

STRUCTURAL CHARACTERIZATION OF POLYETHYLENES BY DSC ANALYSIS AFTER CRYSTALLIZATION SEGREGATION*

Yu Ma and Mao Xu**

State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract The molecular structure of polyethylene (PE) samples with various comonomers including propylene, 1-butene and 1-hexene was investigated by DSC and ^{13}C -NMR techniques. The density of the samples varies from 0.948 g/cm^3 to 0.917 g/cm^3 , and the molecular weight determined by the GPC method is in the range of $1\sim 2 \times 10^5$. The branch point content of the samples was determined by ^{13}C -NMR measurements and was found to be less than 20 per 1000 C atoms along the main chain. Crystallization segregation DSC technique (CSDSC) was used to characterize the branch point distribution or the segment length distribution of PEs. The crystallization segregation was performed in a successive annealing process at decreasing temperatures. The interval of two successive annealing temperatures was 6 K, and the time length of each annealing step was 2.5 h. The CSDSC results clearly indicate that all the PE samples used, including some metallocene PEs, more or less exhibit their non-uniformity in segment length distribution, and bimodal or multimodal CSDSC curves were usually observed. For quantitative characterization of the CSDSC curves and the segment length distribution two parameters, the average melting point, T_{mAV} , and the root-mean-square deviation of melting temperature, $(\Delta T_{\text{m}}^2)^{1/2}$, were proposed. T_{mAV} is corresponding to the average segment length due to branching and $(\Delta T_{\text{m}}^2)^{1/2}$ gives information about the width of the segment length distribution. Experimental results show that both the degree of average melting temperature depression and the width of the distribution seem to increase with increasing the branching content and are dependent on the type of comonomers. Very good reproducibility and additivity of the CSDSC method were evidenced experimentally. It was concluded that the CSDSC technique is a sensitive and convenient method for characterizing the segment length distribution of branched polyethylenes and will be of great interest in structure-property relationship studies of crystalline polymers.

Keywords Polyethylene, Branch point distribution, Segment length distribution, Crystallization segregation, DSC

INTRODUCTION

For ideal linear polyethylenes only their molecular weight and molecular weight distribution should be characterized for controlling and understanding their processing behavior and final properties because of their simple molecular structure. In practice most of the commercially available polyethylene (PE) products are branched ones^[1]. The branching structure of PE molecules, including the long-chain branching and short-chain branching, is usually obtained by controlling the reactor pressure and temperature or by introducing α -olefin comonomers such as propylene, 1-butene, 1-hexene and 1-octene. The purpose is to change the crystallization and melting behavior and the molecular packing of PEs for meeting the different application requirements. For these branched PEs some additional structural parameters should be considered in studies of their structure-property relationships. They are the branch lengths, the degree of branching (the number of branching point per 1000 C atoms of the main chain) and the distribution of branching points along the main chain.

In recent years studies on the distribution of branching points of PEs have been receiving increasing attention and its inhomogeneity has been accepted as a common phenomenon for PEs. In principle one can use

* This work was supported by the Science Foundation of Polymer Physics Laboratory, Chinese Academy of Sciences.

** Corresponding author: Mao Xu (徐 懋), E-mail: xumao@pplas.icas.ac.cn

Received March 22, 2000

the NMR technique to determine the sequence distribution of two monomer units along the main chain. However it is only sensitive to sequence distributions of short range. Usami *et al.*^[12] and Han *et al.*^[13] in their studies of linear low density polyethylenes (LLDPE) with 1-butene and 1-hexene as the comonomers indicated that the amount of 1-butene or 1-hexene units in sequences of two or more was very low according to NMR measurements. One of the important methods for measuring the distribution of branching points is the so-called temperature rising elution fractionation technique (TREF). In TREF, the molecules are separated by selective dissolution after crystallization of the polymer from dilute solutions onto an inert support material during a slow cooling process. The principal idea of this method is the combination of two techniques, viz. crystallization segregation and gradient elution fractionation followed by structure characterization of the fractions. It has been found that TREF is an effective technique for fractionating PEs with respect to their degree of branching, as it is relatively free of molecular weight influences, and a calibration of the elution temperature allows direct calculation of meaningful branching distributions of PEs. Heterogeneity of LLDPE samples in branching distribution and even bimodal or multimodal distributions have been detected by using TREF^[12, 4-6].

