Study of Polyethylene Solution Fractionation and Resulting Fractional Crystallization Behavior

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ABSTRACT: Solution fractionation for four different polyethylenes including high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and very low-density polyethylene (VLDPE) are conducted by stepwise controlling both the temperature and the amount of precipitant. The size exclusion chromatograph (SEC) measurements indicate that solution fractionation technique can successfully separate all the polyethylene samples in accordance with their molecular weight and molecular-weight distributions. In addition, infrared spectroscopy analysis shows that the degree of short-chain branching for each fraction of each polyethylene varies with the fraction's molecular weight. The effect of the molecular weight with different short-chain branching on each fraction's crystallinity represents the characteristics of chain components for different polyethylenes. The crystallinities of HDPE, LLDPE, and LDPE decrease with the increase in their molecular weights; however, for VLDPE, its crystallinity increases with the increase in the molecular weight. The research revealed that the degree of short-chain branching, together with the molecular weight, can greatly affect the crystallinity of polyethylene. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2542–2549, 2004

Key words: solution fractionation; polyethylene; molecular weight; short-chain branching; crystallinity

INTRODUCTION

It is well known that polyethylene is a widely used engineering thermoplastic. Following the development of novel initiation and polymerization technologies, the polyethylene family has added many new members: ultra-high molecular weight polyethylene (UHMWPE), very low-density polyethylene (VLDPE), ultra low-density polyethylene (ULDPE), and metallocene-catalyzed polyethylene (m-PE). These polyethylenes, with recently improved physical properties and processing characteristics, are becoming the focus of much current polymer science research. For polyethylene, crystallinity is one of the important physical parameters that can determine its thermal, mechanical, electrical, and radiation-resistant properties. However, molecular weight, molecular-weight distribution, and the degree of short-chain branching can effectively affect and control its magnitude of crystallinity. For different polyethylenes, due to the difference of comonomers and polymerization techniques, there exist marked chain structure and crystalline morphology differences, resulting in different physical properties. To date, the characterizations of fine crystal structure and its related polymer chain structure for polyethylene were mainly involved in fractionation technology including successive solution fractionation (SSF),[1,2] temperature rising elution fractionation (TREF),[3,4,5,6] thermal fractionation,[7] successive self-nucleation, and annealing fractionation (SSA),[8] or their combination application technology.[9] Among them, TREF is the most used method to separate polyethylene into different fine structure based on its crystallizability. However, this technique has some shortcomings: the cycling time for each sample's separation is relatively long; large amounts of solvent are used that may cause environment pollution; and the equipment of TREF is very expensive, which may limit the large-scale preparation. Compared to TREF, solution fractionation, which can still make a good separation of polyethylene based on molecular weight and molecular-weight distribution, is a relatively simple procedure. Each sample's separation uses less solvent and can be conveniently used for large-scale preparation.

In this article, solution fractionation for polyethylene is studied by stepwise controlling both the temperature and the amount of precipitant. By choosing four different polyethylenes, high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and VLDPE, the solution fractionation routes are determined. Each fraction's molecular weight and molecular weight distribution are measured via size exclusion chromatography (SEC) to understand the fractionation's efficiency. Infrared spectroscopy is employed to measure

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TABLE I
Physical Parameters of Commercial Polyethylene

Items	HDPE	LDPE	LLDPE	VLDPE
Designation	DGDB2480	2102TN00	DFDA7042	DFDA9101
Density[a] (g/cm^3)	0.945	0.921	0.920	0.905
MI[a] (g/10 min)	10.0–15.0	2.1–2.9	1.7–2.3	1.0

[a] The data were taken from chemical data sheets published by the manufacturer.

the degree of short-chain branching for each fraction of each polyethylene. Differential scanning calorimeter (DSC) is used to study the fraction's crystallization behavior and the relation of the crystallinity with the individual molecular chain structure. The study clearly indicates that the solution fractionation is an effective technique for separation based on the molecular chain structure and its component for different polyethylenes. The crystallization behavior and the magnitude of crystallinity for fractions can be markedly affected by their chain component, molecular weight, and molecular-weight distribution.

EXPERIMENTAL

Materials

Different polyethylene samples were obtained commercially from Qilu Petroleum and Chemical Co. (Zibo, China). The physical parameters of each polyethylene used in this study are given in Table I.

