PDF)

AUTHOR INFORMATION

Corresponding Author

Masami Kamigaito – Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan; orcid.org/0000-0001-7584-5524; Email: kamigait@chembio.nagoya-u.ac.jp

Authors

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

Kotaro Satoh – Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-H120 Ookayama, Meguro-ku, Tokyo 152-8550, Japan; orcid.org/0000-0002-3105-4592

Shusaku Nagano – Department of Chemistry, College of Science, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima, Tokyo 171-8501, Japan; orcid.org/0000-0002-3929-6377

Takahiro Seki – Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan; orcid.org/0000-0003-3010-2641

Masazumi Tamura – Research Center for Artificial Photosynthesis, Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan; orcid.org/0000-0002-8293-6093

Yingai Li – Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

Keiichi Tomishige – Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan; orcid.org/0000-0003-1264-8560

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

REFERENCES

(1) Coates, G. W.; Hillmyer, M. A. Polymers from renewable resources. *Macromolecules* **2009**, *42*, 7987–7989.

(2) Yao, K.; Tang, C. Controlled polymerization of next-generation renewable monomers and beyond. *Macromolecules* **2013**, *46*, 1689−1712.

(3) Iwata, T. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. *Angew. Chem. Int. Ed.* **2015**, *54*, 3210–3215.

(4) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable polymers from renewable resources. *Nature* **2016**, *540*, 354−362.

(5) Froidevaux, V.; Negrell, C.; Caillol, S.; Pascault, J.-P.; Boutevin, B. Biobased amines: from synthesis to polymers; present and future. *Chem. Rev.* **2016**, *116*, 14181−14224.

(6) Llevot, A.; Dannecker, P.-K.; Czapiewski, M. von; Over, L. C.; Söyer, Z.; Meier, M. A. R.; Renewability is not enough: recent advances in the sustainable synthesis of biomass-derived monomers and polymers. *Chem. Eur. J.* **2016**, *22*, 11510−11521.

(7) Thomsett, M. R.; Storr, T. E.; Monaghan, O. R.; Stockman, R. A.; Howdle, S. M. Progress in the sustainable polymers from terpenes and terpenoids. *Green Mater.* **2016**, *4*, 115−134.

(8) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From lignin-derived aromatic compounds to novel biobased polymers. *Macromol. Rapid Commun.* **2016**, *37*, 9−28.

(9) Schneiderman, D. K.; Hillmyer, M. A. There is a great future in sustainable polymers. *Macromolecules* **2017**, *50*, 3733–3749.

(10) Nguyen, H. T. H.; Rostagno, P. Qi, M.; Feteha, A.; Miller, S. A. The quest for high glass transition temperature bioplastics. *J. Mater. Chem. A* **2018**, *6*, 9298–9331.

(11) Breitmaier, E. *Terpenes: flavors, fragrances, pharmaca, pheromones.*; Wiley-VCH: Weinheim, **2006**.

(12) Erman, W.F. *Chemistry of the monoterpenes: an encyclopedia handbook.*; Marcel Dekker, Inc.: New York, **1985**.

(13) Connolly, J. D.; Hill, R. A. *Dictionary of terpenoids.*; Chapman & Hall: London, **1991**.

(14) Satoh, K.; Kamigaito, M. *New polymerization methods for biobased polymers, In Bio-based polymers*.; Kimura, Y., Eds.; CMC: Tokyo, **2013**; pp 95−111.

(15) Kamigaito, M.; Satoh, K. *Bio-based hydrocarbon polymers, In Encyclopedia of polymeric nanomaterials.*; Kobayashi, S., Müllen, K., Eds.; Springer: Heidelberg, **2015**; Vol. 1, pp 109−118.

(16) Kamigaito, M.; Satoh, K. *Sustainable vinyl polymers via controlled polymerization of terpenes, In Sustainable polymers from biomass.*; Tang, C., Ryu, C. Y., Eds.; Wiley-VCH: Weinheim, **2017**; pp 55−90.

(17) Satoh, K. Controlled/living polymerization of renewable vinyl monomers into bio-based polymers. *Polym. J.* **2015**, *47*, 527−536.

(18) Satoh, K.; Sugiyama, H.; Kamigaito, M. Biomass-derived heat-resistant hydrogenated alicyclic hydrocarbon polymers: poly(terpenes) and their derivatives. *Green Chem.* **2006**, *8*, 878–882.

(19) Satoh, K.; Nakahara, A.; Mukunoki, K.; Sugiyama, H.; Saito, H.; Kamigaito, M. 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.* **2014**, *5*, 3222−3230.

(20) 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.* **2010**, *132*, 10003−10005.

(21) Matsuda, M.; Satoh, K.; M. Kamigaito Periodically functionalized and grafted copolymers via 1:2-sequence-regulated radical copolymerization of naturally occurring functional limonene and maleimide derivatives. *Macromolecules* **2013**, *46*, 5473−5482.

(22) Matsuda, M.; Satoh, K.; Kamigaito, M. Controlled radical copolymerization of naturally-occurring terpenes with acrylic monomers in fluorinated alcohol. *KGK Kaut. Gummi Kunstst.* **2013**, *66* (5), 51−56.

(23) 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., Part A: Polym. Chem.* **2013**, *51*, 1774−1785.

(24) Ojika, M.; Satoh, K.; Kamigaito, M. 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.* **2017**, *56*, 1789−1793.

