Analysis of Ethylene Copolymers with Long-Chain α-Olefins (1-Dodecene, 1-Tetradecene, 1-Hexadecene): A Transition between Main Chain Crystallization and Side Chain Crystallization

Suphitchaya Kitphaitun, Hiroki Takeshita, and Kotohiro Nomura*
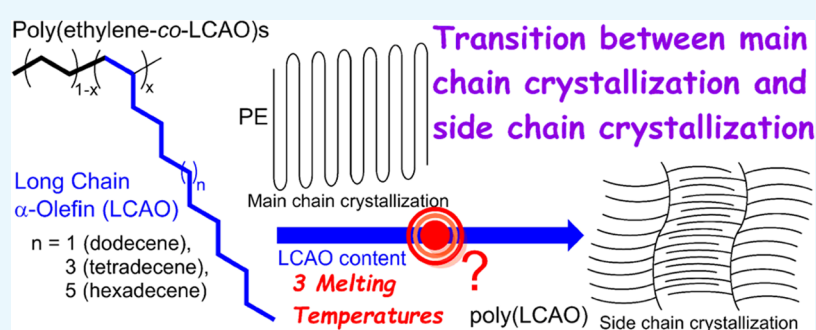
ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: A series of ethylene copolymers with long-chain α-olefins [LCAOs, 1-dodecene (DD), 1-tetradecene (TD), 1-hexadecene (HD)] and various LCAO contents were prepared, and their thermal properties, including effects of LCAO content and side chain length, were explored. The Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$)−MAO catalyst system afforded rather high-molecular-weight copolymers with unimodal molecular weight distributions and uniform compositions (confirmed by DSC thermograms). In addition to the melting temperatures (T_m values) corresponding to the so-called main chain crystallization (samples with low LCAO contents, the T_m value decreased upon increasing the LCAO content) and the side chain crystallization [polymer samples with high LCAO contents, by intermolecular interaction of side chains as observed in poly(DD), poly(TD), and poly(HD)], the other T_m value was observed, especially in poly(ethylene-*co*-HD)s (assumed to be due to co-crystallization of the branch and the main chain through an interaction of the main chain and the long side chains). The presence of another crystalline phase in poly(ethylene-*co*-HD)s was also suggested by a wide-angle X-ray diffraction (WAXD) analysis. These T_m values in poly(ethylene-*co*-TD)s and poly(ethylene-*co*-DD)s with rather high TD or DD contents were affected by the heating conditions in the measurement of DSC thermograms (5 or 10 °C/min), suggesting that the driving force for formation of the crystal packing (observed as T_m) is weak and affected by the alkyl side chain lengths.

INTRODUCTION

Ethylene/α-olefin copolymers (linear low-density polyethylene, LLDPE) have been widely used as commodity plastics in our daily life, and it is well known that the material property is affected by the chain length of the incorporated α-olefin, the α-olefin (comonomer) contents, and the composition (and molecular weight and the distribution, monomer sequence distribution, etc.). It is also known that α-olefin incorporation affects the crystallinity of polyethylene lamellae formed during the crystallization process (main chain crystallization, Figure 1a), and the lamellae thickness, percentage of semicrystalline lamellae, and tie molecules play an important role in the material property. Many studies have thus been conducted for the analysis of ethylene/α-olefin copolymers[1−12] prepared by conventional catalysts including metallocene catalysts[5−10] or the model system.[11,12] Reports with the designed copolymers by the placement of certain alkyl side chains in a controlled manner (the same methylene spacing unit), which were

prepared by adopting acyclic diene metathesis polymerization and subsequent hydrogenation, are known.[13−22] Most of these studies were analyses of semicrystalline copolymers with rather low α-olefin contents, and the copolymers (with 1-butene, 1-hexene, 1-octene, etc.) became amorphous by loss of crystallinity with incorporation of the α-olefin in the main chain. No additional melting temperatures, as described in this text, were observed in these copolymers.

Amorphous poly(α-olefin)s are used in hot melt applications due to their inherent stickiness and softness (high melt-flow
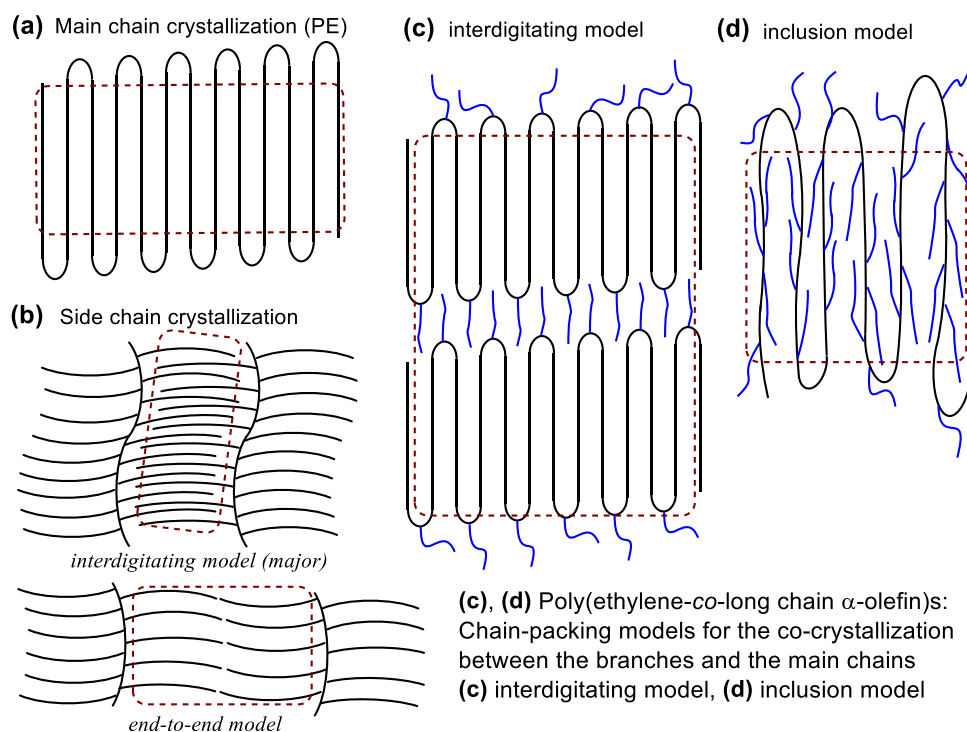
Figure 1. Schematic models for (a) main chain crystallization (observed in semicrystalline polyethylene and ethylene/α-olefin copolymers with low α-olefin content), (b) side chain crystallization [observed in semicrystalline homopolymers of long-chain α-olefins (LCAOs, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, etc.), end-to-end model (major), and interdigitating model],[26,27] and (c, d) assumed chain packing models[22] in the model ethylene copolymers containing C_{21} alkyl chain in every 15th or 19th methylene unit. The dashed-line range depicts the lamellar thickness/layers in each model.

rate with low density). Ultrahigh-molecular-weight polymers, possessing highly entangled bottlebrush architectures, are used as drag reducing agents for improved transport (piping capacity) of crude oil and petroleum products in pipeline methods.[23,24] In contrast, poly(α-olefin)s, especially those consisting of long-chain α-olefins [LCAOs, 1-dodecene (DD), 1-tetradecene (TD), 1-hexadecene (HD), 1-octadecene, etc.],[25−29] are semicrystalline branched (highly entangled) macromolecules with a high graft density, and the polymers are thus recognized as the simplest bottlebrush polymers. The melting temperatures in poly(LCAO)s are affected by the branch length and the stereoregularity (Table 1).[25−28] Recent reports revealed their melt structure, linear rheology, and interchain friction mechanism;[26,27] the polymers crystallize by fully extending their coiled side chains with an arrangement of side chains from adjacent bottlebrush chains (side chain

crystallization, Figure 1b).[26] Although the T_m values in the ethylene copolymers also decreased upon increasing the LCAO incorporation,[10] thermal properties of copolymers with high LCAO contents, transition between the main chain crystallization (the ethylene copolymer with low LCAO contents) and the side crystallization observed in poly-(LCAO)s, have not yet been studied. One of the probable reasons for this is that homopolymerization of LCAO by the ordinary metallocene catalysts affords oligomers,[25,28] and the M_n values in the resultant ethylene copolymers with LCAO thus generally decreased upon increasing the LCAO content.[5−9]

