PAPER

Functionalized cyclic olefin copolymers: chemoselective polymerization of a cyclopropane-containing norbornadiene dimer using a titanium catalyst and post-polymerization modification†

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The synthesis of functionalized polyolefins is important for tuning their properties and expanding their application range. However, the copolymerization of olefins with polar monomers using early transition-metal catalysts remains a formidable challenge. Here, we demonstrate a synthesis strategy through the Ti-catalyzed addition polymerization of a cyclopropane-containing norbornadiene dimer (**1**), followed by post-polymerization modification (PPM). The polymerization of **1** using a constrained-geometry Ti catalyst afforded poly**1** with narrow molecular weight distributions ($Đ$ < 1.3), wherein the molecular weight increased linearly with the monomer conversion. Additionally, the copolymerization of **1** with 1-octene proceeded rapidly, and **1** was consumed faster than 1-octene to form gradient copolymers. The ^{13}C nuclear magnetic resonance (NMR) spectroscopic analysis of the polymers indicated that the coordination−insertion of the alkenyl group of **1** occurred selectively without side reactions at the cyclopropane moiety. The polymerizations were highly controlled and chemoselective owing to the lack of cyclopropane coordination to the active Ti species involved in the polymerization. The PPM of poly(**1**-*co*-1-octene) *via* the protic acid-catalyzed ring-opening reaction of the cyclopropane introduced aromatic, acyloxy, and alkoxy groups in high incorporation ratios without cross-linking reactions. Thus, this work demonstrates a promising procedure for the modification of cyclic olefin copolymers using specific cyclopropane reactivity.

Introduction

Olefin polymerization catalyzed by early transition metal (Ti, Zr, Hf, and Sc) complexes exhibits excellent activity and selectivity, affording well-defined polymer structures (molecular weight, narrow molecular weight distribution, linear structure, regio- and stereoselectivity, and comonomer sequence and its distribution).[1–5] However, copolymerization with polar monomers remains difficult[6–8] because of catalyst poisoning *via* the coordination of Lewis-basic functional groups to the electrophilic metal center. Several functional polyolefins bearing hydroxy,[9–18] sulfanyl,[12] carboxy,[14,19] methoxycarbonyl,[14,19] and dihydroxyboryl[20] groups can be synthesized through their protection using aluminum[9,11–13,15,17,18] and borane[10,16,20] func-

tionalities. Although late transition-metal (Ni and Pd) complexes can be employed for successful copolymerizations with polar monomers,[21,22] a general procedure for producing functional polyolefins through the most reliable and industrially relevant Ti-catalyzed polymerization systems should be developed.

Post-polymerization modification (PPM) is an alternative method for producing functionalized polyolefins,[23–25] and polyolefins containing alkenyl groups are suitable for PPM reactions.[26–37] They are synthesized *via* coordination copolymerizations with diene monomers, *i.e.* isoprene,[29,37] α,ω-dienes,[26–28,30–32,34] myrcene,[33] and dicyclopentadiene;[35,36] however, undesired cross-linking reactions may inherently occur. PPMs *via* C–H bond activation are facilitated by transition metal catalysis or radical mechanisms,[38–42] and polyolefin upcycling has recently been realized.[41–43] Although they are attractive because of the transformation of the most common C–H groups, it is generally difficult to control selectivity and conversion and inhibit side reactions, *i.e.*, cross-linking and polymer chain scission.

We performed the ring-opening metathesis polymerization (ROMP) of a cyclopropane-containing norbornadiene dimer (**1**)

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and the subsequent PPM of the resulting hydrogenated polymer.[44] The cyclopropane moiety is inert to Ru-catalyzed ROMP and hydrogenation, whereas it readily undergoes ring-opening with protic acids. It is rare to coordinate the C–C bonds of non-polar cyclopropanes to transition metal centers (except for a few specific substrates) despite their high ring strain.[45–47] Therefore, we hypothesized and found that monomer **1** undergoes selective addition polymerization at the alkenyl group without cyclopropane ring opening with a highly Lewis-acidic cationic Ti center.

