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Evaluation of the comonomer distribution in ethylene copolymers using DSC fractionation ☆

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Abstract

The microstructures of ethylene random copolymers are evaluated using DSC fractionation by the degree of crystallinity. This method is based on the same principle of separation as temperature-rising elution fractionation (TREF) which uses a crystallization/dissolution procedure; however it does not physically separate the fractions. The resulting copolymers are sorted by crystallite sizes; the crystallite size and lamellae thickness are directly related to the ethylene block length.

Copolymers including E/VA, E/nBA, E/nBA/CO, E/nBA/VA, E/MAA, E/AA and LLDPE have been analyzed by DSC fractionation to elucidate structural differences. We see that (a) specimens with high comonomer content are less crystalline; the ethylene segments are shorter, (b) the comonomer type makes a difference in fractionation if H-bonding is involved, (c) the narrow comonomer distribution, i.e. narrow ethylene-segment-length distribution, has fewer DSC fractions; the broad distribution has more fractions, (d) fractionation by crystallinity is affected if the molecular weight/viscosity is very high, (e) branch content reduces the crystallinity and shortens the ethylene blocks, and (f) there is no direct relation to molecular weight distribution or comonomer content.

Keywords: Comonomer; Copolymer; Crystallite; DSC; TREF

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1. Introduction

The microstructure of ethylene copolymers depends on the comonomer type, the comonomer content, the branch content, the distribution of the comonomers and

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branches along the chains, the crystallinity and aggregates, and the molecular weight distribution of the copolymers. There are many current analytical techniques that are capable of addressing most of these subtleties. This paper focuses on an approach to estimate comonomer distribution using a fractionation technique based on crystallinity. Branch content information can be obtained from ^{13}C NMR.

The crystallinity of semi-crystalline polymers can be recorded by differential scanning calorimetry (DSC). Marx and Cooper [1] showed how the thermal history of annealing affects the breadth and peak positions of the DSC endotherms of poly(ethylene-co-methacrylic acid), E/MAA. It is believed that at the annealing temperature the melting of imperfect thin polyethylene lamellar crystals allows the growth of thicker polyethylene lamellae or perhaps crystallites of fragmentary lamellae which melt approximately 15–20°C above the annealing temperature. According to the Hoffman and Lauritzen [2] theory of growth of lamellar spherulites, annealing allows the formation of crystals with lamellae that approach the equilibrium thickness at the annealing temperature. The higher the annealing temperature, the thicker the lamellae. All of these annealing studies have been focused on the reorganization of the existing crystals. None were designed for systematically sorting by crystallite size.

Studies of the bulk crystallization of ethylene copolymers have provided no clear-cut results on the incorporation of the comonomer unit into the polyethylene crystal lattice. The degree of crystallization was largely due to the differences in specimen treatment. The DSC and X-ray scattering data of MacKnight et al. [3] showed that the acrylic acid and methacrylic acid comonomeric side groups in copolymers of up to 6.3 mol% comonomer are largely excluded from the polyethylene crystal phase. These specimens were annealed at 90°C for 24 h and then either slowly cooled or quickly quenched. The exclusion of side groups was also found by Marx and Cooper [1] in ethylene-co-methacrylic acids in both the neutralized and unneutralized forms; the crystalline morphology is primarily the folded-chain lamellae of polyethylene segments. The specimens were carefully annealed. The SAXS and density data of Kortleve et al. [4], however, showed the presence of acrylic acid and vinyl acetate comonomeric groups in the crystalline regions as crystal defects. These specimens were quickly quenched or slowly cooled in a few cases. It should be noted that acrylic acid and methacrylic acid comonomeric side groups are strongly self-associated into dimers [5]. There is no indication as to whether the side groups reside in amorphous domains.

If a quality problem arises regarding comonomeric composition and branching, it would require the use of a sophisticated and expensive analytical method, such as ^{13}C solution NMR. NMR also has its limitations, i.e. it cannot distinguish the distribution of ethylene block length in runs longer than three ethylene units.

Temperature-rising elution fractionation (TREF) elucidates the comonomer distribution along copolymeric chains. It fractionates the heterogeneous copolymers by stepwise crystallization onto an inert support according to the crystallization temperatures of the copolymer fractions [6]. The fractions can be physically separated by redissolving the crystallized layers from the inert support at ascending temperatures. The DSC annealing/fractionation method we use to assess the microstructures of the ethylene copolymers is based on the principle of TREF, but does not physically separate the fractions. The DSC procedure is clean and clear-cut. The fractionation profile is assessed easily by a subsequent DSC scan. Similar curves, referred to as the thermal history influence, can be found in Gray and Casey's work [7]. The procedure we use is similar to that of thermally treated linear low-density polyethylene by Adisson et al. [8] and Schouterden et al. [9].

2. Experimental

The ethylene copolymers studied in this paper are abbreviated as follows

E/VA	ethylene-co-vinylacetate
E/nBA	ethylene-co-*n*-butylacrylate
E/nBA/CO	ethylene-co-*n*-butylacrylate-co-carbon monoxide
E/nBA/VA	ethylene-co-*n*-butylacrylate-co-vinylacetate
E/MAA	ethylene-co-methacrylic acid
E/AA	ethylene-co-acrylic acid
LLDPE	ethylene-co-1-alkene

2.1. DSC fractionation

Ten-milligram samples of ethylene copolymers crimped in aluminum DSC pans were stepwise annealed in descending 10°C steps from a temperature above their melting at 120–140°C in a TA Instruments 2910 differential scanning calorimeter (DSC), allowing 10 h annealing at each temperature step. Specimens with extremely high molecular weight and viscosity need longer times. The annealed specimens were then scanned at $10°C\,min^{-1}$ from 0 to 150°C. This stepwise annealing produces multiple peaks in the subsequent scan. The area of each peak was determined by integration.