(25) Hashimoto, H.; Takeshima, H.; Nagai, T.; Uchiyama, M.; Satoh, K.; Kamigaito, M. Valencene as a naturally occurring sesquiterpene monomer for radical copolymerization with maleimide to induce concurrent 1:1 and 1:2 propagation. *Polym. Degrad. Stab.* **2019**, *161*, 183−190.

(26) Kaminsky, W.; Boggioni, L.; Tritto, I. *Cycloolefin Polymerization* in *Polymer Science: A Comprehensive Reference*, Vol. 3.; Matyjaszewski, K., Möller, M., Eds.; Elsevier BV: Amsterdam, **2012**; pp 843−873.

(27) Yamazaki, M. Industrialization and application development of cyclo-olefin polymer. *J. Mol. Catal. A: Chem.* **2004**, *213*, 81−87.

(28) Harauchi, Y.; Houkawa, T.; Adachi, S.; Araki, K.; Sawaguchi, T.; Hayano, S.; Uchiyama, S. Recent Developments of Cyclo Olefin Polymers. *Kobunshi Ronbunshu* **2018**, *75*, 477–485.

(29) *Handbook of essential oils: science, technology, and applications.*; Başer, K. H. C. Buchbouer, G. Eds.; CRC Press: Boca Baton, **2016**; pp 814.

(30) De Carvalho, C. C. C. R.; Da Fonseca, M. M. R. Carvone; Why and how should one bother to produce this terpene. *Food Chem.* **2006**, *95*, 413–422.

(31) Leitereg, T. J.; Guadagni, D. G.; Harris, J.; Mon, T. R.; Teranishi, R. Chemical and Sensory Data Supporting the Difference between the Odors and the Enantiomeric Carvones. *J. Agr. Food Chem.* **1971**, *19*, 785–787.

(32) Rothenberger, O. S.; Krasnoff, S. B.; Rollins, R. B. Conversion of (+)-Limonene to (–)-Carvone. *J. Chem. Educ.* **1980**, *57*, 741–742.

(33) Ascue Avalos, G. A.; Toogood, H. S.; Tait, S.; Messiha, H. L.; Scrutton, N. S. From Bugs to Bioplastics; Toal (+)-Dihydrocarvide Biosynthesis by Engineered Escherichia coli. *ChemBioChem* **2019**, *20*, 785–792.

(34) Kobayashi, S.; Lu, C.; Hoye, 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.* **2009**, *131*, 7960–7961.

(35) Kamigaito, M., Satoh, K., Suzuki, S., Kori, Y., Eguchi, Y., Iwasa, K., Shiroto, H. β-Phellandrene polymer, production method for same, and molded article. WO 2015/060310 A1, filed Oct. 21, 2014 and issued Apr. 30, 2015.

(36) Trumbo, D. L. Synthesis and Polymerization of 1-Methyl-4-isopropenyl-6-methylene-1-cyclohexene. *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 599–601.

(37) Lowe, J. R.; Tolman, W. B.; Hillmyer, M. A. Oxidized Dihydrocarvone as a Renewable Multifunctional Monomer for the Synthesis of Shape Memory Polyesters. *Biomacromolecules* **2009**, *10*, 2003–2008.

(38) Lowe, J. R.; Martello, M. T.; Tolman, W. B.; Hillmyer, M. A. Functional biorenewable polyesters from carvone-derived lactones. *Polym. Chem.* **2011**, *2*, 702–708.

(39) Knight, S. C.; Schaller, C. P.; Tolman, W. B.; Hillmyer, M. A. Renewable carvone-based polyols for use in polyurethane thermosets. *RSC Adv.* **2013**, *3*, 20399–20404.

(40) Yang, J.; Lee, S.; Choi, W. J.; Seo, H.; Kim, P.; Kim, G.-J.; Kim, Y.-W.; Shin, J. Thermoset Elastomers Derived from Carvonmenthide. *Biomacromolecules* **2015**, *16*, 246–256.

(41) Sainz, M. F.; Souto, J. A.; Regentova, D.; Johansson, M. K. G.; Timhagen, S. T.; Irvine, D. J.; Buijsen, P.; Koning, C. E.; Stockman, R. A.; Howdle, S. M. A facile and green route to terpene derived acrylate and methacrylate monomers and simple free radical polymerisation to yield new renewable polymers and coatings. *Polym. Chem.* **2016**, *7*, 2882–2887.

(42) Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. Living Cationic Polymerization of Isobutyl Vinyl Ether by Hydrogen Chloride/Lewis Acid Initiating Systems in the Presence of Salts: In-Situ Direct NMR Analysis of the Growing Species. *Macromolecules* **1993**, *26*, 1643-1649.

(43) The NOESY spectrum of poly((–)-HCvD) suggests or at least does not rule out that protons *c* and *e* are spatially close and are located in the diaxial positions (Figure S15).

(44) Aoshima S.; Kanaoka, S. A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **2009**, *109*, 5245–5287.

(45) Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T.; Boyer, C.; Qiao, G. G. Star Polymers. *Chem. Rev.* **2016**, *116*, 6734–6836.

exo-Methylene cyclic conjugated dienes, which are chemically transformed from carvone, a naturally abundant chiral cyclic α,β-unsaturated carbonyl compound, are efficiently polymerized by 1,4-regioselective and stereospecific living cationic polymerization. The chiral monomers result in polymers with weak packing of the rigid main chain in the lamellar layers whereas the racemic mixture results in amorphous polymers, which can be hydrogenated into cycloolefin polymers with enhanced thermal properties.