Solution fractionation procedure

The polyethylene solution was first prepared by dissolving 2.4 g sample in 400 mL xylene by using 0.01 wt% 2,2'-methylene-bis(6-tert-butyl-4-methyl phenol) as antioxidant in a glass column at 130°C stirring for 30 min. The glass column was equipped with a temperature controller and a stirrer to ensure thermostate with a fluctuation of 0.5°C. Then, 372 g of ethylene glycol monoethyl ether as a precipitant was added to the solution. The temperature was kept at 130°C for 120 min to guarantee the system's equilibrium. At that time, the first fraction (Fraction I), occurring as a white gel floating on the top of the solution, was collected. Then, the system was allowed to cool to 100°C at a
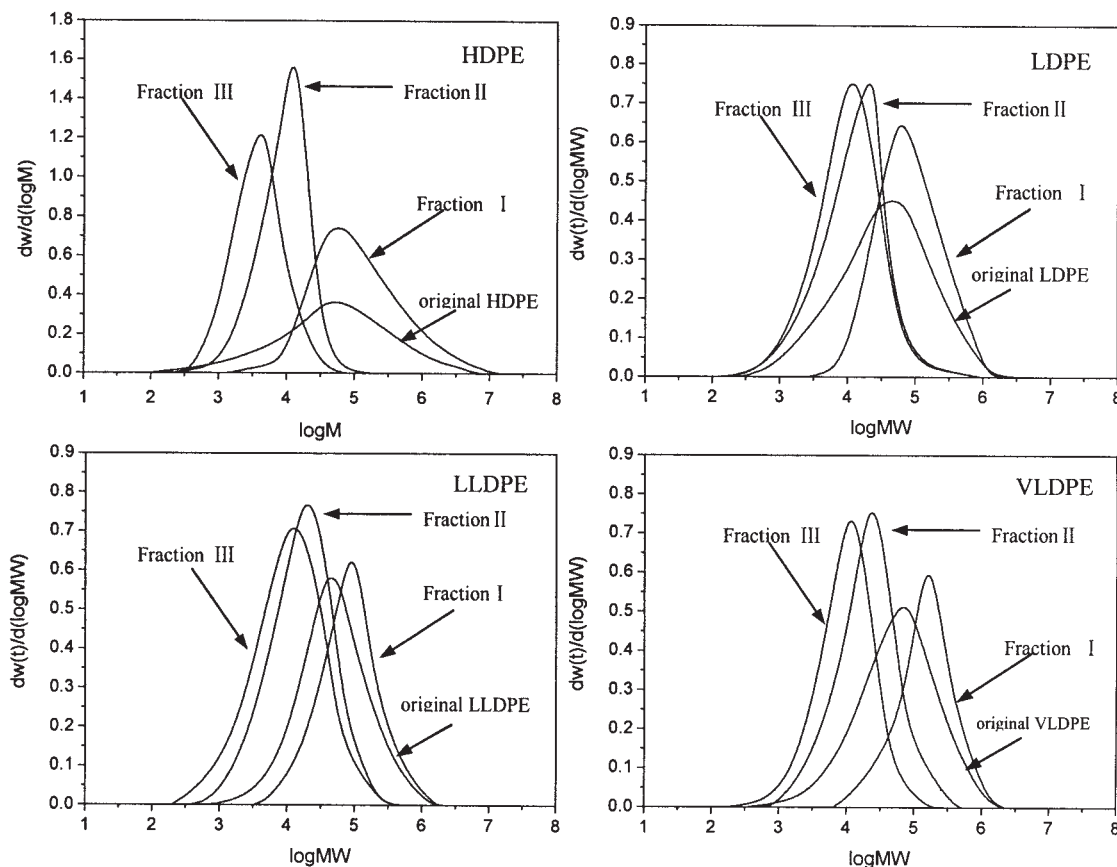

Figure 1 The molecular weight and molecular weight distribution curves for fractions of HDPE, LDPE, LLDPE, and VLDPE.

