Study on the structure and properties of new metallocene high branched polyethylene

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Abstract: The branching composition, distribution and melting crystallization properties of very low density polyethylenes (VLDPE) with different carbon chain length were studied by means of nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). The average sequence length (nE, nH, nB), relative monomer distribution (RMD) and monomer reactivity ratio (rE, rH, rB) were selected to analyze the polymerization characteristics. The crystallization characteristics of wafer thickness (L), relative branching degree (S) and crystallinity (Xc) were discussed by means of SSA thermal classification method. It has been found that the comonomer content and branching degree of VLDPE products with hexene (C6) as co monomers is lower than that of butene (C4) copolymer products; while the crystallinity and lamellar thickness is higher than that of C4 products.
Key words: VLDPE; high branched; metallocene

1. Introduction

Since the metallocene branched polyethylene was prepared, people have found that this kind of polyethylene copolymerized with alpha olefins, can significantly improve the processing performance of metallocene polyethylene, due to the extremely small amounts of branched in the molecular chain. At the same time, film products which prepared by this kind of polyethylene have better film forming and film transparency[1]. As we all know that metallocene catalyzed branched polyethylene has not only a uniform molecular weight and molecular weight distribution, but also a homogeneous branching distribution, it has attracted a great deal of interest from researchers[2,3].More than conventional amount of comonomer was added during VLDPE polymerization, and highly branched polyethylene products with density of 0.880-0.915g/cm^3 could be prepared by metallocene catalyst, The short chain branches in the molecular chain provide excellent mechanical properties, optical properties and heat sealing properties for the VLDPE products, and have broad application prospects in the fields of food packaging, plastic toughening and other fields.

The preparation methods of VLDPE products have been introduced in the foregoing[4], this paper has studied the branched structure of VLDPE products with butene (C4), hexene (C6) as branched comonomer, and their properties are compared. The influences of the type and content of carbon chain of different comonomer on the molecular structure of the copolymer are also discussed.

2. Experiment
2.1 Materials and equipments
VLDPE1 (DQVL1210-H) was produced by Unipol gas-phase process using 1-hexene as comonomer; VLDPE2 (DQVL1210-B) was produced by Unipol gas-phase process using 1-butene as comonomer.

2.2 Equipments
Double screw extruder, TSSJ-25/33, Chenguang Chemical Research Institute; Plastic injection molding machine, K-TEC40, Chenguang Chemical Research Institute; Cantilever beam impact strength tester, XJU-5.5, Chengde Jinjian inspection instrument Co., Ltd.; Universal material testing machine, 5567, INSTRON USA company; MFR tester, CS-127, Chengde Jinjian inspection instrument Co., Ltd.

2.3 Performance testing and structural characterization
The melt flow rate (MFR) was measured by GB/T3682-2000; the density was measured by GB/T1033-2010; tensile yield strength, tensile fracture strength, and tensile nominal strain were measured by GB/T1040-2006.

NMR test: ^{13}C NMR spectra of the samples were obtained with a BRUKER AQS-300 MHz AVANCE spectrometer operating at 75.489 MHz at 100℃. Samples were prepared in 5 mm o.d. Tubes at 60% (w/w) concentration in 1,2,4 trichlorobenzene (TCB). The samples were dissolved at 150℃ for 30min before analyzing in the NMR spectrometer. The conditions for measurement were as follows: pulse interval 3s, acquisition time 1.82s, pulse width 9μs, spectral width 17,985 Hz, number of scans 500.

DSC routine test: The preparation of samples about 6mg in the crucible, the sample is quickly heated from 50℃ to 200℃ under the protection of nitrogen (gas flow 50mL/min), and keep heat preservation at 200℃ for 5min. Reduce temperature to 50℃ at 10℃/min, constant temperature for 5min. Then the temperature is increased to 180℃ at 10℃/min. Record the temperature decease curve and the second heating curve.

Successive self-nucleation annealing test: under the protection of nitrogen (gas flow 50mL/min), (i) Elevate room temperature to 180℃, keep the temperature constant for 5min; (ii) The temperature is reduced to 40℃, and then increased to 130℃, keep the temperature constant for 5min; (iii) The temperature is reduced to 40℃, and then increased to 125℃, keep the temperature constant for 5min; (iv) Repeat (ii) (iii) steps to keep the temperature reduced to 40℃ each time, self nucleation temperature interval is 5℃ from 125℃-70℃, the heating and reducing temperature rate is 15℃/min; (v) when the temperature is 70℃, reduce to 30℃ and then increase to 160℃, record the heating curve.