One report shows that the model ethylene copolymers placing C_{21} alkyl branch on every 15th or 19th methylene units (corresponding to incorporation of linear $C_{22}H_{44}$ with 14.3 or 11.1 mol %, respectively) showed two melting temperatures (ca. 26 and 37 °C), and the ratio was affected by the number of the ethylene spacer.[22] The results were explained using an assumption of formation of side chain crystallization and co-crystallization of the branch and the main chain; two kinds of chain packing models, the end-to-end (interdigitating) model (Figure 1c) and the inclusion model (Figure 1d), were assumed for the explanation.[22]

As described in this article, we observed two different melting temperatures in poly(ethylene-co-HD)s that are different from those observed in poly(HD), and we also obtained the polymer samples possessing three melting temperatures (including the one corresponding to the main chain crystallization). Therefore, we prepared a series of ethylene copolymers with LCAOs with different chain lengths (DD, TD, and HD, Chart 1) and studied their thermal properties including wide-angle X-ray diffraction (WAXD)

Table 1. Summary of the Reported Melting Temperatures (T_m Values) in Poly(α-olefin)s[25−28]

α-olefin	regularity	T_m/°C	references
1-dodecene	atactic	−24	25, 28
1-dodecene	atactic	−25.2	this paper
1-dodecene	isotactic	26	27
1-tetradecene	atactic	7.5	this paper
1-tetradecene	isotactic	43	27
1-hexadecene	atactic	26	25, 28
1-hexadecene	atactic	25.6	this paper
1-octadecene	atactic	42	25, 28
1-octadecene	atactic	42	26
1-octadecene	isotactic	54	27

Chart 1. Ethylene Copolymers with 1-Dodecene [Poly(E-*co*-DD)s], 1-Tetradecene [Poly(E-*co*-TD)s], and 1-Hexadecene [Poly(E-*co*-HD)s]

poly(E-*co*-DD)s   poly(E-*co*-TD)s   poly(E-*co*-HD)s
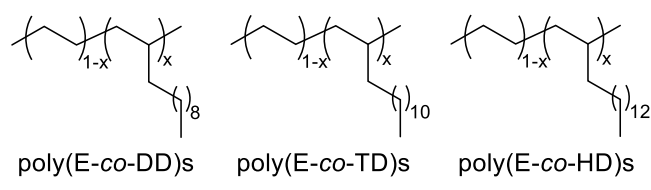
analysis of poly(ethylene-*co*-HD)s films with different HD contents. Through this study, we wish to show the existence of

transition between the main chain crystallization and the side chain crystallization, presumable co-crystallization behaviors.

■ RESULTS AND DISCUSSION

Synthesis of Ethylene Copolymers with 1-Dodecene (DD), 1-Tetradecene (TD), and 1-Hexadecene (HD) and Microstructural Analysis Using ^{13}C NMR Spectra. Ethylene (E) copolymers with 1-dodecene (DD), 1-tetradecene (TD), and 1-hexadecene (HD) were prepared by copolymerization in toluene using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$C$_6$H$_2$) (Cp* = C$_5$Me$_5$) catalyst in the presence of methylaluminoxane (MAO) cocatalyst. The titanium catalyst has been chosen in this study because the catalyst exhibited notable catalytic

Table 2. Ethylene Copolymerization with 1-Dodecene (DD), 1-Tetradecene (TD), and 1-Hexadecene (HD) by the Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$C$_6$H$_2$)−MAO Catalyst System[a]

run	cat./μmol	α-olefin	conc.[b]/M	E/atm	yield/mg	activity[c]	$M_n{}^{[d]} \times 10^{-4}$	$M_w/M_n{}^{[d]}$	cont.[e]/mol %
1	0.001			6	18.1	181 000	insoluble		
2	0.01	DD	0.75	2	329	329 000	8.9	1.86	18.2
3	0.0025	DD	0.75	4	123	492 000	11.4	1.81	15.6
4	0.001	DD	0.30	6	83.5	835 000	25.0	2.05	5.1
5	0.001	DD	0.45	6	88.9	889 000	18.5	1.97	6.6
6[f]	0.001	DD	0.75	6	104	1 040 000	16.7	1.62	15.0 (15.5)[g]
7	0.0025	DD	1.13	6	309	1 240 000	11.4	1.74	16.0
8	0.0025	DD	1.50	6	363	1 450 000	11.6	1.76	17.6
9	0.001	DD	0.30	8	163	1 630 000	30.1	2.09	4.0
10	0.001	DD	0.45	8	177	1 770 000	23.6	1.95	5.3
11	0.001	DD	0.60	8	177	1 770 000	20.6	1.96	6.1
12	0.001	DD	0.75	8	235	2 350 000	16.9	1.89	7.2 (8.0)[g]
13	0.001	DD	0.90	8	283	2 830 000	14.7	1.98	8.5
14	1.0	DD	0.75		477	954	12.7	1.94	100
15	0.01	TD	0.67	2	130	130 000	12.2	1.74	15.4
16	0.0025	TD	0.67	4	58.3	233 000	13.1	1.98	12.0
17	0.001	TD	0.27	8	120	1 200 000	43.5	2.95	3.0
18	0.001	TD	0.40	8	299	2 990 000	35.5	2.49	4.5
19	0.001	TD	0.27	6	387	3 870 000	29.4	2.31	4.8
20	0.001	TD	0.40	5	169	1 690 000	17.6	2.05	8.8
21	0.001	TD	0.40	6	222	2 220 000	23.4	2.25	6.3
22	0.001	TD	0.40	7	234	2 340 000	29.1	2.10	5.2
23	0.001	TD	0.54	6	207	2 070 000	18.1	1.95	8.1
24	0.001	TD	0.67	6	122	1 220 000	14.0	1.87	11.4 (12.0)[g]
25[h]	0.001	TD	0.67	6	136	1 360 000	16.6	1.96	10.0
26	0.001	TD	0.67	8	442	4 420 000	15.2	2.00	6.6
27	0.0025	TD	1.01	6	250	1 000 000	11.2	1.78	13.5
28	0.005	TD	1.34	6	162	323 000	12.1	1.97	15.2
29	1.0	TD	0.67		329	658	17.6	1.98	
30	0.0005	HD	0.58	2	70.8	142 000	11.0	1.66	15.0
31	0.001	HD	0.58	4	176	1 760 000	13.8	1.86	11.4
32	0.0005	HD	0.35	6	97.1	1 942 000	25.9	1.98	6.1
33	0.0005	HD	0.58	6	95.2	1 900 000	18.7	1.96	9.7
34[h]	0.0005	HD	0.58	6	156	3 120 000	15.2	1.96	9.3
35	0.001	HD	0.87	6	190	1 900 000	14.2	1.90	12.5
36	0.001	HD	1.16	6	257	2 570 000	14.1	1.83	14.0
37	0.001	HD	0.23	8	180	1 800 000	43.3	2.57	2.7
38	0.001	HD	0.35	8	244	2 440 000	26.9	2.57	4.4
39	0.0005	HD	0.58	8	180	3 600 000	21.4	1.96	6.4 (7.1)[g]
40	1.0	HD	0.58		134	268	7.8	1.51	