TABLE II
Number- and Weight-Averaged Molecular Weights, Polydispersity Index, and the Degree
of Short-Chain Branching for Fractions of Different Polyethylenes

Polyethylene sample	Yield	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Degree of SCB ($-CH_3/1000°C$)
HDPE					
Fraction I	72.2%	263,588	49,154	5.4	24
Fraction II	17.2%	13,478	8039	1.7	12
Fraction III	8.6%	4828	2405	2.0	11
Original HDPE	—	196,311	11,107	17.7	22
LDPE					
Fraction I	74.2%	135,336	58,294	2.3	33
Fraction II	10.7%	16,164	6608	2.5	39
Fraction III	15.2%	15,974	6026	2.7	41
Original LDPE	—	95,000	16,000	5.9	36
LLDPE					
Fraction I	77.0%	112,000	41,481	2.7	39
Fraction II	9.7%	24,364	9959	2.4	44
Fraction III	13.4%	20,896	8037	2.6	33
Original LLDPE	—	91,000	28,000	3.3	38
VLDPE					
Fraction I	75.1%	178,070	65,796	2.6	43
Fraction II	13.5%	32,069	13,211	2.4	54
Fraction III	11.4%	19,750	7900	2.5	68
Original VLDPE	—	117,626	26,016	4.5	44

cooling rate of 2°C/min and was kept there for 180 min for another equilibrium. The second fraction (Fraction II), precipitating as a white gel to the bottom, was obtained after absorbing the clear solution from the column. The absorbed mixture was added to a beaker containing a large amount of cold acetone. A
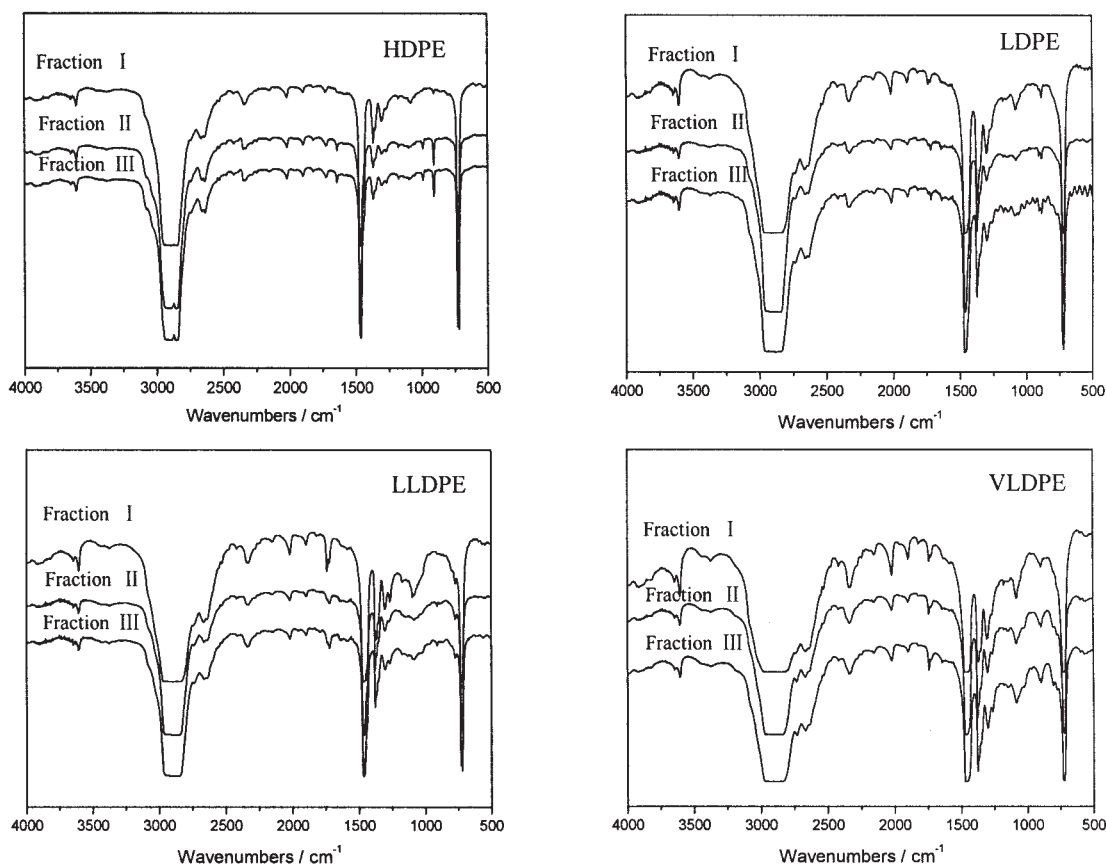