Experiments carried out by varying the annealing time from 30 min/10°C to 24 h/10°C step show that the recrystallization depends very much on the mobility of the polymer chains. The low molecular weights can be fractionated in 1 h/10°C step; the very high molecular weights in 24 h or longer. In general, the fractionations are completed in 4–6 hs; longer times do not change the distribution profiles. We choose 10 h/10°C step which is six times longer than the TREF solubility/recrystallization method at $0.1°C\,min^{-1}$, i.e. $6°C\,h^{-1}$.

2.2. NMR

^{13}C NMR was used to determine the composition, triad distribution where possible, and level of short chain branching for the majority of the polymers studied.

E/VA, E/nBA and E/nBA/CO specimens

^{13}C 100 MHz NMR spectra were obtained using a Varian VXR 400 MHz spectrometer on 15 wt/vol% solutions in 1,2,4-trichlorobenzene (TCB) at 120–

140°C. Benzene-d_6 was also used as a solvent for some E/nBA/CO samples, in which case the temperature was 60°C. Each 3.1 ml of solution contained 60 mg of chromium acetylacetonate (CrAcAc) added as a relaxation agent. An acquisition time of 0.45 s, a 90° pulse length, a spectral width of 35 kHz, a delay of 5 s and inverse gated decoupling were used to insure quantitative results.

E/MAA and E/AA specimens

15 wt/vol% solutions in TCB and a small amount of trifluoroacetic acid (TFAA), or in 1,1,2,2-tetrachloroethane (TCE) and a small amount of TFAA, at 120–140°C were used. Spectra were obtained in the same manner as above, except that CrAcAc was not used and the relaxation delay was increased from 5 s to 35 s.

E/nBA and E/nBA/VA specimens

^{1}H 300 MHz spectra were obtained on 2 wt/vol% solutions in TCE with a Bruker AM spectrometer using an acquisition time of 1.95 s, a 90° pulse, a spectral width of 4.2 kHz and a relaxation delay of 30 s.

3. Results and discussion

The crystallinity of polymers can be recorded by differential scanning calorimetry (DSC). The breadth and the area of the melting endotherms represent the distribution of crystallite size/lamellae thickness. The melting of these crystallites generally overlap in the DSC dynamic scan – a single envelope is observed. From the multiple broad peaks of the ethylene copolymer melting endotherms, we know that the comonomer distribution is heterogeneous. The peak shapes depend very much on their thermal histories. Without control of thermal history, the representation of crystallite size distribution of a single melting envelope is meaningless.

Even the broad melting envelope of low density polyethylene (LDPE) shows the heterogeneity of the branching distribution [1,10,11] which interrupts the polyethylene crystallinity. The broad melting of ethylene copolymers can almost be generalized to two major peaks, as shown in Fig. 1, in spite of the comonomer differences, a higher melting point θ_m decreasing as the extent of comonomer or branching increases, and a lower melting point θ_m staying constant at 42°C due to the room temperature annealing effect. The higher θ_m, depending on the crystallizable fraction, can be described by the Flory equation [12]. Standard differential scanning calorimetry at a fixed heating rate can provide valuable, though limited, information on the fine structure of these ethylene copolymers.

We have fractionated over 60 ethylene copolymers of different comonomer type, comonomer content, branch content, and molecular weight (viscosity) from different manufacturers to look for microstructure subtleties. Primarily, we are looking for comonomer distribution on the polymer chain and branching on ethylene segments from DSC fractionation and ^{13}C NMR data. Not all the branching information will be included in this paper; they are mentioned only to complement the fractionation data. Two representative publications [1,2] on annealing/organiza-

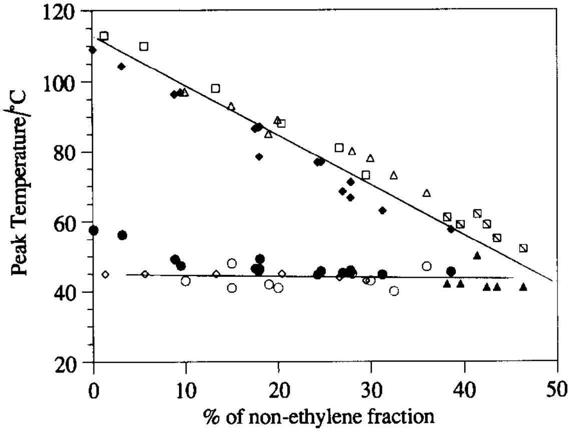

Fig. 1. Melting peaks of ethylene copolymers without heat treatment: E/VA, ● and ◆; E/nBA/CO, ▲ and ▨; E/MAA, ○ and △; E/nBA and E/nBA/VA, ◇ and □.

tion focus on the annealing temperature versus the resulting crystal melting temperature. Their conclusions have led to a fundamental understanding of lamellae thickening and reorganization. At the annealing temperature, the molecules have the mobility to reorganize the existing crystallites – melting thin lamella and imperfect crystallites to produce with time the thicker and more perfect crystallites. It is obvious that the annealing cannot produce an unrealistic large crystallite, because the crystallite size is limited by the ethylene segment length. None of the previous workers have discussed the rest of the crystallizable material after the annealing at a desired temperature. These materials were either quenched and slow cooled before the bulk properties were examined.