[a]Conditions: total volume, 30 mL; MAO, 2.0 mmol; 6 min (runs 14, 29, 40: total 6.0 mL, 30 min); and 25 °C. [b]Initial concentration (mmol/mL). [c]Activity = kg-polymer/mol-Ti·h. [d]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]α-Olefin in copolymer (mol %) estimated using ^{1}H NMR spectra (selected data are shown in SI). [f]Polymerization data cited from ref 31. [g]α-Olefin in copolymer (mol %) estimated using ^{13}C NMR spectra (selected data are shown in SI). [h]Polymerization at 50 °C.
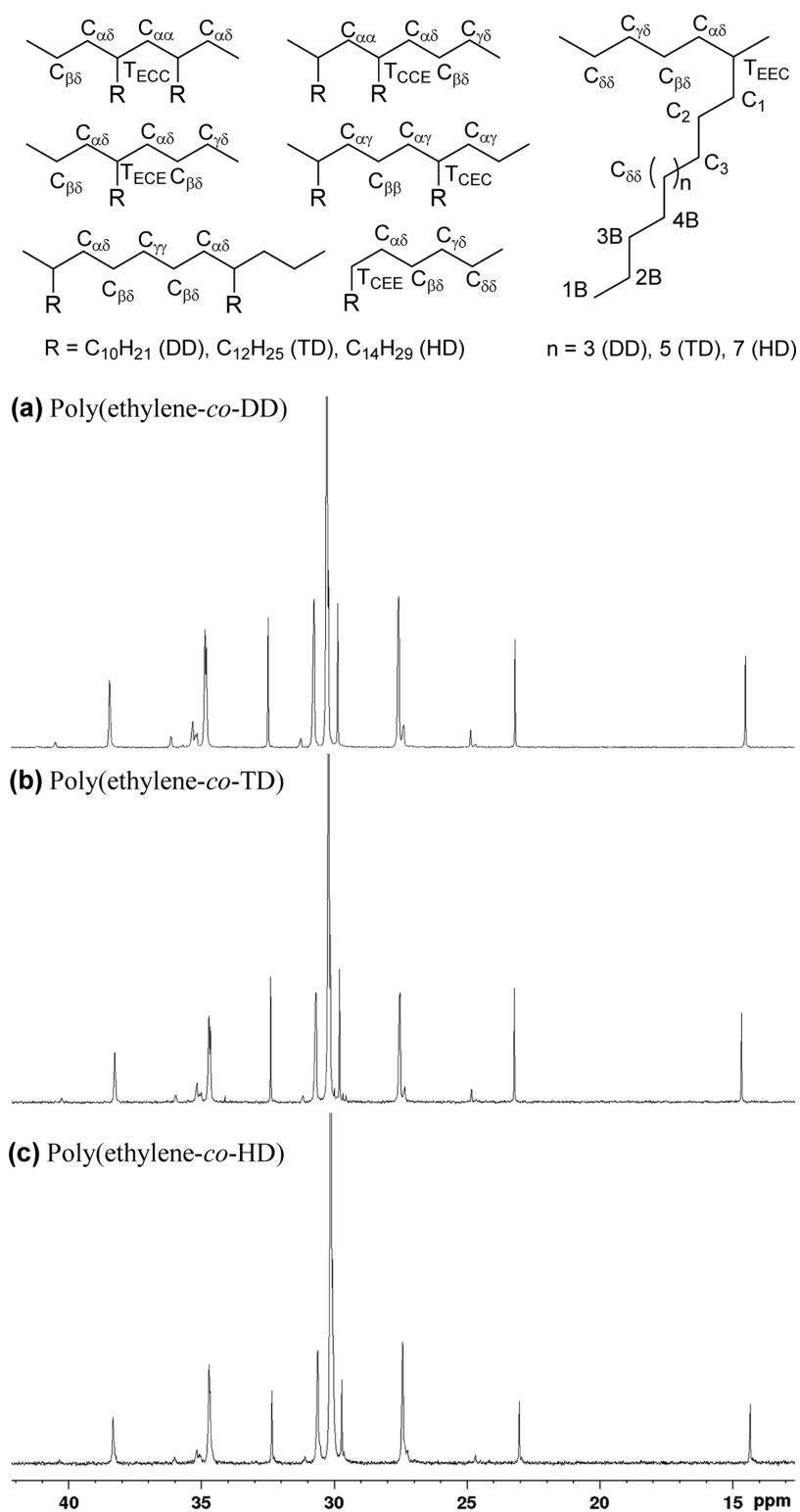
R = C$_{10}$H$_{21}$ (DD), C$_{12}$H$_{25}$ (TD), C$_{14}$H$_{29}$ (HD)   n = 3 (DD), 5 (TD), 7 (HD)

Figure 2. ^{13}C NMR spectra (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C) for (a) poly(E-*co*-DD) (run 6, DD 15.5 mol %), (b) poly(E-*co*-TD) (run 24, TD 12.0 mol %), and (c) poly(E-*co*-HD) (run 39, HD 7.1 mol %). The polymerization data are shown in Table 2, and selected NMR spectra of the ethylene copolymers (for estimations of the comonomer contents) are shown in the SI.

activities for E/DD copolymerization with efficient DD incorporation to afford the copolymers.[30,31] The catalysts of this type are known to be effective for the synthesis of new ethylene copolymers[32−34] with sterically encumbered olefins (disubstituted olefins, branched α-olefins), cyclic olefins, and aromatic vinyl monomers, as well as the synthesis of poly(LCAO)s.[25,28,29] These copolymerizations were conducted with the termination of low comonomer conversions (less than 10%, short period) to obtain the copolymer with uniform compositions (to avoid changes in the LCAO concentrations during the polymerization runs). The results are summarized in Table 2.

Table 3. Monomer Sequence Distributions of Poly(ethylene-co-LCAO)s [LCAO = 1-Dodecene (DD), 1-Tetradecene (TD), 1-Hexadecene (HD)] Prepared by the Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$)−MAO Catalyst System[a,d]

run	α-olefin	content[b]/mol %	triad sequence distribution[c] (%)						dyads[d] (%)			r_E[e]	r_C[e]	$r_E \cdot r_C$[f]
			EEE	EEC+CEE	CEC	ECE	CCE+ECC	CCC	EE	EC+CE	CC			
6	DD	15.3	52.4	29.0	3.04	13.2	2.29		66.9	31.9	1.14	4.32	0.07	0.30
24	TD	12.0	64.0	23.6	0.4	11.7	0.3	trace	75.8	24.0	0.2	5.81	0.02	0.11
37	HD	7.1	74.1	18.8	0.06	7.0	0.08	trace	83.5	16.5	0.04	4.56	0.01	0.05

[a]For detailed polymerization conditions, see Table 2; C = comonomer [1-dodecene (DD), 1-tetradecene (TD), 1-hexadecene (HD)].
[b]Comonomer contents in copolymer estimated using ^{13}C NMR spectra. [c]Calculated using ^{13}C NMR spectra; E = ethylene and C = comonomer (DD, TD, HD). [d][EE] = [EEE] + 1/2[EEC+CEE], [EC] = [CEC] + [ECE] + 1/2{[EEC+CEE] + [CCE+ECC]}, [CC] = [CCC] + 1/2[CCE+ECC]. [e]r_E = [C]$_0$/[E]$_0$ × 2[EE]/[EC+CE], r_C = [E]$_0$/[C]$_0$ × 2[CC]/[EC+CE]. [f]$r_E \cdot r_C$ = 4[EE][CC]/[EC+CE]^2.
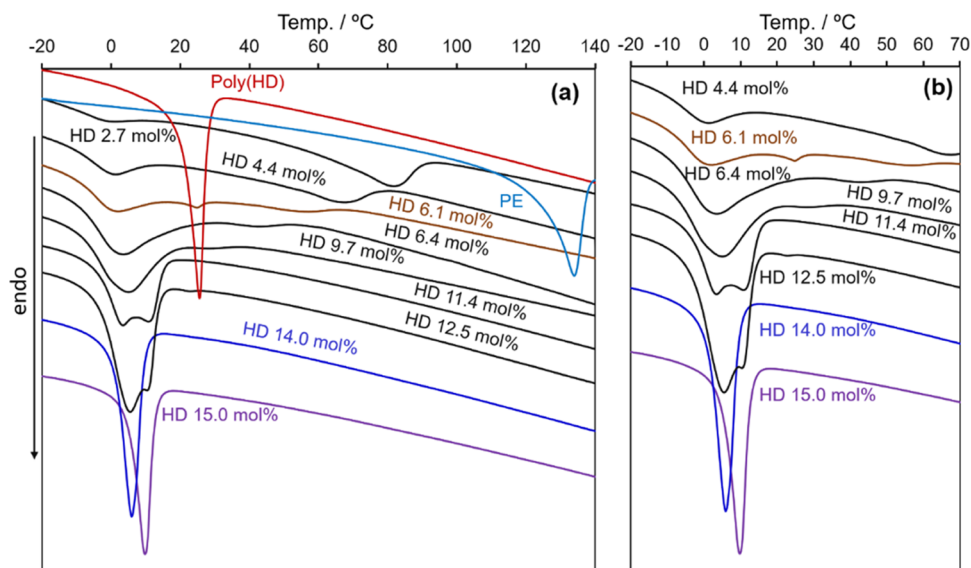

Figure 3. (a) DSC thermograms of poly(E-co-HD)s with different HD contents (second heating at 10 °C/min). (b) Expanded thermograms from −20 to 70 °C. Polymerization data are shown in Table 2, and the additional thermograms are shown in the SI.