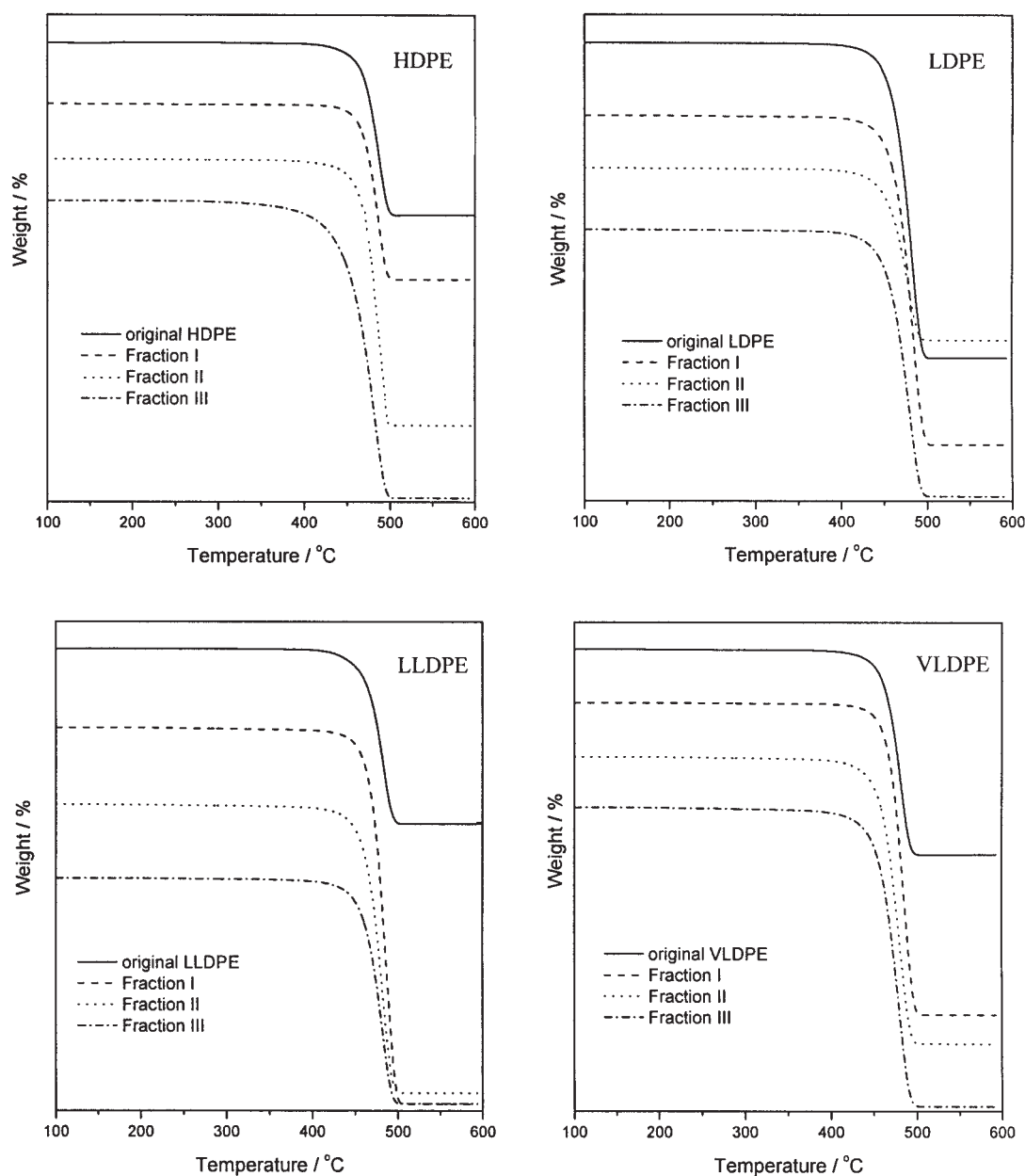Figure 2   The FTIR spectra for fractions of HDPE, LDPE, LLDPE, and VLDPE.

Figure 3 TGA curves for fractions of HDPE, LDPE, LLDPE, and VLDPE.

white precipitate of polyethylene was then collected as the third fraction (Fraction III). All the fractions collected were dried in a vacuum oven at 60°C for 72 h. The same procedure of solution fractionation was used for HDPE, LDPE, LLDPE, and VLDPE as described above.

Size exclusion chromatograph to determine the fraction's molecular weight and molecular weight distribution

The molecular weight and molecular-weight distribution were measured by using a PL220 high-temperature SEC (Shropshire, United Kindom). 1,2,4-Trichlo-

robenzene was used as the elution solvent, with a flow rate of 1.0 mL/min. The operating temperature was 160°C. Polystyrene standards were used for making the calibration curve.