3. Results and Discussion

Adopted Unipol polymerization technique[4], VLDPE1 (DQVL1210-H) was prepared with hexene (C6) as comonomer and VLDPE2 (DQVL1210-B) was prepared with butene (C4) as comonomer. The basic physical properties of the copolymer were tested. The results are shown in table 1.

Table 1 VLDPE physical property comparison table

Properties	VLDPE1	VLDPE2
MFR，g/10min	1.0	1.1
Density，g/cm^{3}	0.911	0.912
Tensile strength at yield，MPa	10.08	9.12
Tensile strength at break，MPa	12.31	11.48
Elongation at break，%	568	594

As it is shown in Table 1, we can see that the two brands of VLDPE have the same density and index, but there are significant differences in tensile properties. In general, the tensile strength of the C6 VLDPE1 is lower than that of C4 VLDPE2, while the elongation at break of VLDPE2 is higher . This is related to the molecular entanglement induced by short branched chain molecules in the molecular chains and the inhibition of molecular chains in the amorphous region[5].

The peaks in the ^{13}C-NMR spectra of two samples are classified and divided into regions, and the peaks are labeled A-G respectively, and the peaks are assigned to each other, as shown in Table 2 and Table 3. According to the method[6], the two products were analyzed by ^{13}C-NMR spectrum, and the absorption peaks were assigned and the chemical shift distribution were divided. Three element sequence distribution was determined by the Seger method[7], andthe calculation results are shown in table 4.

Table 2 Chemical shift assignments in ^{13}C-NMR spectra of VLDPE1

Region	Chemical shift	Carbon atom type	Sequence structure
A	41.3-40.5	ααγ	EEHHHEE
B	40.5-39.4	αα	EEHHEE
C	38.2	CH	EEHEE+EEHEHEE
D	38.2-35.6	CHβ	EEHHEE
E	35.1	4B$_4$	EHE
	34.5	αγ	EHEH+HEHH

	34.2	αδ+	EEHE+EEHH
F	30.5	γδ+	EEEH
	30.0	δ,δ+	(EEE)n
	29.6	3B$_4$	EHE+EHH+HHH
G	27.3	βδ+	EEHE+EEHH

E stands for ethylene polymerization monomer;
H stands for 1- hexene polymerization monomer.

Table 3 Chemical shift assignments in ^{13}C-NMR spectra of VLDPE2

Region	Chemical shift	Carbon atom type	Sequence structure
A	40.0	CH,αα	EEBEE+EEBEBEE+EEBBEE
	40.0-39.4	ααγ	EEBBBEE
B	37.5	CHβ	EEBBEE+EEBBBEE
C	34.8-34.4	α,α,CHβ,γ	EEBEE+EEBEBEE
D+E	32.4-26.9	γ,δ,δ+,β,E2	EEBEE+EEBEB+EEBBEE+ EEBBBEE
F	24.8	ββ	EEBEBEE

E stands for ethylene polymerization monomer;
B stands for 1- butene polymerization monomer.

Table 4 Triadsequence structure distribution of VLDPE1 and VLDPE2

Sample	[EHE]%	[EHH]%	[HHH]%	[HEH]%	[EEH]%	[EEE]%
VLDPE1	3.96	0.20	0	0.18	7.35	88.31
Sample	[EBE]%	[EBB]%	[BBB]%	[BEB]%	[EEB]%	[EEE]%
VLDPE2	4.85	0.15	0	0.12	7.89	86.99

E stands for ethylene polymerization monomer;
H stands for 1- hexene polymerization monomer;
B stands for 1- butene polymerization monomer;
[EHE]、[EHH]、[HHH]、[HEH]、[EEH]、[EEE] stands for three element sequence structure polymerized by ethylene and hexene;
[EBE]、[EBB]、[BBB]、[BEB]、[EEB]、[EEE] stands for three element sequence structure polymerized by ethylene and butene.