As reported recently,[30,31] the ethylene/DD copolymerizations afforded poly(ethylene-co-DD)s possessing rather high molecular weights with unimodal molecular weight distributions (M_n = 8.9−30.1 × 10^4, M_w/M_n = 1.62−2.09) and uniform compositions (confirmed by DSC thermograms shown below). As also reported previously in ethylene/1-hexene copolymerization,[35] the activity (on the basis of polymer yield) was affected by the ethylene pressure and DD concentration charge: the activity increased upon increasing the ethylene pressure. Moreover, the catalytic activity increased upon increasing the DD concentration charge, whereas a decrease in the activity was observed in copolymerization by a conventional catalyst such as linked half-titanocene catalyst [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (called constrained geometry catalyst, CGC) and ordinary metallocene catalysts.[36] As reported recently,[30,31] the activities by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$−4-SiEt$_3$-C$_6$H$_2$) were higher than those by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$).[36] The DD content in the copolymer increased upon increasing the DD concentration charge, and the M_n value decreased with an increase in the DD content. The polymerization of DD resulted in poly(DD) with a rather high molecular weight (run 14, M_n = 1.27 × 10^5).

Similar trends were observed in ethylene copolymerizations with TD and HD, and copolymerization afforded poly(ethylene-co-TD)s (M_n = 1.12−4.35 × 10^5, M_w/M_n = 1.74−2.95) and poly(ethylene-co-HD)s (M_n = 1.10−4.33 × 10^5, M_w/M_n = 1.66−2.57) possessing uniform compositions (confirmed

by DSC thermograms shown below). As observed in the ethylene copolymerization with DD, the activity increased upon increasing the TD or HD concentration charge along with increasing the TD or HD content in the copolymers. The activities conducted at 50 °C were higher than those conducted at 25 °C, as observed in copolymerization with DD and 9-decen-1-ol.[30] The ethylene copolymers (with DD, TD, and HD) with various contents were thus prepared by adopting this catalyst system. Homopolymerizations with TD and HD also afforded poly(TD) and poly(HD) (runs 29 and 40, respectively).

Figure 2 shows selected ^{13}C NMR spectra (1,1,2,2-tetrachloroethane-d_2 at 110 °C) for poly(E-co-DD) (run 6, DD 15.5 mol %), poly(E-co-TD) (run 24, TD 12.0 mol %), and poly(E-co-HD) (run 39, HD 7.1 mol %), and their triad sequence distributions, the dyads, the (relative monomer) reactivity ratios [r_E, r_C values (C = comonomer, DD, TD, HD)], and $r_E \cdot r_C$ values on the basis of microstructure analysis estimated by the NMR spectra are summarized in Table 3.

The r_E and the r_C values can be used to evaluate efficiency in the comonomer incorporation, especially in ethylene/α-olefin copolymerization; the large r_E value (also defined as k_{EE}/k_{EC}, Table 3) expresses less comonomer incorporation. The r_E values are 4.32 (run 6, DD), 5.81 (run 24, TD), and 4.56 (run 39, HD), and the values are close to those of Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) and [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (linked half-titanocene, constrained geometry type);[36] the values are much

smaller than those by Cp_2ZrCl_2.[36] It was revealed that the $r_E \cdot r_C$ values, especially in poly(E-co-TD) and poly(E-co-HD), are small ($r_E \cdot r_C$ = 0.11, 0.05, respectively), suggesting that the percentage of repeated TD or HD insertion was very low. This means that copolymerization proceeds with favored isolated and/or alternating TD and HD insertions. This reflects the low CC values (in dyad level) even with a rather high TD content (CC 0.2%, run 24, 12.0 mol %). This also reflects the observed low catalytic activities in TD or HD polymerizations, as described above (runs 29, 40).

Analysis of Thermal Properties by DSC Thermograms: Effect of Long Side Chains toward Thermal Behaviors. Figure 3 shows DSC thermograms (second heating, 10 °C/min) for poly(E-co-HD)s with various HD contents (2.7−15.0 mol %), and the thermograms for polyethylene (run 1) and poly(HD) (run 40) were also placed. The corresponding plots of the melting temperatures (T_m values) vs the HD content are shown in Figure 4, and the T_m values in the copolymers are summarized in Table 4.
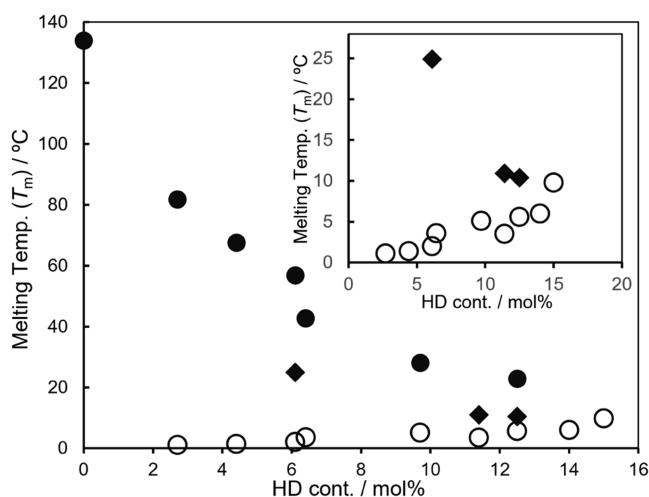

Figure 4. Plots of melting temperatures (T_m values) vs HD contents in poly(E-co-HD)s. ● shows plots corresponding to the main chain crystallization. ○ and ◆ show plots due to other crystallizations (side chain and co-crystallization of side chain and main chain, respectively).

As observed in ordinary ethylene copolymers with α-olefin (such as 1-hexene and 1-octene), the T_m values in poly(E-co-HD)s initially decreased upon increasing the HD content [Figure 3a, plotted as ● in Figure 4, T_m = 134 °C (PE, run 1), 81.8 °C (run 37, HD 2.7 mol %), 67.6 °C (run 38, HD 4.4 mol %), 56.9 °C (run 32, HD 6.1 mol %), 42.8 °C (run 39, HD 6.4 mol %), and 28.1 °C (run 33, HD 9.7 mol %)] with broadening due to loss of crystallinity in the main chain packing.

It was revealed that the copolymers containing 6.1 mol % (and 12.5 mol %) HD possessed three T_m values, although one of these (due to the main chain crystallization) was slightly broad. Importantly, the T_m value observed to be the lowest seems to increase slightly upon increasing the HD content [Figure 3b, plotted as ○ in Figure 4, e.g., T_m = 1.1 °C (run 37, HD 2.7 mol %), 1.4 °C (run 38, HD 4.4 mol %), 2.0 °C (run 32, HD 6.1 mol %), 3.6 °C (run 39, HD 6.4 mol %), 5.1 °C (run 33, HD 9.7 mol %), 5.6 °C (run 35, HD 12.5 mol %), 6.0 °C (run 36, HD 14.0 mol %), and 9.8 °C (run 30, HD 15.0 mol %)]. Since it seems likely that the T_m value probably