Herein, we demonstrate a synthesis procedure for functionalized polyolefins *via* Ti-catalyzed addition polymerization and subsequent PPM. We employ an *ansa*-fluorenylamidotitanium complex, $Me_2Si(Flu)(N^tBu)TiMe_2$ (**2**), which is one of the most reliable catalysts for the living/controlled (co)polymerization of norbornenes (with olefins).[48–51] The (co)polymerization of **1** (with 1-octene) affords cyclopropane-containing cyclic olefin copolymers (COCs), which undergo protic acid-mediated PPM to introduce various functional groups, *i.e.*, aromatic, acyloxy, and alkoxy groups, without any cross-linking and polymer chain scission.

Results and discussion

The dimerization of norbornadiene catalyzed by $CoBr_2(dppe)/ZnI_2/Bu_4NBH_4$ (dppe: 1,2-bis(diphenylphosphino)ethane) afforded monomer **1** as a mixture of *exo–exo* and *exo–endo* isomers with a molar ratio of 80 : 20.[44] The isomeric mixture was used for the polymerizations without their isolation. The homopolymerization of **1** was investigated using **2** with $[Ph_3C][B(C_6F_5)_4]$ as the cocatalyst and $Al^iBu(BHT)_2$ (bis(2,6-di-

tert-butyl-4-methylphenoxy)isobutylaluminum) as the scavenger in toluene at 0 °C for 60 min. The polymerization was initiated by adding $[Ph_3C][B(C_6F_5)_4]$ into a solution of **1**, **2**, and $Al^iBu(BHT)_2$, to afford poly**1** with high molecular weights and narrow molecular weight distributions ($Đ$ < 1.3) in high yields (runs 1 and 2, Table 1). A kinetic study revealed that the conversion of **1** reached 59% in 20 min and 93% in 60 min (Fig. S2†).[52] The size-exclusion chromatography (SEC) of poly**1** sampled at low to high conversions indicated that the peaks shifted toward the high-molecular-weight side, retaining a unimodal distribution ($Đ$ < 1.25) (Fig. 1(A)). The molecular weights estimated at the SEC peak top (M_p) increased linearly with the conversion (Fig. 1(B)). Thus, the polymerization proceeded in a controlled manner without apparent side reactions.
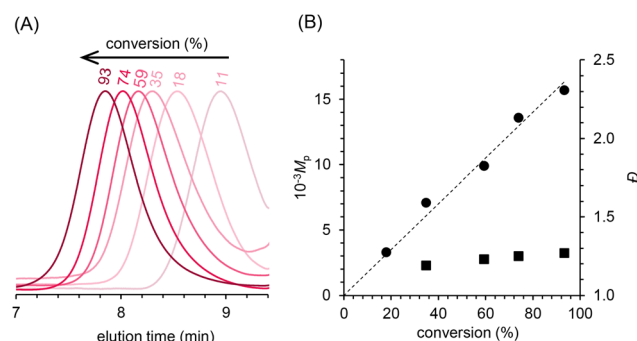

Fig. 1 (A) SEC chromatograms of poly**1** at various conversions (under the same conditions as run 1 in Table 1) and (B) molecular weights estimated at the SEC peak top (M_p, filled circle) and $Đ$ value (filled square) against conversion.

Table 1 Polymerization of **1** and copolymerization of **1** with 1-octene catalyzed by **2**[a]

Run	$[1]_0/[1\text{-octene}]_0$	$[M]_0/[2]_0$[b]	Yield[c] (%)	Composition of **1**[d] (mol%)	$10^{-3}M_n$[e]	$Đ$[e]
1	100/—	135	90	100	17	1.22
2	100/—	270	89	100	26	1.18
3	50/50	90	92	—	14	1.35
4	50/50	135	91	—	18	1.44
5	50/50	270	93	46	38	1.39
6	60/40	270	93	63	36	1.40
7	40/60	270	91	33	40	1.44
8[f]	50/50	540	89	—	62	1.52

[a] **2**, 20 μmol; $[Ph_3C][B(C_6F_5)_4]$, 20 μmol; $Al^iBu(BHT)_2$, 200 μmol; toluene, 30 mL. [b] **M**: total monomer (**1** and 1-octene). [c] The conversions of **1** and 1-octene were quantitative. [d] Calculated using the ^{13}C NMR integral ratio of O7, O8, and the cyclopropane moiety (see Fig. 3(C) and the ESI† for details). [e] SEC ($CHCl_3$, polystyrene standards). [f] **2**: 10 μmol.