The drawbacks of TREF are its complex procedure, the large length of time needed for a complete analysis and the rather high cost of implementation. Therefore quicker and easier methods have been of interest. A practical and promising method for characterizing the branching distribution of PE samples has been proposed^[7-15] by using DSC measurements of samples after suitable thermal treatments. The principle of this technique is the crystallization segregation of polyethylene segments of different length and the DSC detection of the melting behavior of the segregated samples. So it can be called the crystallization segregation DSC technique (CSDSC). This technique is quite convenient, in that the two processes, the crystallization and the DSC detection, can be conducted by using the same DSC instrument. After proper design of the slow cooling program for crystallization segregation a thermogram of high resolution reflecting the heterogeneity of samples in polyethylene segment length can be obtained. It has been demonstrated in comparative studies of various branched PEs^[8-14] that TREF and DSC techniques can provide similar branching distribution information, even though the shapes of their curves are usually not identical, and the DSC technique could be a useful tool for the relative analysis of branch distributions. In this work a series of branched PE samples were studied by the CSDSC technique. A quantitative expression of heterogeneity in polyethylene segment length distribution from DSC measurements was proposed and the possibility of using this technique as an important tool for studies of structure-property relationships of PEs as well as for industrial routine measurements was discussed.

EXPERIMENTAL

Materials

Polyethylene and ethylene copolymers with various α -olefins were used in this study (Table 1). The polyethylene homopolymer sample (EE) and ethylene/propylene (EP), ethylene/1-butene (EB1), and ethylene/1-hexene (EH1 and EH2) copolymers were kindly supplied by Prof. You-lian Hu of the Institute of Chemistry, Chinese Academy of Sciences. They were synthesized on a laboratory scale at 85°C by using $\text{Et(Ind)}_2\text{ZrCl}_2/\text{MAO-SiO}_2$ as catalyst and *n*-hexane as reaction medium. EB2 is a commercial LLDPE of the Panjin Chemical Industry with 1-butene as the comonomer. The ethylene/1-hexane copolymer (EH3) is a product of Exxon Co. All the samples were first dissolved in decahydronaphthalene (~0.2%) and precipitated by adding 95% ethanol. They were then washed with ethanol and dried at 50°C under vacuum for 48 h before use.

Characterization

All the DSC measurements were performed by using a Perkin Elmer DSC-4 apparatus in a nitrogen atmosphere. Indium (m.p. 156.6°C) was used for temperature calibration. The DSC measurements for studying branching distribution were conducted in the following way. The samples were first heated rapidly to a temperature well above their melting temperature, usually around 160~180°C, after that the temperature was programmed to the first annealing temperature. A successive annealing at decreasing temperatures was performed until no thermal effect of crystallization was detected. The interval of two successive annealing temperatures was 6 K and the time

length of each annealing step was 2.5 h. For comparison purposes DSC thermograms used for conventional characterization were obtained under the following conditions. After rapid heating to a temperature above the melting temperature the sample was cooled down to room temperature at a rate of ~ 10 K/min, then the thermogram in a second heating at a rate of 10 K/min was recorded.

Table 1. Basic data of the used PE samples

Sample code	Branch content ^a	ρ^b (g/cm ³)	M_w^c	M_w/M_n^c	T_m^d (°C)
EE	0	0.948	160,600	5.45	133.5
EP	14.95	0.926	104,400	4.52	118.0
EB1	5.35	0.931	204,800	4.40	124.9
EB2	18.30	0.919	-	-	123.5
EH1	5.02	0.934	179,300	5.25	125.4
EH2	6.25	0.928	98,700	18.64	121.4
EH3	13.15	0.917	118,000	4.92	119.8

^a The branch content, the number of branch point per 1,000 C atoms of main chains, was determined by using ¹³C-NMR.