Table 4. Summary of DSC Data (Melting Temperatures, T_m Values) in Poly(E-co-LCAO)s [LCAO = 1-Dodecene (DD), 1-Tetradecene (TD), 1-Hexadecene (HD)][a]

run	α-olefin	content[b]/mol %	T_m[c]/°C	M_n[d] × 10^{-4}	M_w/M_n[d]
1	none	0	134		
9	DD	4.0	81.6	30.1	2.09
4	DD	5.1	63.3	25.0	2.05
10	DD	5.3	59.4	23.6	1.95
11	DD	6.1	53.2	20.6	1.96
5	DD	6.6	44.1	18.5	1.97
12	DD	7.2	28.6	16.9	1.89
13	DD	8.5	24.1	14.7	1.98
6	DD	15.0	−21.4	16.7	1.62
3	DD	15.6	−38.8 (−39.9)[e]	11.4	1.81
7	DD	16.0	−41.3, −50.1 (−42.2, −52.0)[e]	11.4	1.74
8	DD	17.6	−43.1, −50.8 (−43.4, −52.1)[e]	11.6	1.76
2	DD	18.2	−43.0, −53.2 (−43.0, −54.1)[e]	8.9	1.86
14	DD	100	−25.2	12.7	1.94
17	TD	3.0	81.2	43.5	2.95
18	TD	4.5	67.9	35.5	2.49
19	TD	4.8	68.0, −19.7	29.4	2.31
22	TD	5.2	58.5, −13.2 (59.1, −16.6)[e]	29.1	2.1
21	TD	6.3	(52.7, −21.6)	23.4	2.25
26	TD	6.6	40.4, 6.0, −10.7 (40.8, 6.9)[e]	15.2	2
23	TD	8.1	36.9, −11.5 (38.7, −11.4, −14.7)[e]	18.1	1.95
20	TD	8.8	36.2, −9.1	17.6	2.05
24	TD	11.4	23.5, −10.0 (26.2, −8.2)[e]	14	1.87
16	TD	12.0	−14.6, −10.7 (−18.1, −11.6)[e]	13.1	1.98
27	TD	13.5	−11.3 (−11.2)[e]	11.2	1.78
28	TD	15.2	−11.3	12.1	1.97
15	TD	15.4	−10.4	12.2	1.74
29	TD	100	7.5	17.6	1.98
37	HD	2.7	81.8, 1.1	43.3	2.57
38	HD	4.4	67.6, 1.4	26.9	2.57
32	HD	6.1	56.9, 24.9, 2.0	25.9	1.98
39	HD	6.4	42.8, 3.6	21.4	1.96
33	HD	9.7	28.1, 5.1	18.7	1.96
31	HD	11.4	10.9, 3.5	13.8	1.86
35	HD	12.5	22.9, 10.4, 5.6	14.2	1.90
36	HD	14.0	6.0	14.1	1.83
30	HD	15.0	9.8	11.0	1.66
40	HD	100	25.6	7.8	1.51

[a]Polymerization data are shown in Table 1. [b]Estimated using ^{1}H NMR spectra. [c]By DSC thermograms (second heating 10 °C/min). [d]GPC data in o-dichlorobenzene vs polystyrene standards. Selected NMR spectra and DSC thermograms are shown in the SI. [e]By DSC thermograms (second heating 5 °C/min).

reaches that of poly(HD) (25.6 °C, run 40) eventually on increasing the HD content, it is thus assumed that the observed T_m values could be probably due to the so-called side chain crystallization (intermolecular interaction of side chain in the copolymer, as depicted in Figure 1b).[25−28] On the basis of the microstructure analysis (described above), the resultant poly(E-co-HD)s possessed isolated and/or an alternating HD inserted unit in the main chain and the percentage of the HD repeated insertion was very low (Table 3), and the distance
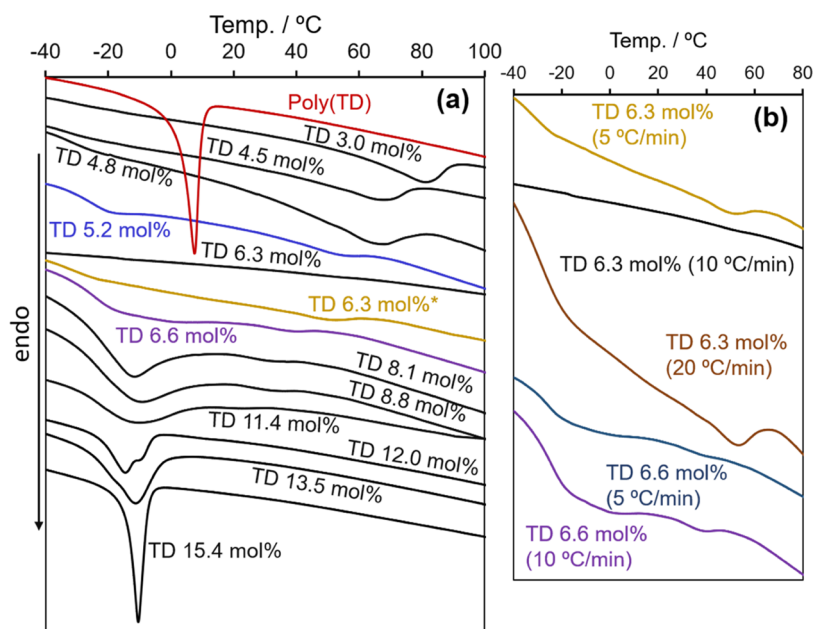
Figure 5. (a) DSC thermograms of poly(E-*co*-TD)s with different TD contents (second heating at 10 °C/min). (b) Expanded thermograms from −40 to 80 °C. Polymerization data are shown in Table 2, and additional thermograms are shown in the SI.

between the HD side chain (*n*-C$_{14}$H$_{25}$) is thus great compared to poly(HD). This suggests that the considered side chain crystallization through the intermolecular interaction could be rather weak (observed as lower T_m values depending upon the HD content). Furthermore, it seems likely that the thermograms with HD contents of 11.4 mol % (run 31) and 12.5 mol % (run 35) were bimodal and became unimodal upon increasing the HD content (Figure 3b, HD 14.0 and 15.0 mol %); a probable linear correlation was also observed (plotted as ◆ in Figure 4). As described in the introduction, two possibilities could probably be considered, the interdigitating model and the inclusion model, as the co-crystallization of the main chain and side chain (in the assumed explanation for the observed T_m value, as also suggested by the WAXD analysis, shown in Figure 9), the latter model may be a probable possibility with speculation of the HD content (such as 11.4−12.5 mol %).

Figure 5 shows DSC thermograms for poly(E-*co*-TD)s with various TD contents (3.0−15.4 mol %) and the thermogram for poly(TD) (run 29). Corresponding plots of the T_m values vs the TD content are shown in Figure 6, and the T_m values are also summarized in Table 4.

As observed in poly(E-*co*-HD)s, T_m values in poly(E-*co*-TD)s decreased upon increasing the TD content [Figure 5a, plotted as ● in Figure 6, e.g., T_m = 81.2 °C (run 17, TD 3.0 mol %), 67.9 °C (run 18, TD 4.5 mol %), 58.5 °C (run 22, TD 5.2 mol %), 40.4 °C (run 26, TD 6.6 mol %), 23.5 °C (run 24, TD 11.4 mol %)] with broadening, especially the TD contents higher than 5.2 mol %. It was revealed that the T_m values were not observed even in a slight trace in the copolymer with 6.3 mol % (run 21) when the thermograms were measured under conventional conditions (10 °C/min, second heating); the value was, however, observed under different conditions (Figure 5b). The values were observed with samples possessing higher TD contents (up to 11.4 mol %) as slight traces (Figure 5a), probably due to weakened crystal packing (main chain). This assumption may also be suggested from the fact that the
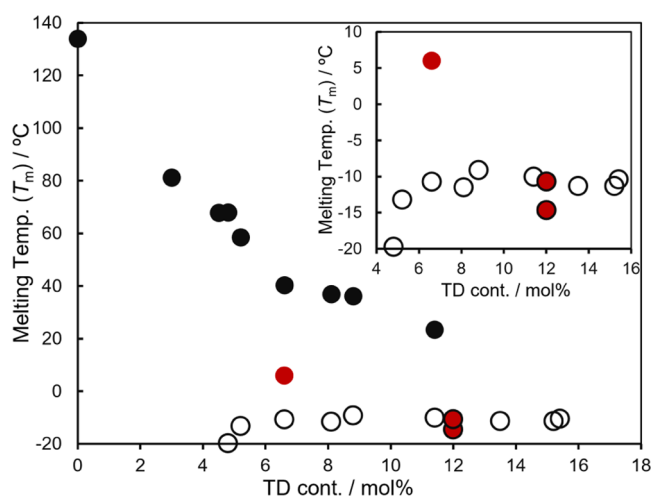

Figure 6. Plots of melting temperatures (T_m values) vs TD contents in poly(E-*co*-TD)s. ● shows plots corresponding to the main chain crystallization. ○ (partly filled in red) shows plots due to the other crystallization.

observed T_m values were affected slightly by the conditions (5, 10 °C/min, Table 4, the thermograms are shown in the SI).