Systematic ways of sorting crystals by their size include Successive Solvent Fractionation (SSF) and Temperature Rising Elution Fractionation (TREF) [6]. Our stepwise annealing/fractionation method elucidates comonomer distribution by sorting ethylene segments into 10 thermal "buckets" or fractions – a narrow distribution would be found in 3–4 buckets, whereas a broad distribution would be more evenly distributed in more buckets. The longer segments, recrystallized to larger lamellar crystals, melt at higher temperatures. The differences in molecular weight distribution and comonomer distribution are illustrated in Fig. 2. We do not see a direct relation of the two.

More work is currently underway using temperature-controlled X-ray to prove the recrystallization exclusion theory which is generally known to exclude side groups larger than methyl from the crystal lattice. Our controlled stepwise annealing method should allow enough time for all comonomer units to be excluded from the ethylene crystal lattice. We feel that the inclusion/exclusion controversy in the literature [3,4] is largely dependent on the treatment of the specimens, i.e. the thermal history. Fast quenching from the melt favors inclusion; annealing and slow cooling favor exclusion. Large comonomer units are excluded; small comonomer

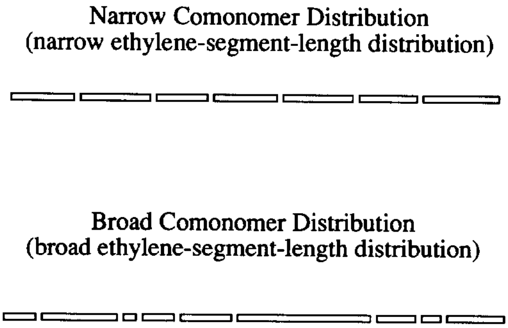

Fig. 2. Narrow and broad comonomer distributions: the blocks represent the ethylene runs and the breaks between the blocks the comonomers.

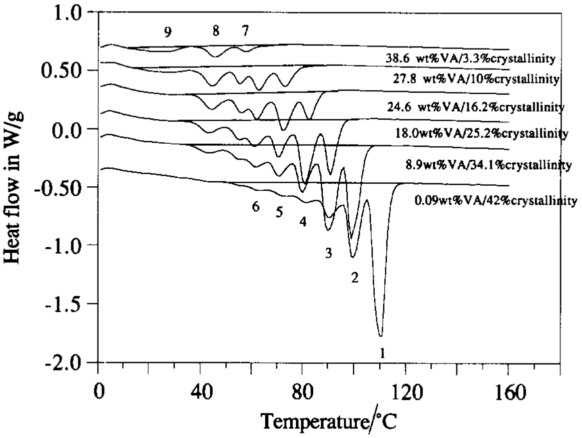

Fig. 3. Profiles of DSC-fractionated E/VAs: composition versus crystallinity.

units might be included. In either model, the ethylene block length and its distribution have a large impact on crystallinity and melting temperature.

3.1. *Crystallinity versus blockiness*

Ethylene copolymers with high comonomer contents show less crystallinity. It is statistically sound that the more comonomer unit present, the more interruption there is of the ethylene blocks if the monomer reactivities are similar. Thus the ethylene blocks are shorter, crystallites are smaller, and melting temperatures lower. Three sets of ethylene copolymers, with comonomer contents ranging from low to high, are used to illustrate the point. Fig. 3 shows that the ethylene vinylacetate (E/VA) copolymer with only 0.99 wt% of vinyl acetate has 42% crystallinity and consists mostly of long blocks of ethylene which appear in fractions 1–2 (θ_m at 110 and 100°C) and minor amounts in fractions 3–6 (θ_m at 90, 80, 70, and 60°C). The

Table 1
Heats of fusion of DSC melting fractions of ethylene/vinyl acetates in J g^{-1}

Composition/wt%		#1	#2	#3	#4	#5	#6	#7	#8	#9
E	VA	θ_m 110°C	θ_m 100°C	θ_m 90°C	θ_m 80°C	θ_m 70°C	$\theta_m \approx 60$°C	$\theta_m \approx 55$°C	θ_m 45°C	$\theta_m \approx 30$°C
99.91	0.09	43.6	21.7	13.4	9.4	6.6	4.5	1.9	1.0	–
91.1	8.9	–	25.0	27.9	15.3	12.0	9.1	5.2	4.3	–
82.0	18.0	–	–	14.2	20.5	12.7	10.8	6.5	6.7	1.5
75.4	24.6	–	–	–	7.8	13.6	9.3	6.3	8.3	1.6
72.2	27.8	–	–	–	–	6.9	7.7	4.3	7.7	2.9
61.4	38.6	–	–	–	–	–	0.4	1.9	4.2	3.3

acetate group appears on average 0.15 times per 1000 CH_2 units, i.e. the CH_2 repeating units are 6666 on average. The ethylene runs are most likely interrupted by short and long chain alkyl branching rather than by acetate groups. The specimen with 38.6 wt% vinyl acetate has only 3.3% crystallinity distributed in fractions 7–9 (θ_m at about 55, 45, and 30°C); the endotherms corresponding to fractions 1–6 are absent. The acetate appears on average 85 times per 1000 CH_2 units, i.e. the CH_2 repeating units are 11.8 on average. For the in-between compositions, the crystallinity and higher melting fractions decrease systematically, as shown in Fig. 3. The fraction sizes for all 6 ethylene/vinylacetate copolymers are summarized in Table 1 and expressed as heats of fusion in J g^{-1}.

