Functionalized Cyclic Olefin Copolymers: Chemoselective Polymerization of Cyclopropane-Containing Norbornadiene Dimer using Titanium Catalyst and Post-Polymerization Modification

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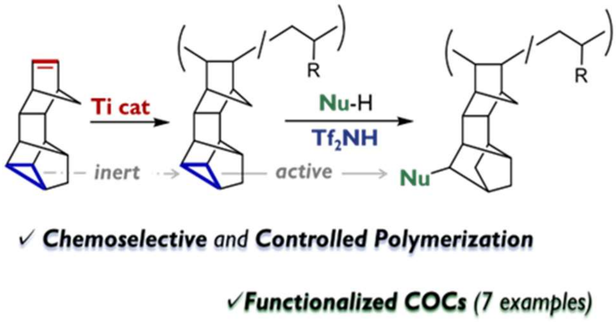


Keywords

cyclic olefin copolymer, post-polymerization modification, norbornadiene dimer, cyclopropane, chemoselective polymerization

Short abstract

We demonstrate a synthesis strategy for functionalized cyclic olefin copolymers using the specific reactivity of cyclopropane, which is inert for Ti-catalyzed coordination insertion polymerization but active for protic acid-catalyzed ring-opening reaction.

Abstract

The synthesis of functionalized polyolefins is important for turning 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 linearly increased against 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. Further, the ^{13}C nuclear magnetic resonance (NMR) spectroscopies indicated the 2,3-addition structure of poly**1** and no side reaction at the cyclopropane moiety. The polymerizations were highly controlled and chemoselective owing to the lack of cyclopropane coordination to the active polymerization Ti species. The PPM of poly(**1**-*co*-1-octene) via the protic acid-catalyzed ring-opening reaction of the cyclopropane introduced aromatic, acyloxyl, 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 distribution, linear structure, regio-, stereoselectivity, 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] functionalities. 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,[26,28,27,30–32,34], myrcene,[33] and dicyclopentadiene;[35,36] however, undesired cross-linking reactions may inherently occur. PPMs via C–H bond activations are facilitated by transition metal catalysis or radical mechanism,[38–42] and polyolefin upcyclings have 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.

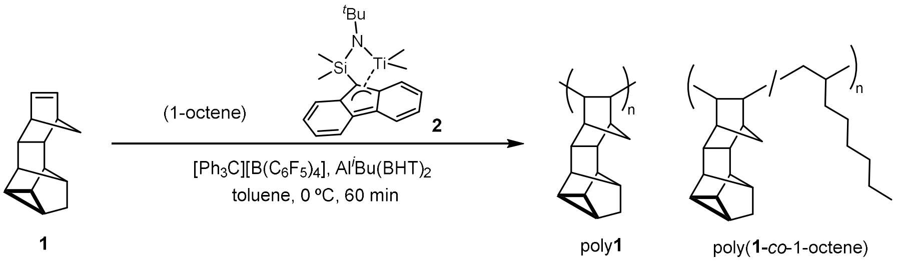
We performed the ring-opening metathesis polymerization (ROMP) of a cyclopropane-containing norbornadiene dimer (**1**) and the subsequent PPM of the resulting hydrogenated polymer.[44] The cyclopropane moiety is inert to the Ru-catalyzed ROMP and hydrogenation, whereas it readily undergoes ring-opening 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 hypothesize that monomer **1** undergoes selective addition polymerization at the C=C bond without cyclopropane ring openings 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 (COC), which undergoes the protic acid-mediated PPM to introduce various functional groups, i.e., aromatic, acyloxy, and alkoxy groups without any cross-linking and polymer chain scissions.

RESULTS AND DISCUSSIONS

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, size exclusion chromatography (SEC), Figure S1). A kinetic study revealed that the conversion of **1** reached 59% in 20 mins and 93% in 60 mins (Figure S2). The SEC chromatograms of poly**1** sampled at low to high conversions shifted toward the high-molecular-weight side, retaining a unimodal distribution ($Đ < 1.25$) (Figure 1(A)). The molecular weights estimated at the SEC peak top (M_p) linearly increased with the conversion (Figure 1(B)). Thus, the polymerization proceeded without apparent side reactions.

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



run	[**1**]$_0$/[1-octene]$_0$	[**M**]$_0$/[**2**]$_0$	yield	composition of **1**	$10^{-3}M_\mathrm{n}$[b]	$Đ$[b]
			%	mol%		
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[c]	50/50	540	89	-	62	1.52

[a] **2**, 20 μmol; $[Ph_3C][B(C_6F_5)_4]$, 20 μmol; Al^{i}Bu(BHT)$_2$, 200 μmol; toluene, 30 mL. [b] SEC ($CHCl_3$, polystyrene standards). [c] **2**: 10 μmol.