As also observed in poly(E-*co*-HD)s, three T_m values were observed in the copolymer with TD 6.6 mol % (run 26), and the lowest T_m value (−10.7 °C) was affected by the TD content. The T_m value was initially low (−16.6, −21.6 °C, runs 21, 22) but seemed to reach a constant value (or slightly increasing) even upon increasing the TD content (plotted as ○ in Figure 6) within these TD content regions. Moreover, the thermogram of the sample with TD 12.0 mol % was bimodal and became unimodal with an increase of TD content (13.5, 15.4 mol %, runs 27, 15, respectively, Figure 5a). Since there is a similar observation in poly(E-*co*-HD)s (Figures 3 and 4), these T_m values could also be assumed to be due to a different packing model (from the main chain and side chain, plotted as red circles in Figure 6) although the interaction seems to be

weak compared to HD due to a rather short side chain branching.

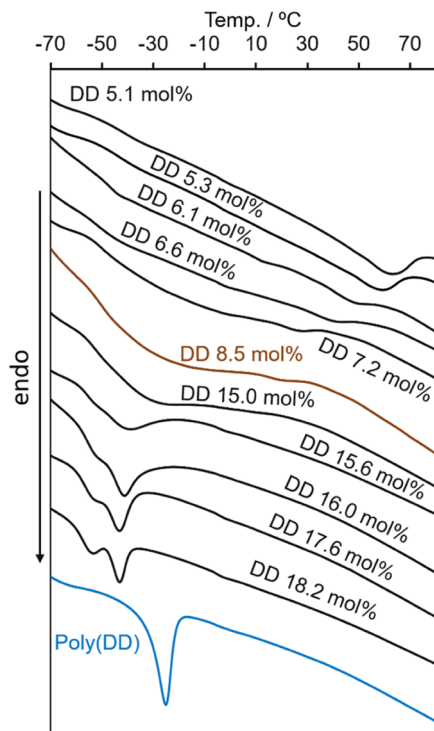Figure 7 shows DSC thermograms (second heating, 10 °C/min) for poly(E-co-DD)s with various DD contents (4.0−18.2

Figure 7. DSC thermograms (between −70 and 80 °C) of poly(E-co-DD)s with different DD contents (second heating at 10 °C/min). Polymerization data are shown in Table 2, and the additional thermograms are shown in the SI.

mol %) and the thermogram for poly(DD) (run 14). Corresponding plots of the T_m values vs the DD content are shown in Figure 8, and the values are also summarized in Table 4. As observed in poly(E-co-HD)s and poly(E-co-TD)s, the T_m
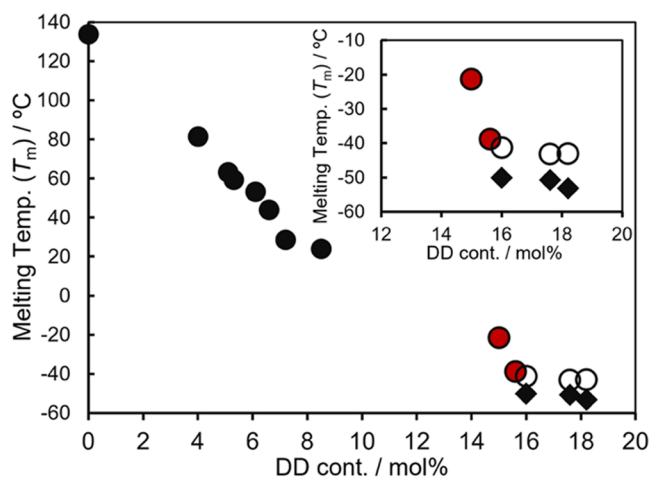
values initially decreased upon increasing the DD content [Figure 7a, plotted as ● in Figure 8, e.g., T_m = 81.6 °C (run 9, DD 4.0 mol %), 63.3 °C (run 4, DD 5.1 mol %), 59.4 °C (run 10, DD 5.3 mol %), 44.1 °C (run 5, DD 6.6 mol %), 24.1 °C (run 13, DD 8.5 mol %)] with broadening, especially DD contents higher than 6.1 mol %.

In contrast to the thermograms of the copolymers with HD, TD, the sample with DD 15.0 mol % (and DD 15.6 mol %) showed one broad T_m value (plotted as red circles, Figure 8), and the thermogram became bimodal on increasing the DD content; the values were also affected by the heating conditions (5, 10 °C/min, Table 4, the thermograms are shown in the SI). The thermogram of the T_m value at −43 °C seemed to become sharp upon increasing the DD content (runs 2, 8, Figure 7). The observed difference could probably be explained due to the rather short alkyl branching in DD compared to those in HD and TD, which showed an apparent low T_m value with poly(DD) (−25.2 °C) compared to poly(TD) (7.5 °C) and poly(HD) (25.6 °C); the observed fact seems to be explained as an effect of the side chain length in the crystallization in poly(LCAO)s.[26,27] However, we only have a simple assumption (probably due to side chain and co-crystallization of the main chain and side chain) as the explanation for the observed bimodal thermograms.

WAXD Analysis of Poly(E-co-HD) Films. Wide-angle X-ray diffraction measurements were performed at BL-6A in the Photon Factory of High Energy Accelerator Research Organization (Tsukuba, Japan), and the diffraction angle was calibrated with a diffraction pattern of silver behenate. Samples were sandwiched between thin polyimide films with a 1 mm aluminum spacer and placed on a temperature-controlled hot stage. After being heated at 120 °C, the samples were cooled to −20 °C at a rate of 10 °C/min. The spectra measured at 263 K (−10 °C) are shown in Figure 9.

In addition to the diffractions at 20.79 and 22.97° [corresponding to (110) and (200) diffractions observed in polyethylene, main chain crystallization] in the poly(ethylene-co-HD) sample with low HD content (HD 2.7 mol %, run 37) and similar diffraction at 20.85° [corresponding to (100) in poly(HD), side chain crystallization], another diffraction
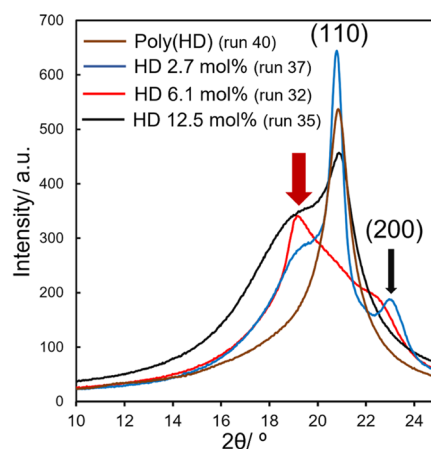

Figure 8. Plots of melting temperatures (T_m values) vs DD contents in poly(E-co-DD)s. ● shows plots corresponding to the main chain crystallization. ○ (partly filled in red) shows plots that are probably due to the other crystallization (or side chain crystallization in the sample with DD content of 15.6 mol %).

Figure 9. Wide-angle X-ray diffraction (WAXD) spectra of poly-(ethylene-co-HD)s [HD content 2.7 mol % (run 37), 6.1 mol % (run 32), 12.5 mol % (run 35)] and poly(HD) (run 40) films measured at 263 K. Detailed polymerization data are summarized in Table 2, and the corresponding DSC thermograms are shown in Figure 3. The DSC data are summarized in Table 4.

(shown by the red arrow in Figure 9) was observed at 19.16° in poly(ethylene-*co*-HD) samples (HD 2.7−12.5 mol %), especially in the sample with HD 6.1 mol %, which was observed to have three melting temperatures in the DSC thermograms. The results thus clearly suggest the presence of another crystalline phase in these copolymer samples.