We found similar behavior for ethylene/*n*-butyl acrylate (E/nBA), ethylene/methacrylic acid (E/MAA), and ethylene/*n*-butyl acrylate/carbon monoxide (E/nBA/CO) copolymers and terpolymers. In Figs. 4 and 5, the compositions indicated in wt% are from ^1H and ^{13}C NMR data. The longest ethylene segment ($\theta_m \approx 110$°C)

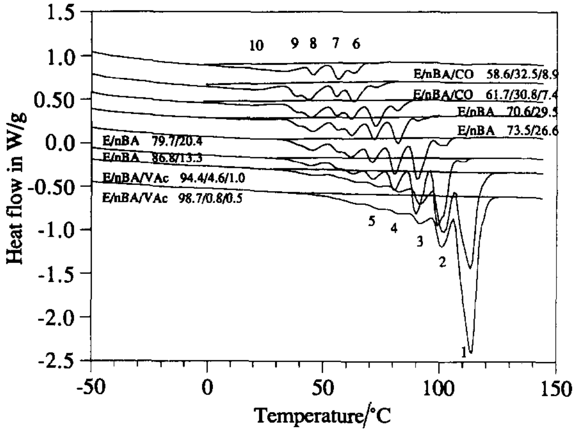

Fig. 4. Profiles of DSC-fractionated E/nBA, E/nBA/VA and E/nBA/CO: composition versus crystallinity.

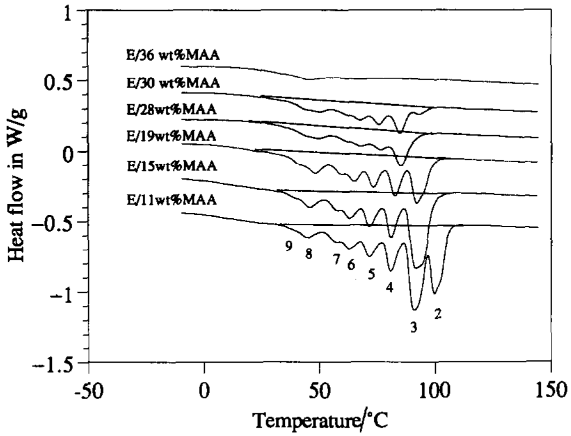

Fig. 5. Profiles of DSC-fractionated E/MAA: composition versus crystallinity.

appears in substantial amounts in two E/nBA/VAc terpolymers (Fig. 4). Comonomers interrupt ethylene chains 1.7 and 7.0 times per 1000 CH_2, respectively, i.e. CH_2 repeating units are 588 and 143 on average. The fewer the interruptions, the longer the ethylene segment. The next four E/nBA copolymers have comonomer interruptions of 16.7, 27.9, 39.6 and 45.6 times per 1000 CH_2 groups, i.e. CH_2 repeating units are 60, 36, 25 and 22 on average. The crystallinities of these E/nBA are reduced quickly, as are the ethylene block lengths. Introduction of carbon monoxide CO to the backbone of the ethylene chains interrupts the crystallinity in the same way. Starkweather [13] found that the melting point of ethylene/CO copolymer decreases rapidly as the CO content falls below 50%, e.g. from 244°C at 50% to 110°C at 35% CO. In the 1 : 1 E/CO alternate copolymer, the crystallizable unit is CH_2CH_2CO, the non-crystallizable unit the adjacent CH_2CH_2. At lower CO content, the material behaves like polyethylene whose structure has been disturbed by the presence of carbonyl groups. The two E/nBA/CO terpolymers in Fig. 4 have 114.5 and 136.6 comonomer interruptions per 1000 CH_2, i.e. CH_2 repeating units are 8.7 and 7.3 on average. Therefore, the ethylene blocks are substantially shorter as indicated by the absence of fractions 1–4. The fraction sizes of the 8 ethylene/*n*-butyl acrylates are summarized in Table 2 and expressed in heats of fusion in J g^{-1}.

The ethylene/methacrylic acid (E/MAA) copolymers can be fractionated the same way. The randomness of the acid copolymers is controlled by comonomer feeding speed rather than relative reactivity. Nevertheless, the DSC fractions reveal the degree of randomness in the final products. There is evidence that the acid copolymers are strongly self-associated in the condensed state at ambient temperatures through the formation of intermolecular carboxylic acid dimers [5]. In the stepwise annealing process, the ethylene segments of a copolymer, having first been melted, are allowed to recrystallize at a series of controlled temperatures. The intermolecular hydrogen bonding is weakened by thermal energy if not broken