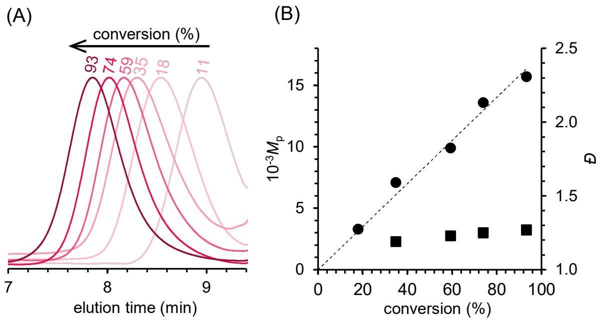


Figure 1. (A) SEC chromatograms of poly**1** at various conversions (under the conditions of run 2 in Table 1) and (B) molecular weights estimated at the SEC peak top (M_p, filled circle) and $Đ$ value (filled square) against conversion.

Further, the copolymerization of **1** and 1-octene ($[\mathbf{1}]_0$:[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 $[\mathbf{1}]_0$/[1-octene]$_0$ of 60/40 and 40/60 yielded the corresponding poly(**1**-*co*-1-octene) with high M_ns in high yields (runs 6 and 7). The kinetic study indicated that **1** and 1-octene were completely consumed within 15 and 20 min, respectively (run 5, and Figure S3(A)). Further, the SEC chromatograms shifted toward the high-molecular-weight side with the conversions while retaining the unimodal distribution (Figures S3(B) and S3(C)). The pseudo-first-order kinetic plots showed linear relationships for **1** and 1-octene. Further, the ratio of the copolymerization rate, $k_1/k_{(1\text{-octene})}$, was estimated to be 3.4 (Figure 2(B)), indicating the high polymerizability of **1** despite the bulky structure and the formation of a gradient copolymer sequence. Comparing the polymerization rate of **1** under identical conditions, the consumption rate of **1** in the copolymerization was 3.6 times faster than that of 1-octene (Figures 2(A) and 2(B)). Thus, the 1-octene polymer terminal rapidly reacted with **1** in the copolymerization.

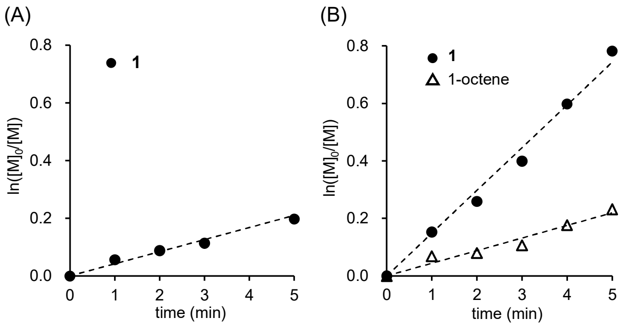


Figure 2. The pseudo-first-order kinetic plots of (A) the polymerization of **1** under the conditions of run 2 and (B) the copolymerization of **1** with 1-octene under the conditions of run 5.

The structures of poly**1** and poly(**1**-*co*-1-octene) were analyzed by nuclear magnetic resonance (NMR) spectroscopies (Figures 3 and S4–S7). Figure 3 shows their ^{13}C NMR spectra compared with those of hydrogenated **1** (H-**1**). The measurements were conducted using high-resolution instrument (225 MHz for ^{13}C), using Cr(acac)$_3$ as the relaxation reagent to quench the nuclear Overhauser effects. 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 (Figure 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*, C4' and C5' for the *exo–endo*, and C4, C5, and C6' (overlapped) 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, 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 splitting 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 2,7-linkage.[52] However, in this study, the clear assignment of ^{13}C signals, particularly for the methylene signals derived from C14 and C14' not from C12 and C13, ruled out the possibilities of such isomerization polymerization. Further, the signals of poly(**1**-*co*-1-octene) were reasonably assigned by comparing those of poly(1-octene) (Figures 3(C) and S7). The composition ratios were calculated using the integral ratio between O7, O8, and the cyclopropane moiety. The methylene carbon of the 1-octene sequence (O1α) was observed at 41–42 ppm at a low intensity, whereas 1-octene-derived methylene carbons (O1αδ) that bonded to **1** appeared at 30–32 ppm. Collectively, these ^{13}C NMR analyses confirmed that (1) the polymerization of **1** proceeded chemoselectively via the 2,3-addition (at C12 and C13) without side reactions at the cyclopropane moieties and the bridgehead methylenes. Further, (2) the copolymerization of **1** with 1-octene efficiently proceeded via the preferential crossover propagation to form the gradient copolymers.