(A) / (B)
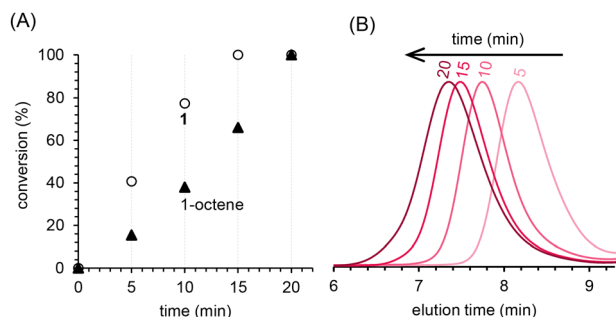
Fig. 2 (A) Time *versus* conversion plots of the copolymerization of **1** (open circle) with 1-octene (filled triangle) (under the same conditions as run 5 in Table 1) and (B) the corresponding SEC chromatograms of the obtained poly(**1**-*co*-1-octene)s.

The copolymerization of **1** and 1-octene ($[\mathbf{1}]_0 : [\text{1-octene}]_0 = 50 : 50$) proceeded efficiently and was completed within 60 min under similar conditions to afford poly(**1**-*co*-1-octene) with high M_n (14 000–62 000) and narrow $Đ$ values (<1.6) in high yields (runs 3–5 and 8). The M_n values increased with the $[\mathbf{M}]_0/[\mathbf{2}]_0$ (**M** : **1** and 1-octene) values while maintaining the unimodal distributions. Additionally, the copolymerizations at $[\mathbf{1}]_0/[\text{1-octene}]_0$ of 60/40 and 40/60 yielded the corresponding poly(**1**-*co*-1-octene) with high M_n values in high yields (runs 6 and 7). The kinetic study indicated that **1** and 1-octene were completely consumed within 20 min (run 5, Fig. 2(A) and Table S1†). The conversion of **1** and 1-octene reached 41% and 15%, respectively, for 5 min, indicating the higher polymerizability of **1** despite the bulky structure and the formation of a gradient copolymer sequence. The SEC chromatograms shifted toward the high-molecular-weight side with the conversions while retaining the unimodal distribution (Fig. 2(B)), support-

ing that the copolymerization also proceeded in a controlled manner.