Table 2
Heats of fusion of DSC fractions of E/nBA copolymers in J g^{-1}

Composition/wt%				#1	#2	#3	#4	#5	#6	#7	#8–#10
				θ_m 110°C	θ_m 100°C	θ_m 90°C	θ_m 80°C	θ_m 70°C	θ_m 62°C	θ_m 55°C	θ_m 45–20°C
E	nBA	VAc	CO								
98.7	0.8	0.5	–	79.8	22.7	15.6	10.8	8.6	5.0	4.9	–
94.4	4.6	1.0	–	47.4	26.6	16.6	11.3	9.2	6.2	4.0	4.5
86.8	13.3	–	–	1.2	28.5	23.6	14.8	11.2	9.7	5.1	11.1
79.7	20.4	–	–	0.2	3.2	16.3	14.9	11.2	9.2	5.5	14.4
73.5	26.6	–	–	–	0.2	1.7	10.5	8.9	7.9	4.9	16.0
70.6	29.5	–	–	–	–	–	3.6	10.7	6.8	5.2	15.3
61.7	30.8	–	7.4	–	–	–	–	1.8	7.8	4.1	17.1
58.6	32.5	–	8.9	0.2	–	–	–	0.3	3.6	5.7	14.4

completely in the melt state. The recrystallization through the ethylene chain-folding mechanism can be slower than for ethylene copolymers that are free of intermolecular bonding. We compare three types of copolymers in the next paragraph. The fractionated E/MAAs in the 11 wt%–40 wt% range in Fig. 5 showed the expected relation between crystallinity and composition.

It should be noted that for E/MAA, as well as for other ethylene copolymers, at low comonomer content short-chain branching is a significant source of interruptions of the ethylene segments. For example, in the 11 wt% MAA sample, there are ≈15 branches 5 carbons in length or shorter per 1000 CH_2 units. In this same sample there would be 21 MAA groups per 1000 CH_2 units. This is illustrated in Fig. 6 which shows the ^{13}C NMR spectrum of an 11 wt% E/MAA copolymer. The identifications of all branches are given in the figure caption.

3.2. Comonomer type

The comonomer side groups are considered as branches in the chain with a different chemical nature. The $-CO_2CH_2CH_2CH_2CH_3$ in E/nBA and $-OCOCH_3$ in E/VA are slightly different in size, but both are esters. However, the $-CO_2H$ in E/MAA and E/AA, known to form dimers with neighboring $-CO_2H$ groups through hydrogen bonding [5], are different from the ester side group. The interchain ties result in higher viscosity and lower chain mobility. This affects the reorganization of crystallites. It has been reported [14] that hydrogen bonding in nylons remains in the melt state and is responsible for the memory effect in many extrusion experiments. We assume that melting in ethylene acid copolymers can weaken the H-bonding, if not destroy it completely. Three ethylene copolymers with similar compositions but different comonomer types are compared in Fig. 7. The fractionated profiles of E/27.8 wt% VA (11.1 mol%) and E/29.5 wt% nBA (8.4 mol%) are almost identical; whereas the profile of E/28.7 wt% MAA (11.6 mol%) shows that it was not fractionated well – the fraction melting temperatures are shifted and the separation is poor. The methyl ester of the acid

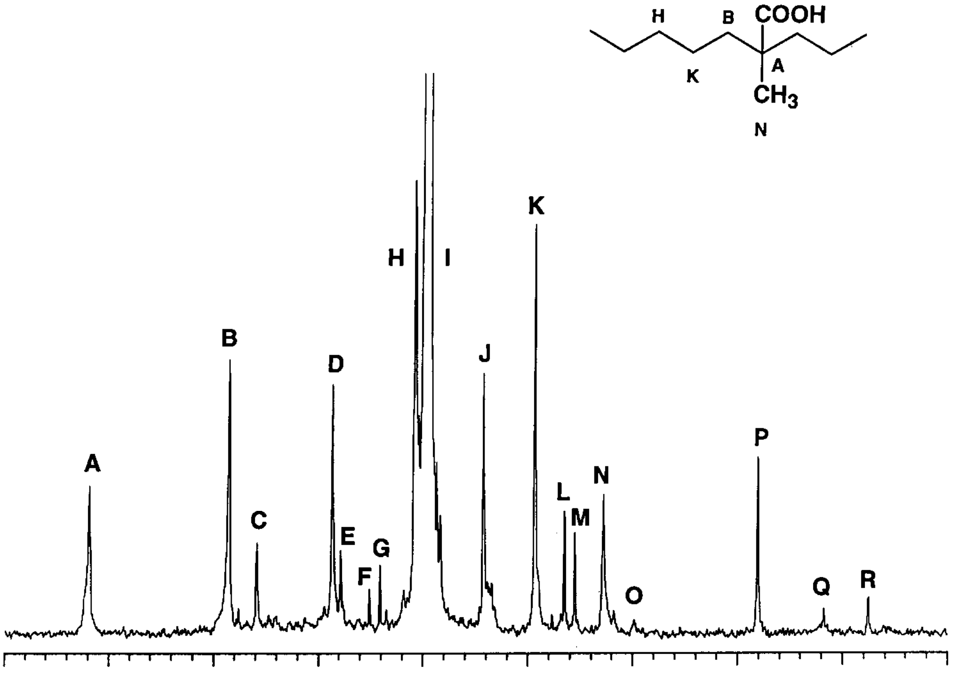

Fig. 6. ^{13}C NMR spectrum of E/11 wt% MAA. The resonance assignments are: A, B, H, K, N, as indicated on figure; C, methine of butyl or longer branch; E, butyl branch C_4, α to ethyl; D, α to a butyl or longer branch; F, amyl branch C_3; G, hexyl or longer branch C_3; J, β to an ethyl or longer branch; L, butyl branch C_2; M, amyl or longer branch C_2; O, β to MAA groups; P, methyl from branches butyl or longer, including chain ends; Q, methyl of ethyl branch; R, methyl of ethyl group attached to a quaternary carbon.