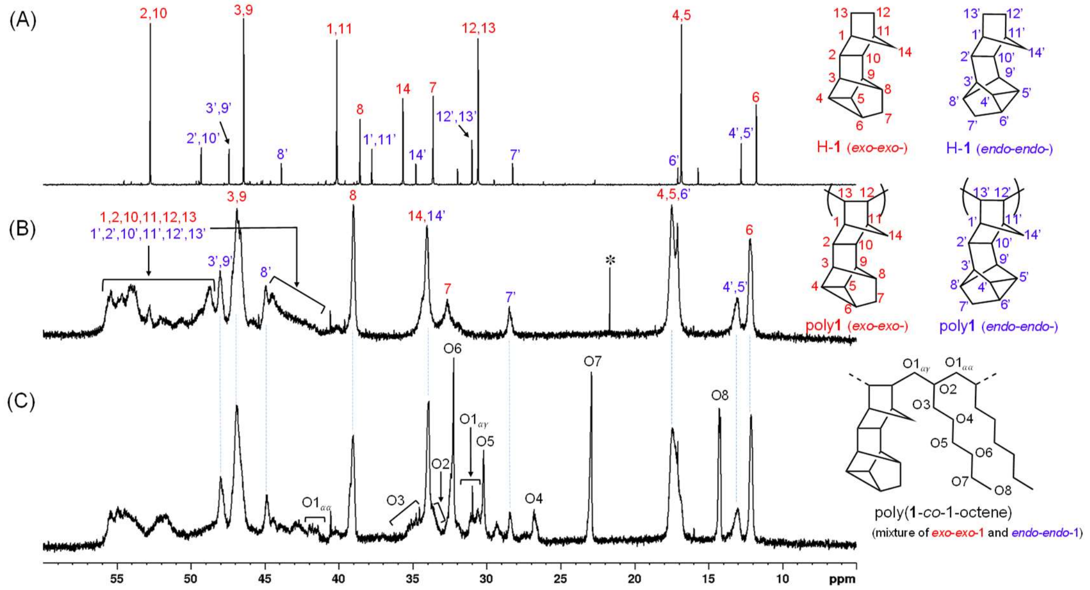
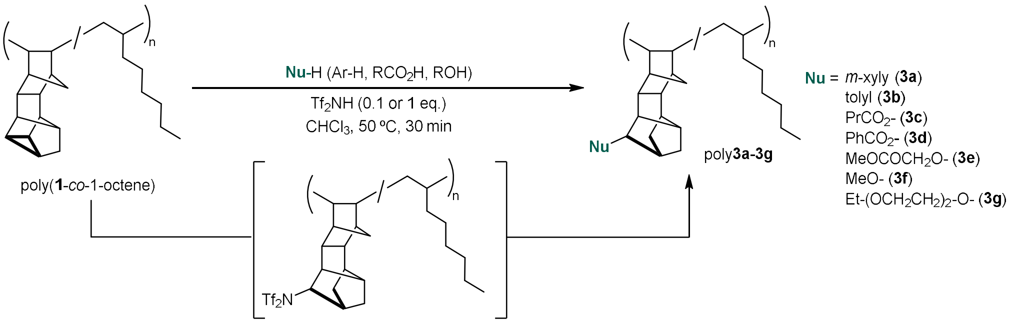


Figure 3. ^{13}C NMR spectra of (A) H-**1**, (B) poly**1** (run 2, Table 1), and (C) poly(**1**-*co*-1-octene) (run 6, Table 1).