^b Measured by the density gradient tube method

^c Determined by high temperature GPC

^d Determined by conventional DSC method

The ¹³C-NMR spectra were recorded at 125°C on a 75.48 MHz Bruker DMX-300 NMR spectrometer with broad-band decoupling. The solvent used was 1,2,4-trichlorobenzene and the concentration was around 10% by weight. The molecular weight and polydispersity of the samples were measured at 135°C by using a Waters high temperature GPC instrument. The columns were calibrated with polystyrene standards and 1,2,4-trichlorobenzene was used as the eluent solvent.

RESULTS AND DISCUSSION

The basic characteristics of the PE samples used are listed in Table 1. The density of the samples varies from 0.948 g/cm³ to 0.917 g/cm³, and the molecular weight, M_w , is in the range of $1\sim 2 \times 10^5$. The branch point content of the samples determined by ¹³C-NMR measurements is less than 20/1000C.

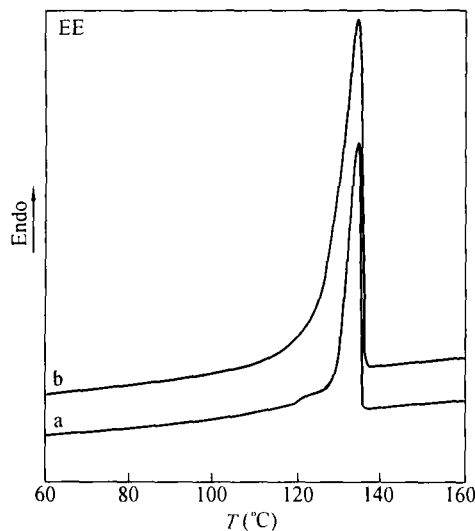


Fig. 1 CSDSC curve (a) and conventional DSC curve (b) of sample EE

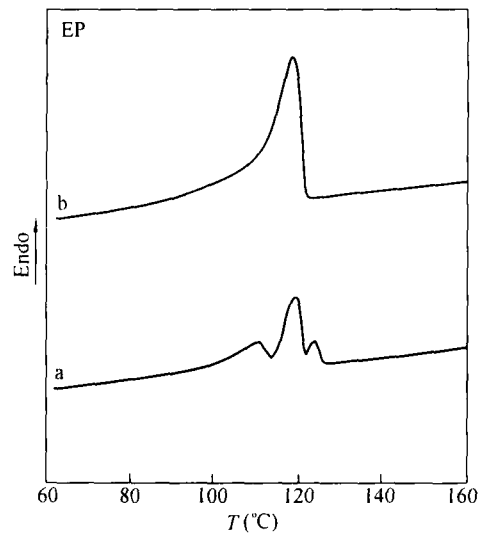


Fig. 2 CSDSC curve (a) and conventional DSC curve (b) of sample EP

The CSDSC thermograms of all the samples are given in Figs. 1~4. The conventional DSC curves, which are also presented for comparison, exhibit a single melting peak for most samples except EH3. They are

unsymmetrical peaks with long extensions in the low temperature side. In the case of EH3 an additional broad peak at 109.4°C was detected.