The structures of poly**1** and poly(**1**-*co*-1-octene) were analyzed by nuclear magnetic resonance (NMR) spectroscopy (Fig. 3 and S2–S5†). Fig. 3 shows their ^{13}C NMR spectra compared with those of hydrogenated **1** (H-**1**). The measurements were conducted with a high-resolution instrument (225 MHz for ^{13}C) using Cr(acac)$_3$ as the relaxation reagent to quench the nuclear Overhauser effect. The signals corresponding to the cyclopropane moiety, methylene, and other methine carbons for poly**1** appeared at 12–18, 28–35, and 38–57 ppm, respectively (Fig. 3(B)). No quaternary carbons were detected. The characteristic three methine signals for the cyclopropane moieties observed at 12, 13, and 17 ppm corresponded to C6 for the *exo–exo* isomer, C4′ and C5′ for the *exo–endo* isomer, and
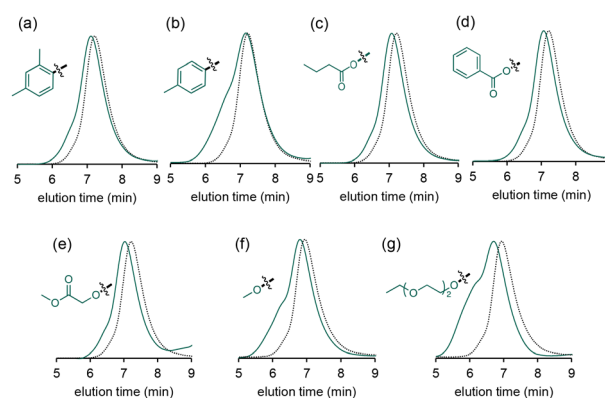
Fig. 4 SEC chromatograms before and after the PPM; functionalized poly(**1**-*co*-1-octene)s (poly**3a–3g**) (green solid line) and prepolymer, poly(**1**-*co*-1-octene), (black dotted line). The chromatograms of (a)–(g) correspond to runs 1–7 in Table 2.
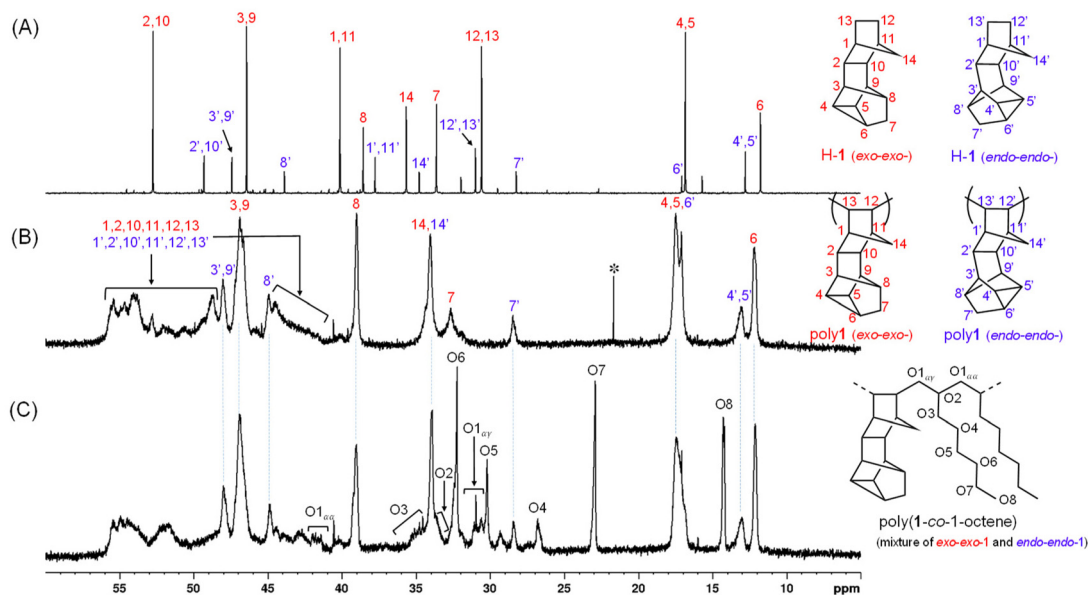
Fig. 3 ^{13}C NMR spectra of (A) H-**1**, (B) poly**1** (run 2, Table 1), and (C) poly(**1**-*co*-1-octene) (run 6, Table 1).

Table 2 PPM of poly(**1**-*co*-1-octene) (run 5, Table 1, 46% composition of **1**) with various weak nucleophiles (Nu–H) using Tf$_2$NH

Run	Nu–H[a] (equiv.)	Tf$_2$NH (equiv.[a])	Yield (%)	Incorp.[b] (%)	$10^{-3}M_n$[c]	Đ[c]	T_{d10}[d] (°C)
1[e]	*m*-Xylene (150)	0.1	70	80	43.6	1.38	427
2[e]	Toluene (150)	0.1	69	62	45.6	1.56	430
3	Butyric acid (5)	0.1	93	85	45.5	1.36	311
4	Benzoic acid (5)	0.1	70	82	44.8	1.34	310
5	Methyl glycolate (5)	0.1	92	99	53.8	1.25	384
6	Methanol (5)	1	87	80	70.2	1.51	387
7	2-(2-Ethoxyethoxy)ethanol (5)	1	82	70	89.4	1.62	368

[a] Equivalent relative to the cyclopropane moiety. [b] Incorporation ratio of the Nu unit in the copolymers estimated by ¹H NMR. [c] SEC (CHCl₃, polystyrene standards). [d] 10% weight loss temperature estimated by TGA. [e] Nu–H used as both the reagent and solvent.