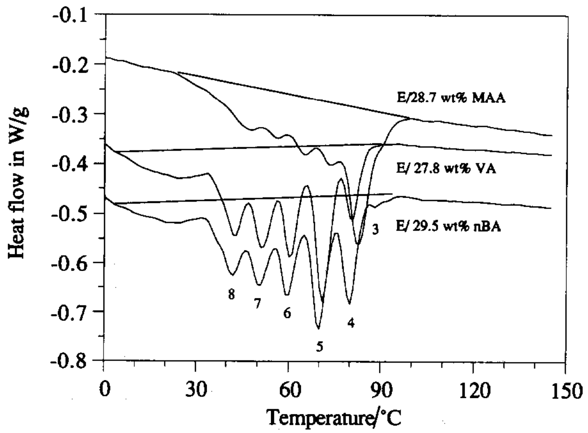

Fig. 7. Profiles of DSC-fractionated ethylene copolymers, similar compositions but different in comonomer type: E/MAA, E/VA and E/nBA.

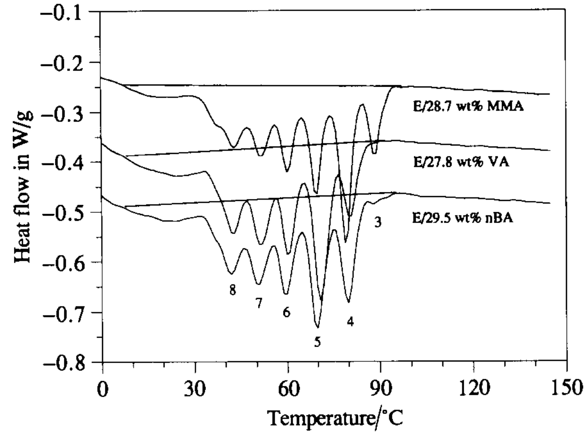

Fig. 8. Profiles of DSC-fractionated ethylene copolymers, similar compositions but different in comonomer type: methyl ester of acid copolymer E/MMA, E/VA and E/nBA.

copolymer E/28.7 wt% MAA does not have this problem. We are able to compare the ethylene-segment-length distributions of the three in Fig. 8 without the complication of H-bonding. The methyl ester of the acid copolymer, E/MMA, is indeed blockier than E/nBA which is in turn blockier than E/VA.

3.3. Narrow versus broad comonomer distribution

To show the practicality of the DSC fractionation method for describing the comonomer distribution, we have compared the distribution of two copolymers which are known with their difference in ethylene segment length distributions: broad and narrow. A narrow distribution indicates that the ethylene segment lengths are about the same; a broad distribution means there is a big difference in ethylene segment lengths. Two DSC-fractionated E/hexene-1 copolymers are compared. The narrow E/hexene-1, produced in the single-site catalysis process, is a copolymer with butyl side groups evenly distributed on the chains, a narrow distribution. It has 3.95 wt% comonomer content which converts to a short chain branching (SCB) frequency of 7.8 per 1000 CH_2 units, a weight average molecular weight M_w of 97 800, and a polydispersity of 2.21. The broad E/hexene-1 specimen, produced in conventional catalytic process, is a comonomer with butyl side groups randomly distributed on the chains. It has 6.34 wt% comonomer content which converts to 11.3 SCB frequency per 1000 CH_2 units, a M_w of 157 000, and a polydispersity of 5.04. Although the so-called broad specimen happens to be 50% higher in weight-average molecular weight, the comonomer distribution on the chains is very different from the so-called narrow specimen. As shown in Fig. 9, the narrow has mostly higher melting fractions with lesser amounts in lower melting fractions; the broad has more fractions. The melting points of the fractions in the narrow ($\theta_m = 125$, 120 and 115°C) are also different from those in the broad ($\theta_m = 130$, 115°C) and represent 66.6% and 54.4% of the total crystallinity, respectively.

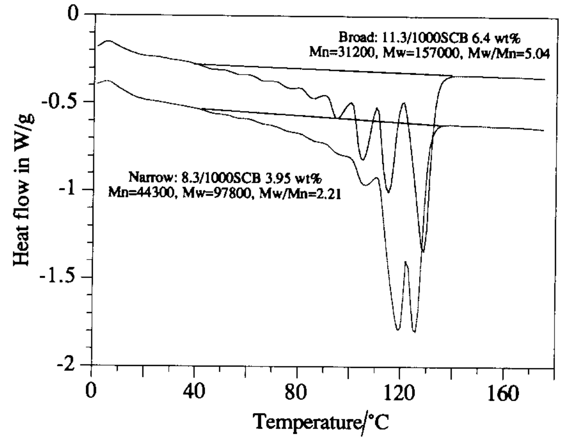

Fig. 9. Profiles of DSC-fractionated E/Hexene-1: broad and narrow ethylene-segment-length distributions.