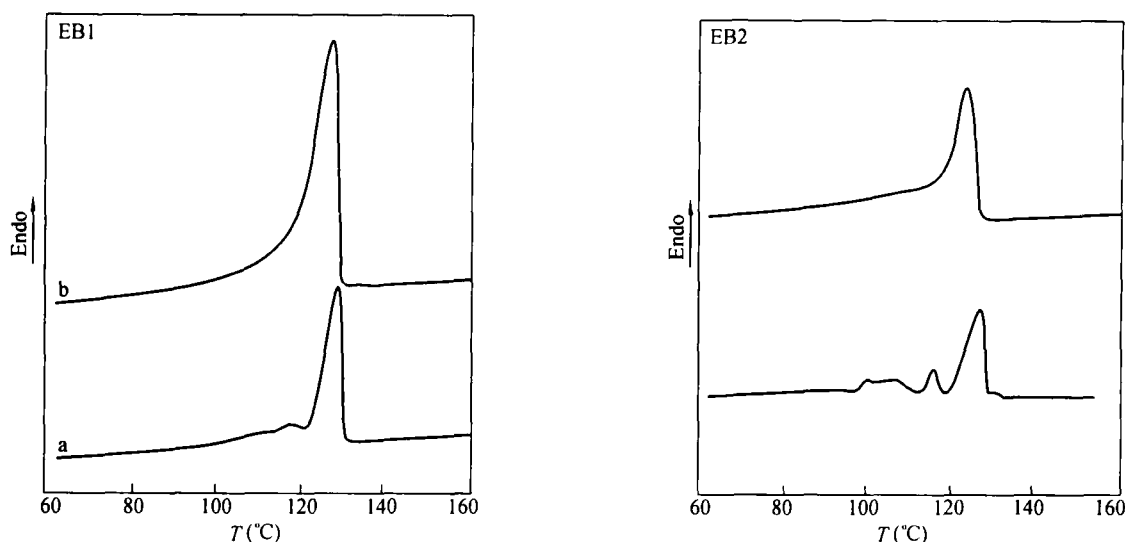


Fig. 3 CSDSC curve (a) and conventional DSC curve (b) of samples EB1 and EB2

Although EE is an almost linear homo-polyethylene, no branch points were detectable by the ^{13}C -NMR technique, the crystallization segregation procedure does have some influence on its melting curve (Fig. 1). The melting peak becomes narrow and shifts slightly to higher temperature. A very small peak at 126°C as a shoulder of the main melting peak can be observed. The sample EP shows three well separated melting peaks after crystallization segregation (Fig. 2) and the highest peak is the middle one. The two EB samples have two and five melting peaks respectively in their CSDSC curves (Fig. 3), and both have a predominant peak at about 126.7°C. All the EH samples exhibit a multimodal melting curve after segregation (Fig. 4). The EH1 and EH2 both have a main melting peak at the high temperature side, while the EH3 shows five peaks of quite uniform height. The peak positions determined from CSDSC curves of all the samples are summarized in Table 2. It seems that the PE samples may exhibit melting peaks only at some definite temperatures characteristic of each ethylene/ α -olefin copolymer systems.

It is well accepted that the melting temperature of PE is directly related with the lamella thickness of polyethylene crystallites and it rises with increasing the thickness. A step-wise annealing of samples at subsequent decreasing temperatures may result in the crystallization segregation of polyethylene segments according to their length. It means, in principle, that the CSDSC technique can be used to obtain information about the segment length distribution or the branching point distribution of PE samples. If the branching points are introduced uniformly along the PE chains, the latter are divided into segments of equal length, then the only effect of branching on the CSDSC curve is the shift of the single narrow melting peak downward to low temperatures. When the branching distribution is inhomogeneous, or the PE segments are different in length, then a very broad melting peak or multiple melting phenomenon of branched PEs will be detected by the CSDSC technique in addition to the depression of the melting temperature. Our results clearly indicate that all the PE samples we used, including some metallocene PEs, more or less exhibit their non-uniformity in segment length due to chain branching, and the CSDSC technique is a sensitive and convenient method for characterizing the segment length distribution of branched polyethylenes.