Differential scanning calorimeter to study the fraction's crystalline behavior

A modulated differential scanning calorimeter (2910 MDSC, TA Instruments) equipped with a refrigerated cooling system (RCS) was used in the study. The temperature was calibrated with indium (156.6°C) and the heat flow was calibrated with the specific heat of

TABLE III
Thermal and Crystalline Behaviors for Fractions of Different Polyethylenes

Polyethylene sample	T_m (°C)	Crystallinity (%)	T_D (°C)
HDPE			
Fraction I	128.5	57.68	486.2
Fraction II	128.2	77.40	486.9
Fraction III	124.2	81.42	482.5
Original HDPE	128.3	64.49	487.1
LDPE			
Fraction I	105.2	40.03	483.9
Fraction II	106.0	46.02	478.1
Fraction III	106.5	48.03	479.7
Original LDPE	105.4	43.4	481.8
LLDPE			
Fraction I	121.3	43.91	487.2
Fraction II	122.5	44.89	481.8
Fraction III	122.7	45.46	481.6
Original LLDPE	121.2	44.33	483.2
VLDPE			
Fraction I	123.4	39.55	486.3
Fraction II	123.1	28.22	480.7
Fraction III	121.4	26.2	479.4
Original VLDPE	123.1	33.38	481.8

fusion of indium (28.71 J/g) at a scanning rate of 10°C/min. The furnace was purged with dry nitrogen at a flow rate of 50 mL/min. About 5.0 mg of sample was sealed in an aluminum pan, and the scanning procedure was conducted from −20 to 170°C. The sample's crystallinity was calculated by eq. (1) by using software supported by TA Instruments[10]

$$X_c = \frac{\Delta H_u}{\Delta H_{100}} \times 100\% \qquad (1)$$

where ΔH_u is the integrated melting enthalpy between 0 and 140°C from the DSC endothermic curve and ΔH_{100} is the melting enthalpy of polyethylene crystal with 100% crystallinity, which was set as 287.3 J/g in this study.[11]

Calculation of the degree of short-chain branching using infrared spectroscopy

Infrared spectrograms were recorded from the absorption region of 4000–500 cm^{-1} with a WQF-310 Fourier transform infrared (FTIR) spectroscope (Beijing, China). A minimum of 100 scans was used with a resolution of 2 cm^{-1}. The degree of short-chain branching of polyethylene was determined by using the methyl group absorption band at 1378 cm^{-1}. Detailed calculation procedures were used according to the literature.[12,13]

Thermal gravimetric analysis to study the fraction's thermal stability

A Q50 thermal gravimetric analyzer (TGA; TA Instruments, New Castle, DE) was employed to identify the thermal stability for fractions of polyethylene. The mass of polyethylene sample used was in the range of 12.0–18.0 mg. The heating step was adopted from 30 to 600°C at a rate of 15°C/min, and the furnace was purged with dry nitrogen at a flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Fraction's molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution curves for the polyethylenes and their fractions are shown in Figure 1. Number- and weight-averaged molecular weights and the polydispersity index are given in Table II. Evidently, after solution fractionation, each fraction's molecular weight and molecular-weight distribution show some variations. Compared to the original samples, the molecular weights of Fraction I for all four different polyethylenes increase, and the molecular weights of Fraction II and Fraction III decrease. Additionally, narrowing molecular-weight distributions can be clearly observed for all three fractions. As is known, the addition of precipitant into thermal-stated polyethylene solution can lower the solute's solubility. As a result, Fraction I, with larger molecular weight portion, can be obtained first. Then, under the fixed composition of the mixture solution, continuous reduction of the temperature from 130 to 100°C can further decrease the molecular interaction between polyethylene and solvent; therefore, Fraction II, which contains the smaller molecular weight portion, is obtained. After the temperature decreases to 25°C, the lowest molecular-weight portion of polyethylene is finally precipitated, which is Fraction III. Compared to Fraction II and Fraction III, the molecular-weight distribution for Fraction I is relatively larger, indicating that those molecules with higher molecular weight are more sensitive to the precipitant. The result may also imply that solution fractionation via the control of the temperature is more precise than via the control of the amount of precipitant. It is shown that solution fractionation technique, indeed, is an effective way to separate different polyethylenes based on their molecular weight and molecular-weight distribution.