3.4. Third comonomer present

The presence of small amounts of a third comonomer further interrupts the ethylene crystallinity. We studied two E/VA specimens prepared under identical reactor conditions with identical vinyl acetate contents of 18.0 wt%, but one (E/VA #2) was copolymerized with 2 mol% of a third comonomer, propylene. The DSC-fractionated profiles in Fig. 10 shows that E/VA #2 has fewer long ethylene blocks (fractions 3 and 4, θ_m at 90 and 80°C). The absence of fractions 1 and 2 (θ_m at 110 and 100°C) in both specimens E/VA #1 and #2 indicates that 18 wt% of

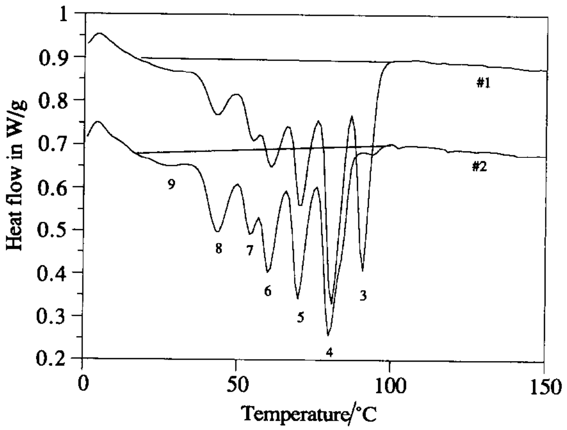

Fig. 10. Profiles of DSC-fractionated E/VA: #1, (18.04 wt% VA); and #2, (17.99 wt% VA).

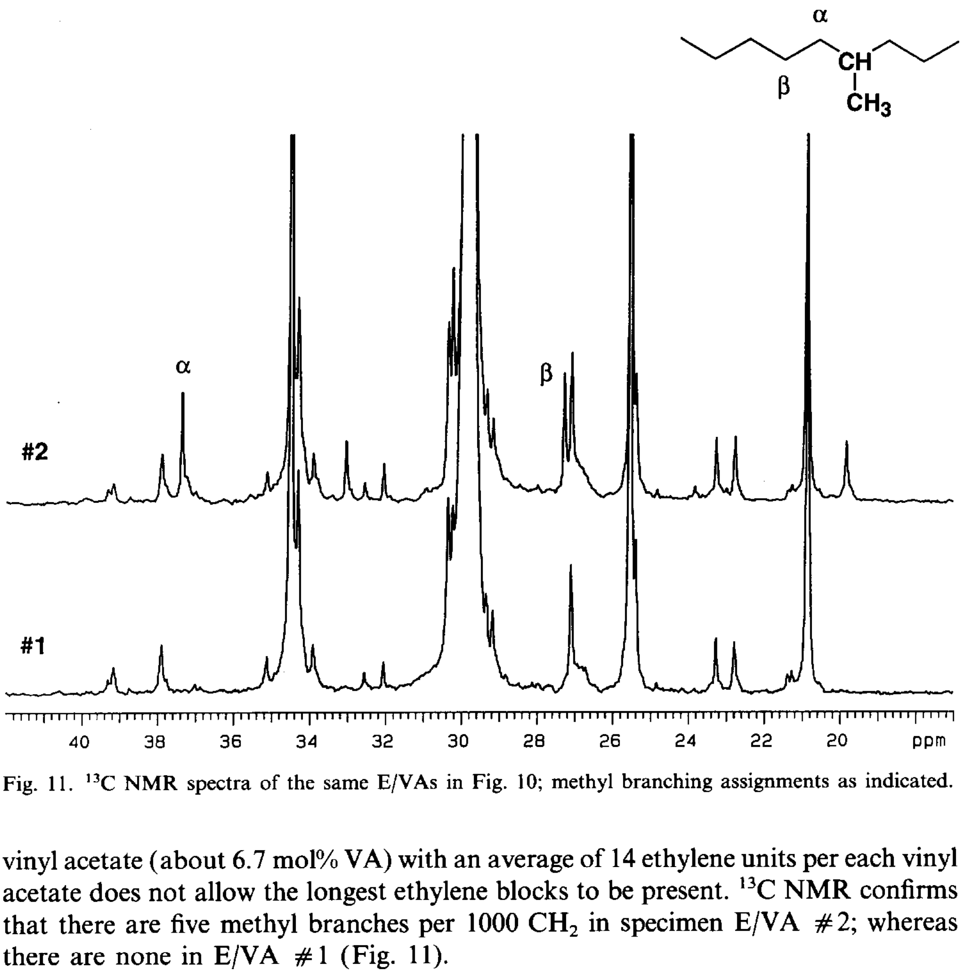

Fig. 11. ^{13}C NMR spectra of the same E/VAs in Fig. 10; methyl branching assignments as indicated.

vinyl acetate (about 6.7 mol% VA) with an average of 14 ethylene units per each vinyl acetate does not allow the longest ethylene blocks to be present. ^{13}C NMR confirms that there are five methyl branches per 1000 CH_2 in specimen E/VA #2; whereas there are none in E/VA #1 (Fig. 11).

Another example of a third comonomer reducing ethylene crystallinity is shown in Fig. 12. The DSC profiles of two ethylene/*n*-butyl acrylate/carbon monoxide (E/nBA/CO) terpolymers are compared: specimen #1 with a composition of 57.9/29.2/12.9 wt% is less blocky than specimen #2 with a composition of 58.9/30.7/10.4 wt%. The 2.5 wt% more carbon monoxide in #1 has shortened the ethylene segments significantly – the total crystallinity reduces from 10.6% (in #2) to 5.7% (in #1); DSC fraction 5 ($\theta_m = 72°C$) is absent in #1; fraction 6 ($\theta_m = 62°C$) is smaller in #1. The interruption of ethylene segments by the CO group has been reported before [13]. A tiny melting peak of a long ethylene segment ($\theta_m = 110°C$) is noticed in #1, but not in #2. This may be the branched ethylene homopolymer.