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 ^{1}H NMR spectroscopy (Figure S8–14), SEC (Figure 4) and thermogravimetric analysis (TGA) (Figure 5). The PPM using 10 mol% of Tf$_2$NH with *m*-xylene as both 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 ^{1}H NMR signal derived from the cyclopropane methine protons (0.8 ppm) disappeared, and aromatic signals (6.8–7.3 ppm) appeared, confirming the introduction of a *m*-xylyl group in a high incorporation ratio. The SEC chromatogram shifted toward the high-molecular-weight side, maintaining the unimodal distribution (Figure 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 a polyalkylation at the tolyl group (Figure 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 (Figures 4(c), (d), and (e)). The ^{1}H NMR signals for -C*H*-O- appeared at 4.5 ppm (for poly**3c** and poly**3d**) and 3.3 ppm (for poly**3e**), and the incorporation ratios were estimated to be 82%–99% (Figures S10–S12). The PPM with methanol and 2-(2-ethoxyethoxy)ethanol was difficult because of the possible iccurrence of side reactions with Tf_2NH. Thus, we generated an intermediate via the ring-opening reaction with an equimolar amount of Tf_2NH at 50°C for 10 min. Subsequently, 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 (Figures 4(f) and (g)), poly**3f** and poly**3g** were obtained in high yields with high incorporation ratios.

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_2NH.



run	Nu-H (eq.)[a]	Tf$_2$NH	yield	incorp.[b]	$10^{-3}M_n$[c]	$Đ$[c]	T_{d10}[d]
		eq.[a]	%	%			°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 Nu unit in the copolymers estimated by ^{1}H NMR. [c]SEC (CHCl$_3$, polystyrene standards). [d]10% weight loss temperature estimated by TG-DTA. [e]Nu-H used as both reagent and solvent.

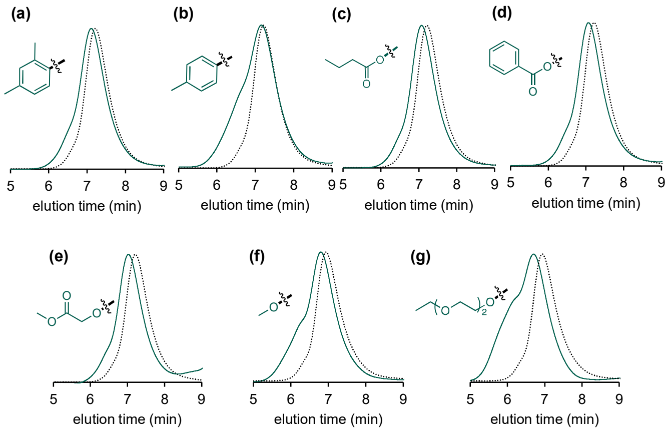


Figure 4. SEC chromatograms before and after the PPM; functionalized poly(**1**-*co*-1-octene)s (poly**3a**–**3g**) (green solid line) and prepolymer, poly(**1**-*co*-1-octene), (black dotted line). The chromatograms of (a)–(g) correspond to runs 1–7 in Table 2.

The thermal stability was investigated by 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 the thermal decomposition at approximately 250°C –300°C, because of the possible heterolytic cleavage of the O–C bond to generate non-classical carbocation.[53–55] Thus, the thermal stability could be controlled by the introduced substituents.

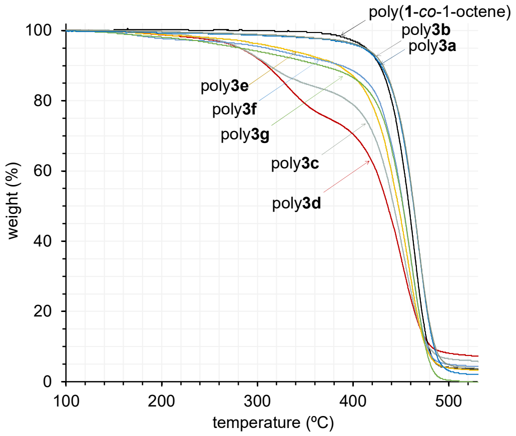


Figure 5. TGA curves of poly(**1**-*co*-1-octene) (run 2, Table 1) and poly**3a**–**3g**.

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** linearly increased against the conversion. The copolymerization of **1** and 1-octene proceeded quickly reaching complete conversion within 20 min, and **1** was consumed 3.4 times faster than 1-octene. Thus, the crossover propagation was dominant to form a gradient copolymer sequence. The ^{13}C NMR analysis of poly**1** and poly(**1**-*co*-1-otene) indicated that the polymerization proceeded via 2,3-insertion without isomerizations or cyclopropane ring-opening during the polymerization. The ring-opening reaction of the cyclopropane moiety in poly(**1**-*co*-1-otene) with aromatic compounds, carboxylic acids, and alcohols 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, whreas the aryl-substituted polymers exhibited relatively high thermal stability with T_{d10} values of approximately 430°C. Thus, this work demonstrated that the chemoselective polymerization of **1** using 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, and writing of the original draft. T.S.: investigation. 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.

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