CONCLUDING REMARKS

A series of ethylene (E) copolymers with α-olefin containing rather long side chains [LCAO, 1-dodecene (DD), 1-tetradecene (TD), 1-hexadecene (HD)] with various comonomer contents were prepared, and their thermal properties, including the effects of LCAO contents and side chain length, were explored. The Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$)−MAO catalyst system enabled the synthesis of the copolymers with unimodal molecular weight distributions (Table 2) and with uniform compositions (confirmed by DSC thermograms). In addition to the melting temperatures (T_m values) corresponding to the so-called main chain crystallization (samples with low LCAO contents) and side chain crystallization [as observed in poly(DD), poly(TD), and poly(HD), polymer samples with high LCAO contents],[25−29] the other T_m values were observed, especially in poly(E-*co*-HD)s; the wide-angle X-ray diffraction (WAXD) data clearly suggest the presence of another crystalline phase. These T_m values in poly(E-*co*-TD)s and poly(E-*co*-DD)s with rather high TD or DD contents were affected by the heating conditions in the measurement of DSC thermograms (5, 10 °C/min, Table 4, the additional thermograms are shown in the SI), suggesting that the driving force for generating crystal packing (observed T_m) should be weak and affected by the length of the alkyl side chains. Presently, as described in the text, we speculate using the inclusion model (Figure 1d) rather than the interdigitating model (Figure 1c), proposed as a model polyethylene containing C$_{21}$H$_{43}$ alkyl branching placed at every 15th or 19th carbon,[22] for the observed additional T_m values on the basis of rather high HD (TD) contents; the presence, observed as a different diffraction peak, could be strongly suggested by the WAXD analysis. As far as we know, the study on thermal properties in a series of poly(E-*co*-LCAO)s with various LCAO contents has never been reported, and the results should thus be helpful for a better understanding, further study of details (by a physical approach), and the design of new polymers by the copolymerization approach.

EXPERIMENTAL SECTION

General Procedure. All experiments were conducted under the atmospheric pressure of nitrogen in a dry box (Vacuum Atmospheres Co.). All chemicals used in these experiments were of reagent grade and were purified using standard purification procedures. 1-Dodecene (DD, Tokyo Chemical Industry Co., Ltd.), 1-tetradecene (TD, Aldrich Chemical Co.), and 1-hexadecene (HD, Tokyo Chemical Industry Co., Ltd.) were stored in bottles in a dry box upon addition of molecular sieves and were passed through an alumina short column prior to use. Ethylene (purity >99.9%; Sumitomo Seika Co., Ltd.) of polymerization grade was used as received. Toluene (anhydrous grade, Kanto Kagaku Co., Ltd.) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16 and 13X) in a dry box and was used without further purification. AlMe$_3$-Free MAO (d-MAO) white solids employed as a cocatalyst were prepared by

removing toluene and AlMe$_3$ from commercially available methylaluminoxane (MAO) [TMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] *in vacuo* in a dry box (at ca. 50 °C for removing toluene and AlMe$_3$ and then heated at >100 °C for 1 h for completion).[25,30,31,35,36] Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$) was prepared according to a previous report.[30]

All ^{1}H and ^{13}C NMR spectra for analysis of the resultant copolymers were recorded on a Bruker AV500 spectrometer (500.13 MHz, ^{1}H; 125.77 MHz, ^{13}C), and all chemical shifts are given in ppm and are in reference to SiMe$_4$. ^{13}C NMR spectra for the resultant copolymers were recorded with proton decoupling (the pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°) by ca. 6000 accumulation of transients. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the resultant copolymers were measured by gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) in *o*-dichlorobenzene (containing 0.05 wt/v % 2,6-di-*tert*-butyl-*p*-cresol) at 140 °C (column TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d., molecular weight ranging from <10^2 to <2.8 × 10^8; RI-8022 detector). The molecular weights were calculated using a standard procedure based on the calibration with standard polystyrene samples. Thermal properties of the resultant copolymer were evaluated using a differential scanning calorimeter (DSC, Hitachi DSC-7020) under a nitrogen atmosphere. First, the polymer samples were preheated from 30 to 250 °C with an increasing rate at 20 °C/min and then cooled to −100 °C with a rate of 10 °C/min. Then, the samples were second-heated from −100 to 250 °C at a rate of 5 or 10 °C/min and then cooled to 30 °C at a rate of 20 °C/min. The T_m values were determined from the middle of the phase transition of the second heating scan. Wide-angle X-ray diffraction measurements were performed at BL-6A in the Photon Factory of High Energy Accelerator Research Organization. The diffraction angle was calibrated with a diffraction pattern of silver behenate. Diffraction data were collected using a PILATUS 100 K (DECTRIS Ltd., Switzerland). Samples were sandwiched between thin polyimide films with a 1 mm aluminum spacer and placed on a temperature-controlled hot stage (Linkam Scientific Instruments Ltd., THMS-600). After being heated at 120 °C, the samples were cooled to −20 °C at a rate of 10 °C/min, and the spectra were measured at 263 K.

Ethylene Copolymerization with Long-Chain α-Olefins [LCAOs, 1-Dodecene (DD), 1-Tetradecene (TD), 1-Hexadecene (HD)]. Copolymerization of ethylene with long-chain α-olefins (LCAOs) was conducted in toluene. A typical procedure is as follows. Into a 100 mL scale stainless steel autoclave placed in a dry box, d-MAO (116 mg, 2.0 mmol), LCAO (prescribed amount), and toluene (total 29.0 mL) were added. The reaction apparatus was taken out and the reactor was then filled with ethylene (1 atm). A toluene solution (1.0 mL) containing Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$) (prescribed amount) was then added into the reactor at a prescribed temperature. Ethylene was immediately pressurized (prescribed amount) by closing the valve, and the reaction mixture was magnetically stirred for 6 min. After the reaction, the reactor was immediately cooled in an ice bath and the remaining ethylene was purged. The reaction mixture was then poured into a mixed HCl (10 mL) and isopropanol (^{i}PrOH) (100 mL) solution and stirred at room temperature for 15 min. The obtained polymer was washed with hot ^{i}PrOH and stirred

for 30 min to remove the remaining LCAO monomers. The precipitates in the mixed solution were then collected through suction filtration and washed with ^{i}PrOH. The resultant copolymer was then dried *in vacuo* at room temperature for 6 h.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06560.

> Experimental procedure for the synthesis of ethylene copolymers with 1-dodecene, 1-tetradecene, and 1-hexedecene including general procedures; selected NMR spectra of the copolymers; and additional DSC thermograms of the copolymers (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Kotohiro Nomura − *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan;* Ⓞ orcid.org/0000-0003-3661-6328; Email: ktnomura@tmu.ac.jp

Authors

Suphitchaya Kitphaitun − *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*

Hiroki Takeshita − *Department of Materials Science, Faculty of Engineering, The University of Shiga Prefecture, Hikone, Shiga 522-8533, Japan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c06560

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) For selected examples, refs 1−4: Alamo, R. G.; Mandelkern, L. Thermodynamic and structural properties of ethylene copolymers. *Macromolecules* **1989**, *22*, 1273−1277.

(2) Hosoda, S.; Nomura, H.; Gotoh, Y.; Kihara, H. Degree of branch inclusion into the lamellar crystal for various ethylene/α-olefin copolymers. *Polymer* **1990**, *31*, 1999−2005.

(3) Müller, A. J.; Arnal, M. L.; Spinelli, A. L.; Cañizales, E.; Puig, C. C.; Wang, H.; Han, C. C. Morphology and crystallization kinetics of melt miscible polyolefin blends. *Macromol. Chem. Phys.* **2003**, *204*, 1497−1513.

(4) Stadler, J. F.; Takahashi, T.; Yonetake, K. Lattice sizes, crystallinities, and spacing between amorphous chains - characterization of ethene-/ α -olefin copolymers with various comonomers and comonomer contents measured by wide angle X-ray scattering. *e-Polymers* **2009**, *9*, No. 040.

(5) Selected reports by the metallocene (and linked half-titanocene) catalysts, refs 5−10: Walter, P.; Trinkle, S.; Suhm, J.; Mäder, D.; Friedrich, C.; Mülhaupt, R. Short and long chain branching of polyethene prepared by means of ethene copolymerization with 1-eicosene using MAO activated Me$_2$Si(Me$_4$Cp)(N^{t}Bu)TiCl$_2$. *Macromol. Chem. Phys.* **2000**, *201*, 604−612.

(6) Pollard, M.; Klimke, K.; Graf, R.; Spiess, H. W.; Wilhelm, M.; Sperber, O.; Piel, C.; Kaminsky, W. Observation of chain branching in polyethylene in the solid state and melt via ^{13}C NMR spectroscopy and melt NMR relaxation time measurements. *Macromolecules* **2004**, *37*, 813−825.

(7) Kaminsky, W.; Piel, C.; Scharlach, K. Polymerization of ethene and longer chained olefins by metallocene catalysis. *Macromol. Symp.* **2005**, *226*, 25−34.