At present, there are many methods to characterize the polymerization characteristics of ethylene and alpha olefins. In this paper three methods are used to analyze the polymerization characteristics, the average sequence length[6] (nE, nH, nB), the monomer distribution[8](RMD), and monomer reactivity ratio[9](rE, rH, rB).
Formula for average sequence length: nE=2×y(E)/y(EH)
$$nH=2×y(H)/y(EH)$$
$$nB=2×y(B)/y(EB)$$

Table 5 Structural parameters of VLDPE1 and VLDPE2

Sample	nE	nH	nB	yE%	yH%	yB%
VLDPE1	30.1	1.01	-	96.36	3.64	-
VLDPE2	26.8	-	1.08	95.88	-	4.12

nE stands for the average sequence length of ethylene;
nH stands for the average sequence length of hexene;
nB stands for the average sequence length of butene;
yE% stands for the mole content of ethylene;
yH% stands for the mole content of hexene;
yB% stands for the mole content of butene;

As summarized in Table 5, the average sequence length of two samples are both 1, and three element sequence structure are below 0.2% (taking into account the error range, can be regarded as 0%) which have been shown in Table 4. It can be inferred that C4 and C6 comonomers are isolated in the distribution chain in two brands of VLDPE products , and there is no comonomer distribution of adjacent structure. Although they have the same density, the C4 comonomer content is higher than that of C6 comonomer content, about 13.2% higher in molar fraction. This is because the molar fraction of the alpha olefin comonomer decreases with the increase of the chain length[10] in the case of lowering the PE density in the same range.

Formula of relative monomer distribution (RMD):

RMD=$100 \times 0.5 \times y(EH)/[y(H) \times y(E)]$

RMD=$100 \times 0.5 \times y(EB)/[y(B) \times y(E)]$

Formula of reactivity ratio: rE=$y(EE)/[y(E)-y(EE)]$

rH=$y(HH)/[y(H)-y(HH)]$

rB=$y(BB)/[y(B)-y(BB)]$

Table 6 Polymerization characteristic parameters of VLDPE1 and VLDPE2

Sample	RMD%	rE	rH	rE×rH	rB	rE×rB
VLDPE1	102.8	39.13	0.0199	0.78	-	-
VLDPE2	102.1	28.98	-	-	0.0283	0.82

RMD stands for relative monomer distribution;
rE stands for reactivity ratio of ethylene;
rH stands for reactivity ratio of hexene;
rB stands for reactivity ratio of butene.

In the two polymerization systems, RMD is both higher than 100% and has obvious alternating copolymerization characteristics. At the same time, it can be seen that rE×rH is 0.78, rE×rB is 0.82, which are close to 0. It also shows that copolymerization has the tendency of alternating polymerization. From the chemical composition and distribution uniformity of polymers, the alternating copolymerization is larger than that of random copolymerization and block copolymerization[11]. Therefore, both VLDPE1 and VLDPE2 have good chemical composition and distribution uniformity.

For branched polyethylene, the thermal properties are closely related to the branched structure, and the crystallinity of polyethylene with different branching degree is different. The melting crystallization properties of VLDPE1 and VLDPE2 are compared by DSC test method, By using a special method[13], crystallinity (Xc) and the average lamellar thickness (lc) is studied, which the results are shown in Table7.

Table 7 DSC routine test data of VLDPE1 and VLDPE2

Sample	Tm,℃	Tc,℃	ΔHm,J/g	Xc,%	lc,nm
VLDPE1	118.5	104.2	116.8	35.8	13.12
VLDPE2	117.2	96.48	104.3	34.1	11.65

Tm stands for melt point；Tc stands for crystallization temperature；ΔHm stands for melting enthalpy；Xc stands for crystallinity；lc stands for the average lamellar thickness.

The crystallization properties of VLDPE are usually determined by comonomer content and ethylene sequence length. By ^{13}C-NMR test, the comonomer content of C6 as comonomer is high. So the values of Tm, Tc, ΔHm, Xc of VLDPE1 are obviously higher than those of VLDPE1 which is C4 as comonomer.While

sequence of VLDPE molecular chain is long, so the long methylene sequences in the crystal are more easily folded in order to format more thickness and larger lamellae. Therefore the copolymerization of C6 VLDPE1 has higher lc value.