The CSDSC curves are usually very complicated in shape. The number of the melting peaks and their position, height and width may all change from curve to curve. In addition to a schematic description of these curves it is necessary to have parameters reflecting the basic information of the curves, and these parameters can

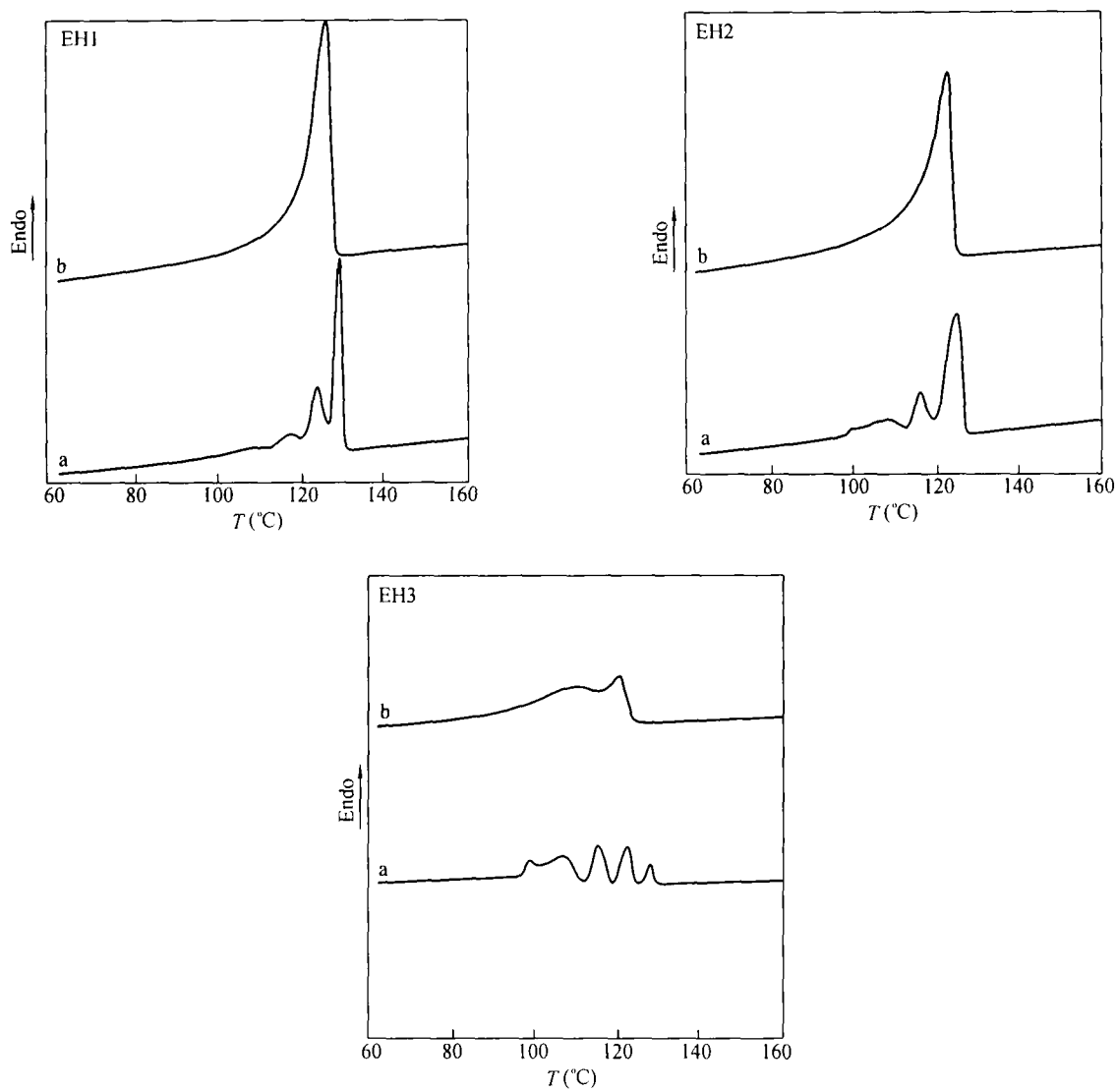


Fig. 4 CSDSC curve (a) and conventional DSC curve (b) of samples EH1, EH2 and EH3