(8) Piel, C.; Starck, P.; Seppälä, J. V.; Kaminsky, W. Thermal and mechanical analysis of metallocene-catalyzed ethene−α-olefin copolymers: The influence of the length and number of the crystallizing side chains. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1600−1612.

(9) Stadler, F. J.; Piel, C.; Klimke, K.; Kaschta, J.; Parkinson, M.; Wilhelm, M.; Kaminsky, W.; Münstedt, H. Influence of type and content of various comonomers on long-chain branching of ethene/α-olefin copolymers. *Macromolecules* **2006**, *39*, 1474−1482.

(10) Janicek, M.; Cermak, R.; Obadal, M.; Piel, C.; Ponizil, P. Ethylene copolymers with crystallizable side chains. *Macromolecules* **2011**, *44*, 6759−6766.

(11) Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; García-Franco, C. A.; Lyon, M. K. Well-Defined, Model Long Chain Branched Polyethylene. 2. Melt Rheological Behavior. *Macromolecules* **2002**, *35*, 3066−3075.

(12) Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; García-Franco, C. A.; Sun, T.; Ruff, C. J. Well-defined, model long chain branched polyethylene. 1. Synthesis and characterization. *Macromolecules* **2000**, *33*, 2424−2436.

(13) Selected reports by the acyclic diene metathesis (ADMET) polymerization, refs 13−22: Pribyl, J.; Wagener, K. B.; Rojas, G. ADMET polymers: synthesis, structure elucidation, and function. *Mater. Chem. Front.* **2021**, *5*, 14−43.

(14) Wei, Y.; Graf, R.; Sworen, J. C.; Cheng, C.-Y.; Bowers, C. R.; Wagener, K. B.; Spiess, H. W. Local and collective motions in precise polyolefins with alkyl branches: A combination of ^{2}H and ^{13}C solid-state NMR spectroscopy. *Angew. Chem., Int. Ed.* **2009**, *48*, 4617−4620.

(15) Rojas, G.; Inci, B.; Wei, Y.; Wagener, K. Precision polyethylene: Changes in morphology as a function of alkyl branch size. *J. Am. Chem. Soc.* **2009**, *131*, 17376−17386.

(16) Inci, B.; Wagener, K. B. Decreasing the alkyl branch frequency in precision polyethylene: Pushing the limits toward longer run lengths. *J. Am. Chem. Soc.* **2011**, *133*, 11872−11875.

(17) Hosoda, S.; Nozue, Y.; Kawashima, Y.; Suita, K.; Seno, S.; Nagamatsu, T.; Wagener, K. B.; Inci, B.; Zuluaga, F.; Rojas, G.; Leonard, J. K. Effect of the sequence length distribution on the lamellar crystal thickness and thickness distribution of polyethylene: Perfectly equisequential ADMET polyethylene vs ethylene/α-olefin copolymer. *Macromolecules* **2011**, *44*, 313−319.

(18) Nozue, Y.; Kawashima, Y.; Seno, S.; Nagamatsu, T.; Hosoda, S.; Berda, E. B.; Rojas, G.; Baughman, T. W.; Wagener, K. B. Unusual crystallization behavior of polyethylene having precisely spaced branches. *Macromolecules* **2011**, *44*, 4030−4034.

(19) Inci, B.; Lieberwirth, I.; Steffen, W.; Mezger, M.; Graf, R.; Landfester, K.; Wagener, K. Decreasing the alkyl branch frequency in precision polyethylene: Effect of alkyl branch size on nanoscale morphology. *Macromolecules* **2012**, *45*, 3367−3376.

(20) Matsui, K.; Seno, S.; Nozue, Y.; Shinohara, Y.; Amemiya, Y.; Berda, E. B.; Rojas, G.; Wagener, K. B. Influence of branch incorporation into the lamella crystal on the crystallization behavior of polyethylene with precisely spaced branches. *Macromolecules* **2013**, *46*, 4438−4446.

(21) Li, H.; Rojas, G.; Wagener, K. B. Precision long-chain branched polyethylene via acyclic diene metathesis polymerization. *ACS Macro Lett.* **2015**, *4*, 1225−1228.

(22) Matsui, K.; Li, H.; Nozue, Y.; Rojas, G.; Bell, M.; Shinohara, Y.; Amemiya, Y.; Wagener, K. B. A Study of ADMET polyethylene with 21-carbon branches on Every 15th compared to every 19th Carbon: What a difference four extra backbone methylenes make. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 3090−3096.

(23) Ivchenko, P. V.; Nifant'ev, I. E.; Tavtorkin, A. V. Polyolefin drag reducing agents. *Pet. Chem.* **2016**, *56*, 775−787.

(24) Gómez Cuenca, F.; Marín, M. G.; Folgueras Díaz, M. B. Energy-savings modeling of oil pipelines that use drag-reducing additives. *Energy Fuels* **2008**, *22*, 3293−3298.

(25) Nomura, K.; Pengoubol, S.; Apisuk, W. Synthesis of ultrahigh molecular weight polymers by homopolymerisation of higher α-olefins catalysed by aryloxo-modified half-titanocenes. *RSC Adv.* **2016**, *6*, 16203−16207.

(26) López-Barrón, C. R.; Tsou, A. H.; Younker, J. M.; Norman, A. I.; Schaefer, J. J.; Hagadorn, J. R.; Throckmorton, J. A. Microstructure of crystallizable α-olefin molecular bottlebrushes: Isotactic and atactic poly(1-octadecene). *Macromolecules* **2018**, *51*, 872−883.

(27) López-Barrón, C. R.; Tsou, A. H.; Hagadorn, J. R.; Throckmorton, J. A. Highly entangled α-olefin molecular bottle-brushes: Melt structure, linear rheology, and interchain friction mechanism. *Macromolecules* **2018**, *51*, 6958−6966.

(28) Nomura, K.; Pengoubol, S.; Apisuk, W. Synthesis of ultrahigh molecular weight polymers with low PDIs by polymerizations of 1-decene, 1-dodecene, and 1-tetradecene by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)−borate catalyst. *Molecules* **2019**, *24*, No. 1634.

(29) Nomura, K.; Pengoubol, S.; Apisuk, W. Synthesis of ultrahigh molecular weight polymers containing reactive functionality with low PDIs by polymerizations of long-chain α-olefins in the presence of their nonconjugated dienes by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)−borate catalyst. *Polymers* **2020**, *12*, No. 3.

(30) Kitphaitun, S.; Yan, Q.; Nomura, K. Effect of SiMe$_3$, SiEt$_3$ *para*-substituents for exhibiting high activity, introduction of hydroxy group in ethylene copolymerization catalyzed by phenoxide-modified half-titanocenes. *Angew. Chem., Int. Ed.* **2020**, *59*, 23072−23076.

(31) Kitphaitun, S.; Yan, Q.; Nomura, K. Effect of *para*-substituents in ethylene copolymerizations with 1-decene, 1-dodecene, and with 2-methyl-1-pentene using phenoxide modified half-titanocenes−MAO catalyst systems. *ChemistryOpen* **2021**, *10*, 867−876.

(32) Nomura, K.; Liu, J.; Sudhakar, P.; Kitiyanan, B. Nonbridged half-metallocenes containing anionic ancillary donor ligands: New promising candidates as catalysts for precise olefin polymerization. *J. Mol. Catal. A: Chem.* **2007**, *267*, 1−29.

(33) Nomura, K. Half-titanocenes containing anionic ancillary donor ligands as promising new catalysts for precise olefin polymerization. *Dalton Trans.* **2009**, *34*, 8811−8823.

(34) Nomura, K.; Liu, J. Half-titanocenes for precise olefin polymerisation: Effects of ligand substituents and some mechanistic aspects. *Dalton Trans.* **2011**, *40*, 7666−7682.

(35) Nomura, K.; Oya, K.; Imanishi, Y. Ethylene/α-olefin copolymerization by various nonbridged (cyclopentadienyl)(aryloxy) titanium(IV) complexes − MAO catalyst system. *J. Mol. Catal. A: Chem.* **2001**, *174*, 127−140.

(36) Kakinuki, K.; Fujiki, M.; Nomura, K. Copolymerization of ethylene with α-olefins containing various substituents catalyzed by half-titanocenes: Factors affecting the monomer reactivities. *Macromolecules* **2009**, *42*, 4585−4595.