The degree of short-chain branching for fractions

The FTIR spectra for fractions of HDPE, LDPE, LLDPE, and VLDPE are shown in Figure 2. The degrees of short-chain branching based on the calculation by using FTIR data for all fractions are given in Table II. From Figure 2, variations of FTIR spectra at 1378 cm^{-1} for different fractions clearly suggest that the fractions obtained with different molecular weights have different degrees of short-chain branching. However, as can
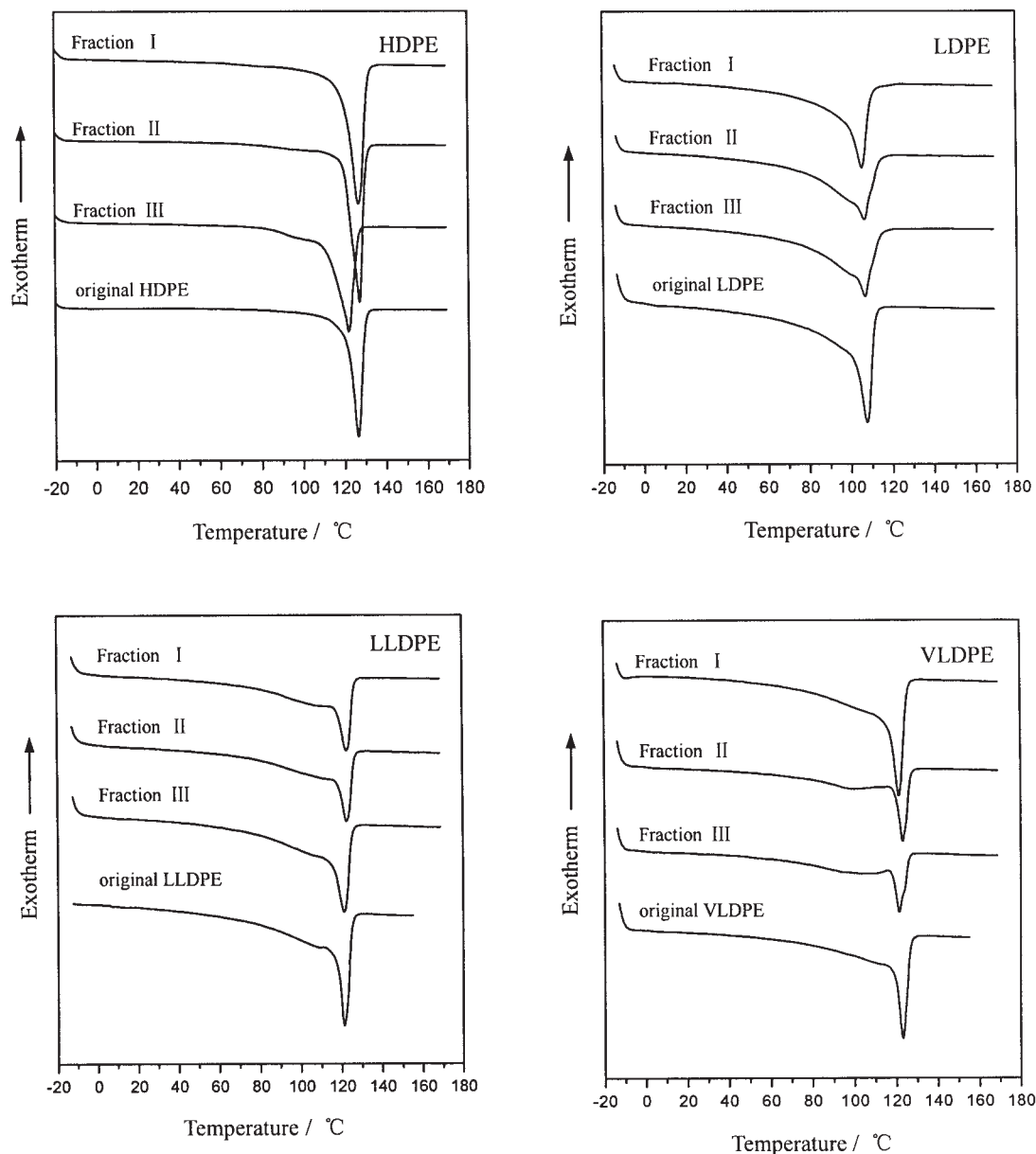
Figure 4 DSC curves for fractions of HDPE, LDPE, LLDPE, and VLDPE.