Table 2. Multiple melting behavior of segregated samples

Sample code	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m4} (°C)	T_{m5} (°C)
EE	134.0 ^a	126.0			
EP	123.6	119.2 ^a	110.3		
EB1		126.7 ^a	116.5		
EB2	130.7	126.8 ^a	115.6	107.4	100.3
EH1	128.5 ^a	123.2	116.0		
EH2		123.5 ^a	114.9	107.2	98.5
EH3	128.0	122.1 ^a	115.3 ^a	107.5	98.5

^a The highest melting peak(s)

be used for a quantitative description of the segment length distribution and also for comparison between samples. Balbontin *et al.*^[12] divided the whole melting temperature range into four regions (< 80°C, 80~100°C, 100~120°C and > 120°C). The areas under a CSDSC curve in the four temperature regions were calculated and their relative amounts in the total area were used to characterize the branching distribution of the samples.

Lehtinen *et al.*^[15] suggested using “DSC index values” to describe the distribution. These values were defined as the ratios of the peak heights of each melting peak to that of the highest peak in the thermogram. These methods are not widely used because of their inconvenience and the not very clear physical meaning of the parameters.

Two parameters, the average melting point T_{mAV} and the root-mean-square deviation of melting temperature $(\Delta T_m^2_{AV})^{1/2}$, are proposed here to characterize the CSDSC curve and the segment length distribution of samples. They can be directly determined from experimental curves (Fig. 5) and are defined as follows.

$$T_{mAV} = \Sigma \Delta H_i T_{mi} / \Sigma \Delta H_i \tag{1}$$

$$(\Delta T_m^2_{AV})^{1/2} = [\Sigma \Delta H_i (T_{mi} - T_{mAV})^2 / \Sigma \Delta H_i]^{1/2} \tag{2}$$

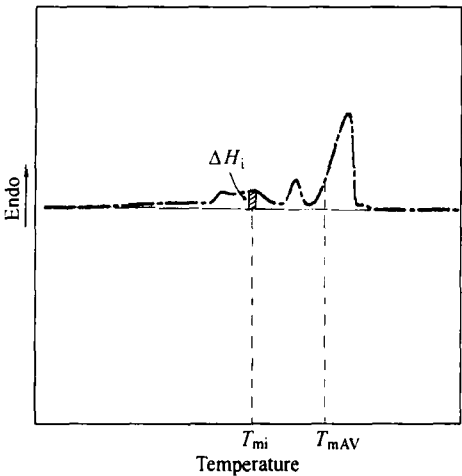


Fig. 5 Scheme for calculating T_{mAV} and $(\Delta T_m^2_{AV})^{1/2}$

The average melting point corresponds to the average segment length due to branching and the root-mean-square deviation $(\Delta T_m^2_{AV})^{1/2}$ gives information about the width of the segment length distribution. The values of the two parameters for all the samples were calculated from the experimental curves, and the results are given in Table 3. It was expected that the sample EE showed the highest average melting point among the samples. The $(\Delta T_m^2_{AV})^{1/2}$ value of sample EE is as low as 7.57 K which indicates a narrow distribution of segment lengths around its average value. While the other PE copolymers have a relatively high value of $(\Delta T_m^2_{AV})^{1/2}$ in the range of about 10.0~13.5 K. Both the degree of melting temperature depression and the width of the distribution seem to increase with increasing branching content and are dependent on the type of the comonomers.