C4, C5, and C6′ (overlapping) for the *exo–exo* and *exo–endo* isomers, respectively. The methylene carbons (C7 and C7′) bonded to the cyclopropane moiety were observed at 28 ppm (for *exo–endo*) and 32 ppm (for *exo–exo*). The bridgehead methylene carbons (C14 and C14′) in proximity to the main chain for both isomers overlapped at 34 ppm. There were no other signals for methylene carbons. The high-intensity signals for methine C8 and methine C3 and C9 appeared at 39 and 47 ppm, respectively, with reasonable integral ratios. The other methine carbons of the polymerizable norbornene moiety (C1, C2, C10, C11, C12, and C13) were broad and split signals because of the stereoregularity of the main chain. It was reported that a σ-bond metathesis reaction occurred during the Zr-catalyzed addition polymerization of norbornene to form a 2,7-linkage.[53] However, in this study, the clear assignment of ¹³C signals, particularly for the methylene signals derived from C14 and C14′, not from C12 and C13, ruled out the possibility of such isomerization polymerization. Furthermore, the signals of poly(**1**-*co*-1-octene) were reasonably assigned by comparing them with those of poly(1-octene) (Fig. 3(C) and S5†). The composition ratios were calculated using the integral ratio of O7, O8, and the cyclopropane moiety (see the ESI† for details). The methylene carbon of the 1-octene sequence (O1α) was observed at 41–42 ppm with a low intensity, whereas 1-octene-derived methylene carbons (O1αδ) that bonded to **1** appeared at 30–32 ppm. Collectively, these ¹³C NMR analyses confirmed that the polymerization of **1** proceeded chemoselectively *via* the coordination–insertion at C12 and C13 without side reactions at the cyclopropane moieties and the bridgehead methylenes.

Next, we investigated the post-polymerization modification (PPM) of poly(**1**-*co*-1-octene) (run 5, Table 1) *via* the Tf$_2$NH-

catalyzed ring-opening reactions of the cyclopropane with weak nucleophiles, *i.e.*, aromatic compounds, carboxylic acids, and alcohols. The resulting functionalized COCs were analyzed by ¹H NMR spectroscopy (Fig. S6–12†), SEC (Fig. 4), and thermogravimetric analysis (TGA) (Fig. 5). The PPM using 10 mol% Tf$_2$NH with *m*-xylene as both the reagent and solvent at 50 °C for 30 min afforded a white powder polymer in 70% yield (run 1, Table 2). After the PPM, the ¹H NMR signal derived from the cyclopropane methine protons (0.8 ppm in Fig. S3†) disappeared, and aromatic signals (6.8–7.3 ppm) appeared (Fig. S6†), confirming the introduction of an *m*-xylyl group in a high incorporation ratio. The SEC chromatogram shifted toward the high-molecular-weight side, maintaining
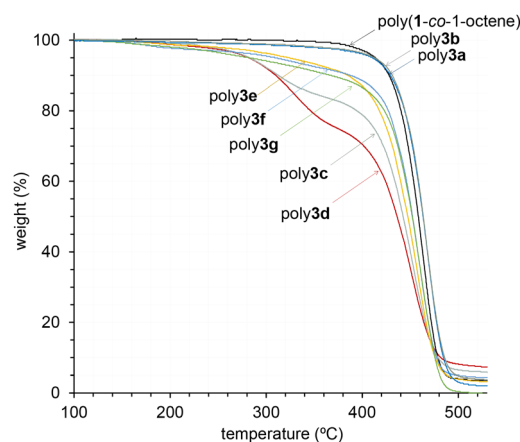
Fig. 5 TGA curves of poly(**1**-*co*-1-octene) (run 2, Table 1) and poly**3a**–**3g**.