In order to further analyze the influence of VLDPE branching structure on crystallization properties, two samples are treated by successive self-nucleation annealing (SSA), as shown in Figures 1 and 2.
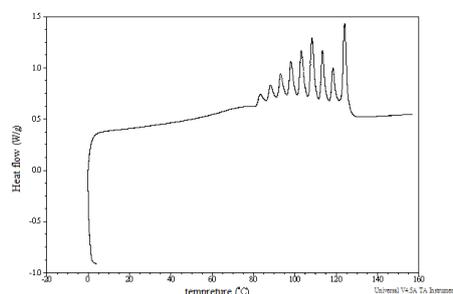
Fig.1 SSA curves of VLDPE1
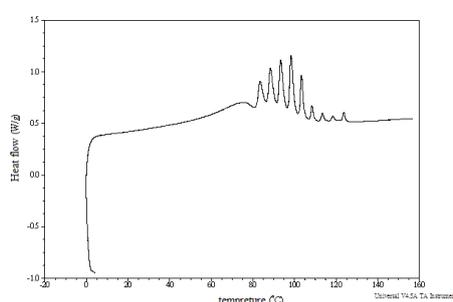
Fig.2 SSA curves of VLDPE2

SSA can classify the branched chains with different crystallization ability, and more finely characterize the chip thickness and distribution. As shown in Figure 1 and 2, there are multiple melting peaks of different melting points in the melting curve, which are correspond to lamellaes fomed by different molecular chain structure units. And the melting enthalpy represents the content of this part of lamellae[14].The grade distribution of two grades has obvious differences. VLDPE1 has a strong melting peak at 110-125℃, and the melting peak of VLDPE2 is the strongest at 82-100℃.

Based on the melting peak temperature, the relative degree of branching (S) and lamellae thickness (L) of the corresponding components are calculated by means of the literature[12,13,15]. The results are shown in Table 8 and 9.

Table 8 Results of thermal classification of VLDPE1

Parameter	Melting peak temperature，℃								
	84.2	89.2	94.8	98.5	102.2	107.2	112.6	117.5	124.9
Hm,J/g	3.99	4.95	5.12	6.35	7.32	9.98	7.36	5.02	11.36
L,nm	4.59	5.03	5.63	6.12	6.70	7.67	9.10	10.96	15.85
S	32.13	28.90	25.23	22.90	20.51	17.29	13.81	10.65	5.87
Hm/ΣH,%	6.49	8.06	8.33	10.33	11.91	16.24	11.98	8.17	18.49

Hm stands for melting enthalpy；L stands for lamellae thickness；S stands for relative branching degree；Xc stands for crystallinity；Hm/ΣH stands for the proportion of each melting peak area to the entire melting peak area.

From the datas in Table 8 and 9, it can be seen that there is a significant difference between the two grades of VLDPE products after thermal classification:

The strongest absorption peak of melting peak temperature of VLDPE1 (C6 copolymer) is from 107.2℃ to 124.9℃, and the highest fraction content reached 18.49% at 124.9. While the corresponding fractions have less branched content (S=5.87), more regular and long methylene sequence (L=15.85nm), larger lamellae thickness molecules.

Table 9 Results of thermal classification of VLDPE2

Parameter	Melting peak temperature，℃								
	84.1	88.7	94.7	98.8	103.8	108.9	114.6	117.9	123.1
Hm,J/g	7.56	8.12	9.85	9.94	8.34	3.12	2.56	1.36	2.68
L,nm	4.58	4.98	5.62	6.16	6.98	8.07	9.78	11.15	14.30
S	28.93	26.21	22.66	20.24	17.28	14.26	10.89	8.93	5.86
Hm/ΣH	14.12	15.17	18.40	18.57	15.58	5.83	4.78	2.54	5.01

The melting peak temperature of copolymerization of VLDPE2 (C4 copolymer) is at 84.1-103.8℃ which the highest appears at 98.8℃ and the content reaches 18.57%. This part of the thin lamellae fractions correspond to the irregular molecular chain structure (L=6.16nm).

From the comparison datas in the table we can also see that the fractions of VLDPE1 are mainly concentrated in the high melting peak temperature range which have larger lamellae thickness and higher crystallinity, while the fractions of VLDPE2 are in the lower melting peak temperature range which owe smaller lamellae thickness and lower crystallinity. So in the same density, VLDPE2 have even lower crystallinity which consistent with the previous results.

4. Conclusions

1) The contribution of different carbon chain lengths to the density amplitude of PE resin is significantly different. In the case of lower PE density, the molar fraction of C6 comonomer is lower.

2) The VLDPE products have obvious differences in branch chain content and crystallization property. In the products of C4 copolymerization, the degree of molecular chain branching is higher and the thickness of lamellae is smaller.

5. References

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