Table 3. T_{mAV} and $(\Delta T_m^2_{AV})^{1/2}$ values of polyethylene samples			
Sample code	T_{mAV} (°C)	$T_{mAV}(EE) - T_{mAV}$ (K)	$(\Delta T_m^2_{AV})^{1/2}$ (K)
EE	129.8	0	7.57
EP	111.0	18.8	10.76
EB1	120.3	9.5	10.04
EB2	115.7	14.1	12.74
EH1	120.7	9.1	10.39
EH2	114.2	15.6	11.39
EH3	105.7	24.1	13.51

The reproducibility of the CSDSC method was checked by repeated measurements of two samples. One is the sample EB2 and the another one is a mixture (1/1 by weight) of samples EH1 and EH3. The results are given in Figures 6 and 7, respectively, and their calculated values of T_{mAV} and $(\Delta T_m^2_{AV})^{1/2}$ are listed in Table 4. The shapes of the CSDSC curves for repeated measurements with different specimens of the same sample are identical, and the values of T_{mAV} and $(\Delta T_m^2_{AV})^{1/2}$ calculated from the repeated measurements are very consistent

with each other within the experimental error of the conventional DSC measurements. For a reasonable characterization technique, the additivity of experimental data is important. It was checked by comparing the experimental data of a mixture of two samples with those calculated from the data of the two component samples according to their content in the mixture and the additivity rule. Figure 8 shows the two CSDSC curves and their T_{mAV} and $(\Delta T_{mAV}^2)^{1/2}$ data are given in Table 4. The differences in T_{mAV} and $(\Delta T_{mAV}^2)^{1/2}$ are only 0.38 K and 0.01 K, respectively. It means that the effect of cocrystallization of segments of different lengths during a step-wise annealing procedure on the CSDSC results is negligible or at least is not important and keeps almost unchanged even in blending of samples of quite different segment length distribution.

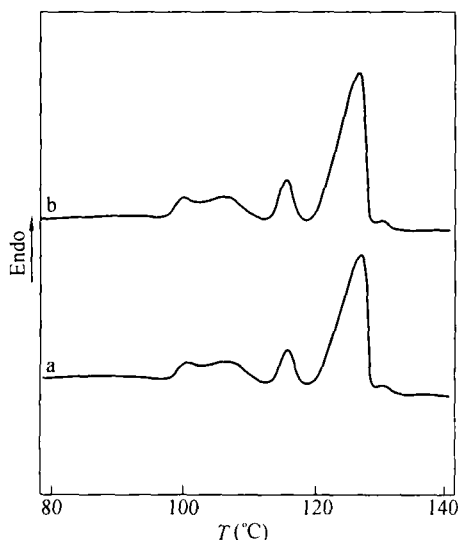


Fig. 6 Repeated CSDSC measurements of sample EB2
a) Specimen 1, b) Specimen 2

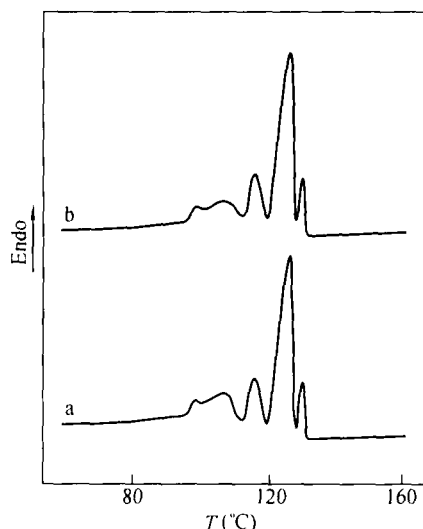


Fig. 7 Repeated CSDSC measurements of sample EH1/EH3
a) Specimen 1, b) Specimen 2

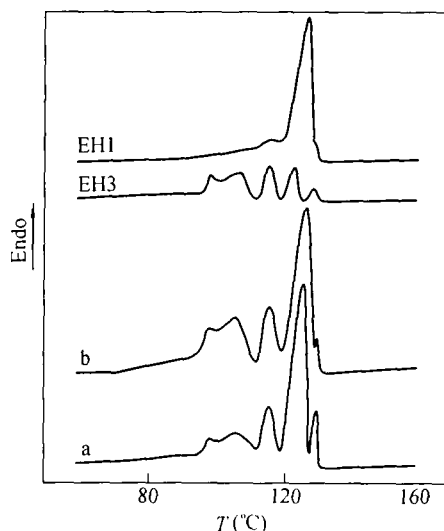


Fig. 8 Additivity test of CSDSC measurements for blend of EH1 and EH3,
a) Experimental curve
b) Calculated according to the additivity rule