the unimodal distribution (Fig. 4(a)), indicating that neither polymer reactions nor polymer chain scission occurred. The PPM with toluene under similar conditions afforded the corresponding polymer. The SEC chromatograms became slightly broader presumably, because of the occurrence of polymer reactions *via* polyalkylation at the tolyl group (Fig. 4(b)). The PPMs with butyric acid, benzoic acid, and methyl glycolate in chloroform as the solvent under similar conditions afforded poly**3c**–**3e** in high yields with a clear shift of the SEC chromatograms to the high-molecular-weight side (Fig. 4(c), (d), and (e)). The ^{1}H NMR signals for –C*H*–O– appeared at 4.2 ppm (poly**3c**), 4.5 ppm (poly**3d**), and 3.1 ppm (poly**3e**), and the incorporation ratios were estimated to be 82%–99% (Fig. S8–S10†). The PPM with methanol and 2-(2-ethoxyethoxy)ethanol was difficult because of the possible occurrence of side reactions with Tf$_2$NH. Thus, we generated an intermediate *via* the ring-opening reaction with an equimolar amount of Tf$_2$NH at 50 °C for 10 min. Subsequently, the alcohols were added, and the mixture was stirred at 50 °C for 30 min. Although the SEC analysis indicated that the reaction between polymer chains slightly occurred (Fig. 4(f) and (g)), poly**3f** and poly**3g** were obtained in high yields with high incorporation ratios.

The thermal stability was investigated using TGA analysis. Poly(**1**-*co*-1-octene), poly**3a**, and poly**3b** showed high thermal stabilities; their 10% weight-loss temperatures (T_{d10}) were 427 °C, 427 °C, and 430 °C, respectively. The cyclopropane moiety and the C–C bonds between the aryl groups and the **1** moiety were thermally stable. Acyloxy- and alkoxy-substituted polymers, poly**3c**, poly**3d**, poly**3e**, poly**3f**, and poly**3g**, were less thermally stable. In particular, the acyloxy-substituted polymers, poly**3c** and poly**3d**, underwent thermal decomposition at approximately 250 °C–300 °C, because of the possible heterolytic cleavage of the O–C bond to generate a non-classical carbocation.[54–56] Thus, the introduced substituents largely affected thermal stabilities.

Conclusion

We have demonstrated the synthesis of functionalized cyclic olefin copolymers *via* the polymerization of **1** and the subsequent PPM. The addition polymerization of **1** using the Ti catalyst proceeded chemoselectively owing to the lack of cyclopropane coordination to the active Ti$^+$ polymerization species. Despite the bulky polycyclic structure, the polymerization of **1** proceeded at 0 °C and reached high conversions (>90%) within 60 min to afford poly**1** with narrow *Đ* values. The molecular weight of poly**1** increased linearly with the conversion. The copolymerization of **1** and 1-octene proceeded quickly, reaching complete conversion within 20 min, and **1** was consumed faster than 1-octene to form a gradient copolymer sequence. The ^{13}C NMR analysis of poly**1** and poly(**1**-*co*-1-octene) indicated that **1** polymerized *via* the coordination–insertion of the alkenyl group without undergoing the metathesis reaction or ring-opening reaction of the cyclopropane moiety. The ring-opening reaction of the cyclopropane moiety in poly(**1**-*co*-1-octene) with aromatic compounds, carboxylic acids, and alco-

hols introduced aromatic, acyloxy, and alkoxy groups, respectively, without cross-linking or polymer chain scission. The TGA revealed that weight loss for acetoxy- and alkoxy-substituted polymers started at approximately 200 °C, whereas the aryl-substituted polymers exhibited relatively high thermal stability with T_{d10} values of approximately 430 °C. Thus, this work demonstrated that the chemoselective and controlled (co)polymerizations of **1** using the Ti catalyst and the subsequent ring-opening reaction of the cyclopropane is a promising process for synthesizing functionalized polyolefins.

Author contributions

Y.I.: investigation, visualization, validation, writing of the original draft, and review and editing. T.S.: investigation and review and editing. S.-i.M.: conceptualization, project administration, funding acquisition, investigation, visualization, writing of the original draft, and review and editing. All authors have read and approved the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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