be seen from Table II, for HDPE, the fraction with larger molecular weight possesses a higher degree of short-chain branching, but for LDPE, the fraction with smaller molecular weight has a higher degree of short-chain branching. For VLDPE, the same result as with LDPE can be observed. Interestingly, for LLDPE, all fractions present basically the same values of short-chain branching. In this study, HDPE is a copolymer of ethylene with a small amount of 1-butene monomers synthesized under low pressure. Therefore, there should exist a smaller portion of short-chain branching along their main polymer chain. LDPE is a homopolymer synthesized with ethylene monomer only. Due to chain transfer among macromolecules and molecular rearrangement caused by backbiting of free

radicals[14] during polymerization, LDPE may carry both mostly longer chain branching and a smaller portion of short-chain branching. LLDPE and VLDPE are produced by copolymerization of ethylene and α-olefin, such as 1-butene and 1-hexene. Even with the different polymerization mechanisms, the degree of short-chain branching for them should increase with the decrease in the molecular weight. These conclusions were well documented by articles[15,16] and further confirmed with our results.

Fraction's thermal stability

TGA curves for fractions of HDPE, LDPE, LLDPE, and VLDPE are shown in Figure 3. The decomposition
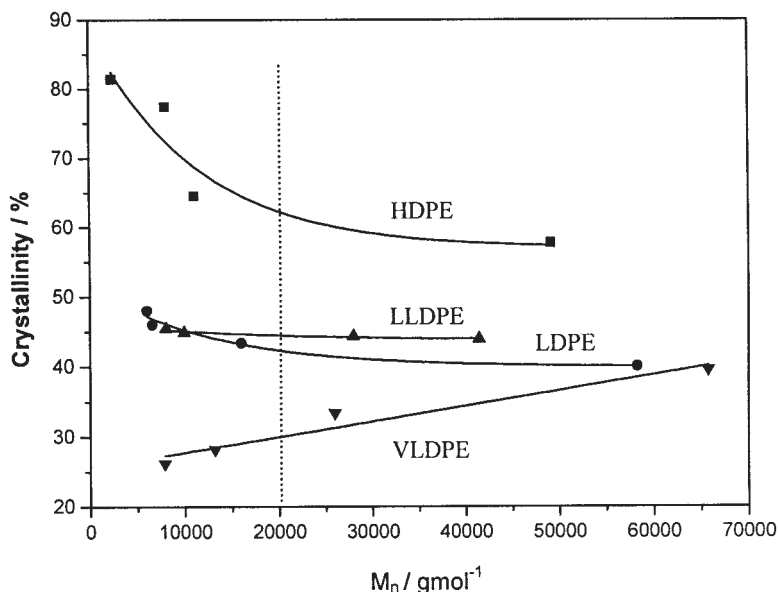
Figure 5 The relationship between fraction's crystallinity and their number-averaged molecular weights for different polyethylenes.

temperatures for all fractions are listed in Table III. Evidently, the decomposition temperatures for fractions of the polyethylenes, except for HDPE, present a slight reduction with the decrease in the molecular weight. It is well known that thermal stability of polymers depends closely on its chain structure and intra-, intermolecular interactions that, in turn, rely on its molecular weight and molecular weight distribution. The different polyethylene fraction's TGA data further confirm these conclusions. That is, for the same polymer product, the higher the molecular weight, the better the thermal stability would be. On the other hand, as the change of decomposition temperature for all fractions is not significant compared to their parent polyethylene, it is reasonable to assume that the solution fractionation process may have less of an effect on the thermal stability for each fraction of different polyethylenes.

Fraction's crystalline behavior

DSC endothermic curves for fractions of HDPE, LDPE, LLDPE, and VLDPE are shown in Figure 4, and related crystalline parameters are listed in Table III. The relationship between the fraction's crystallinity and their number-averaged molecular weights is presented in Figure 5. As can be seen from Figure 5, the crystallinity of HDPE, LLDPE, and LDPE gradually decreases with the increase in their molecular weights. That is, following the augmentation of the molecular weight, the physical entanglement density via macromolecular interaction can accordingly increase; in addition, the related degree of short-chain branching