Table 4. Results of repeated measurements and additivity test

Sample code	Measurements	T_{mAV} (°C)	$(\Delta T_{m,AV}^2)^{1/2}$ (K)
EB2	Specimen 1	115.75	12.57
	Specimen 2	115.61	12.91
	Average	115.68	12.74
EH1/EH3	Specimen 1	114.44	13.18
	Specimen 2	114.60	13.60
	Average	114.52	13.39
EH1/EH3	Calculated	114.90	13.40

All these results indicate that CSDSC is a convenient method for studying branch distribution of polyethylenes and is methodologically reasonable. A comparison of its characteristics with those of TREF will be helpful for the rational utilization of these two techniques. It should be realized that the two methods are measuring different properties related with the molecular structure of polymers. TREF is reporting the amount of molecules in any temperature interval of elution, and its results may include all molecules of the polymer sample as in the case of PEs. However TREF alone can only present the intermolecular heterogeneity in molecular structure, as the molecules are fractionated according to their average branch point content or average segment length. CSDSC gives the amount of segments as a function of the melting temperature of their crystallites. As a result its information may only relate with the crystallizable segments of the sample, however both the intermolecular and the intramolecular heterogeneity in the length of crystallizable segments affect the CSDSC data. In this sense CSDSC is not suggested for studies where a complete structural description of molecules is required. However in many studies of crystalline polymers their crystallinity, crystalline morphology and melting behavior are of great interest, which are mainly controlled by the amount and distribution of the crystallizable segments. In these cases CSDSC must be one of the most important techniques for studying structure-property relationships.

REFERENCES

- 1 "Modern Plastics Encyclopedia Handbook", ed. by Modern Plastics Magazine, McGraw-Hill, Inc., 1994, p.27
- 2 Usami, T., Gotoh, Y. and Takayama, S., *Macromolecules*, 1986, 19: 2722
- 3 Han, X.W., Liu, X.M., Zhao, J.K., Bao, X.H., Chen, W., Deng, Y. and Jing, Z.H., *Chinese J. Polym. Sci.*, 1999, 17: 141
- 4 Wild, L., Ryle, T., Knobelock, D. and Peat, I., *J. Polym. Sci., Polym. Phys. Ed.*, 1982, 20: 441
- 5 Mirabella, Jr., F.M. and Ford, E.A., *J. Polym. Sci., Polym. Phys., Ed.*, 1987, 25: 777
- 6 Wild, L., *Adv. Polym. Sci.*, 1991, 98: 1
- 7 Hosoda, S., *Polymer J.*, 1988, 20: 383
- 8 Wild, L. and Chang, S., *Shankernarayanan, M.J.*, *Polym. Prep.*, 1990, 31: 270
- 9 Kamiya, T., Ishikawa, T., Kambe, S., Ikeyami, N., Nischibu, H. and Hattori, T., "ANTEC Conference Proceedings", 1990, p.871
- 10 Adisson, E., Ribeiro, M., Deffieux, A. and Fontanille, M., *Polymer*, 1992, 33: 4337
- 11 Karoglanian, S.A. and Hassison, I.R., *Thermochim. Acta*, 1992, 212: 143
- 12 Balbontin, G., Camurati, I., Dall'Occo, T., Finotti, A., Franzese, R. and Vecellio, G., *Angew. Makomol. Chem.*, 1994, 219: 139
- 13 Mara, J.J. and Menard, K.P., *Acta Polymer.*, 1994, 45: 378
- 14 Starck, P., *Polymer International*, 1996, 40: 111
- 15 Lehtinen, C., Starck, P. and Lofgren, B., *J. Polym. Sci., Polym. Chem. Ed.*, 1997, 35: 307