also increases. These factors can greatly affect the chain segments' folding in three-dimensional directions and cause more defects in the crystalline region. Consequently, the crystallinity of polyethylene can be reduced. On the other hand, in the same molecular weight range, such as in the range of 20,000 as presented in Figure 5, it is obvious that the crystallinity closely relies on the different sort of polyethylene. It is evident that the crystallinity for HDPE at the same molecular weight range is the highest, and the crystallinity for LLDPE is higher than that of LDPE, but VLDPE's crystallinity is the lowest. The marked difference in the crystallinity in the same molecular-weight range for polyethylenes indicates that the degree of short-chain branching, in other words, the actual macromolecular chain component, is another important parameter that can tremendously affect the crystallinity for polyethylene. Based on the data from Table II, the molecular weight for Fraction II of HDPE is about 13,478, and its degree of short-chain branching is only 12. However, for Fraction II of LDPE, the molecular weight is about 16,164, and the related degree of short-chain branching can reach 39. For LLDPE, its molecular weight of Fraction III is about 20,896 and the degree of short-chain branching is 33. Exceptionally, for Fraction III of VLDPE, its molecular weight is about 19,750, but its degree of short-chain branching reaches as high as 68. The results again soundly demonstrate the significant contribution of the short-chain branching to the magnitude of crystallinity of polyethylene. That is, the higher the degree of short-chain branching, the lower the crystallinity for polyethylenes. This is because as the degree of short-

chain branching increases, the irregular chain segments cannot fold sequentially into crystalline lattice; as a result, it may initiate more defect formation and increase the amorphous region, leading to lowering the crystallinity. Here, it is worth mentioning VLDPE's crystalline behavior. In contrast to other commercial polyethylenes, its crystallinity increases with the increase in molecular weight. The phenomenon can still be attributed to the special contribution of its molecular chain character. According to Table II, for VLDPE, due to its low molecular weight portion carrying a relatively higher degree of short-chain branching, the large amount of short-chain branching is separated together with those lower molecular weight portions. This leaves less short-chain branching in the higher molecular weight portion, and in turn, increases the crystallinity following the increase in the molecular weight.

CONCLUSION

Solution fractionation is an effective way to conduct separation for different polyethylenes based on their molecular weight and molecular weight distribution. Solution fractionation controlled by lowering temperature is more precise than by controlling the amount of precipitant. After solution separation, the fractions for different polyethylenes can still maintain good thermal stability; even the fraction's molecular weight alters greatly. For HDPE, LLDPE, and LDPE, their crystallinities decrease with the increase in the molecular weight; however, for VLDPE, its crystallinity increases with the increase in its molecular weight. The results can be attributed to the completely different molecular chain components. The short-chain branching is an important factor affecting the crystallinity; the higher the short chain branching, the lower the crystallinity for polyethylene.

REFERENCES

1. Vandermiers, C.; Moulin, J. F.; Damman, P.; Dosière, M. Polymer 2000, 41, 2915.
2. Springer, H.; Hengse, A.; Hinrichsen, G. J Appl Polym Sci 1990, 40, 2173.
3. Wild, L. Adv Polym Sci 1991, 98, 1.
4. Deffoor, F.; Groenincky, G.; Schouterden, P.; Van Der Heijden, B. Polymer 1992, 33, 3878.
5. Soares, J.S.P.; Hamielec, A.E. Polymer 1995, 36, 1639.
6. Yau, W. W.; Gillespie, D. Polymer 2001, 42, 21, 8947.
7. Adisson, E.; Ribeiro, M.; Deffieux, A. Fontanille, M. Polymer 1992, 33, 20, 4337.
8. Müller, A.J.; Hernandez, Z.H.; Arnal, M.L.; Sanchez, J.J. Polym Bull 1997, 39, 4, 465.
9. Zhang Mingqian, Lynch D. T., Sieghard E W. J Appl Polym Sci 2000, 75, 960.
10. Blundell, D. J.; Beckett, D. K.; Wilcocks, P. H. Polymer 1981, 22, 704.
11. Wunderlich, B.; Cormier, C. M. J Polym Sci Part A2 1967, 5, 987.
12. Neves, C.J.; Monteiro, E.; Habert, A.C. J Appl Polym Sci 1993, 50, 817.
13. Lei, W. Y.; Gu, F.; Zhang, W. Polymer Physics Experiment; Northwestern Polytechni University Press; China, 1994.
14. McCord, E.F.; Shaw, W.H., Jr.; Hutchinson, R.A. Macromolecules 1997, 30, 2, 246.
15. Wild, L.; Ryle, T.R.; Knobeloch, D.C.; Peat, I.R. J Polym Sci: Polym Phys Ed 1982, 20, 441.
16. Hosoda, S. Polym J 1988, 20, 5, 383.