3.5. *No direct relation to MWD*

The observed comonomer distribution is not due to differences in molecular weight distribution. Copolymers with different molecular weights, polydispersities

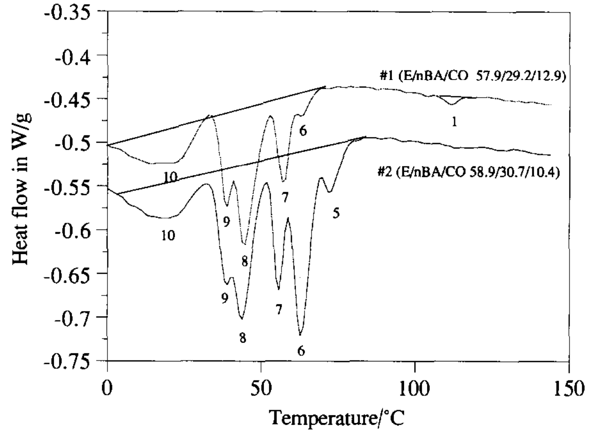

Fig. 12. Profiles of DSC-fractionated E/nBA/CO terpolymers, different in third comonomer content.

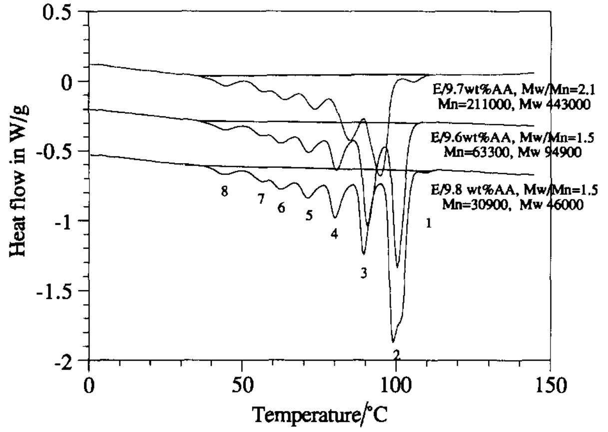

Fig. 13. Profiles of DSC-fractionated E/AA, similar composition but different molecular weight.

and compositions can have identical fraction profiles, unless the difference in molecular weight is huge. The effect of molecular weight on DSC fractionation is illustrated by the ethylene/acrylic acid (E/AA) copolymers in Fig. 13. Three E/AA specimens that have identical compositions but huge differences in number and weight average molecular weights, separated from parent E/AA by McHugh and Pratt at Johns Hopkins University using supercritical fluid extraction technique [15], do show a difference in fraction profiles. E/AA with half a million M_w did not fractionate well using our current conditions – peak positions are shifted and separations are poor. Viscosity is high at the annealing temperatures and there is possible entanglement at this molecular weight. Using longer annealing time has shown some improvement.

3.6. Branch content

Two E/nBA copolymers of the same composition of 34 wt% nBA show quite different profiles in Fig. 14 and Table 3. In the first specimen E/nBA #1, fraction 4 (θ_m at 80°C) has only 0.7% of the total crystallinity and fraction 5 (θ_m at 70°C) is also smaller at 12.5%, whereas E/nBA #2 has 4% and 16.9%, respectively. The absence of fractions 1–3 is the result of the high nBA content. The ^{13}C NMR data indicate that the two are identical in sequence distribution based on triads and in composition. However, the two differ in the number of ethyl branches: specimen #1 has 12.5 ethyl per 1000 CH_2 units and specimen #2 has 5.4 ethyl per 1000 CH_2 units. The extra branching in specimen #1 has interrupted and shortened the ethylene chains, thus reducing the amounts of crystals formed at higher annealing temperatures. In addition to the DSC and NMR data, E/nBA specimen #2 does not show the same clarity in its appearance as specimen #1, due to the blockiness of the ethylene segments and the increased crystallinity which cause light scattering.

3.7. Separation of a polymer blend

The separation power of the DSC fractionation technique by the ethylene block lengths is further demonstrated in a blend of HDPE and E/VA copolymer in

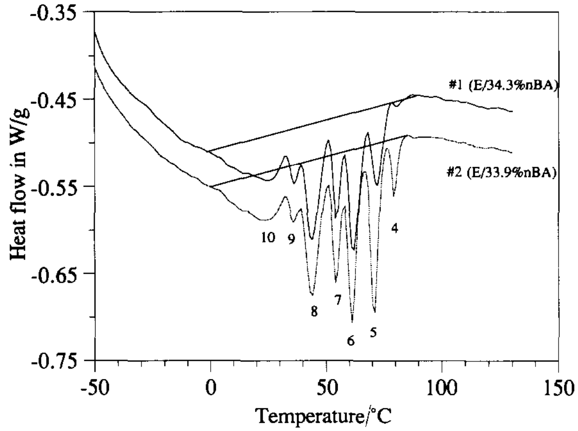

Fig. 14. Profiles of DSC-fractionated E/34 wt% nBA copolymers, different in branch content.

Table 3
Heats of fusion of DSC fractions of two E/nBA copolymers in J g^{-1}

Id.	Composition/wt%		#4	#5	#6	#7	#8	#9	#10
			θ_m 80°C	θ_m 70°C	θ_m 61°C	θ_m 54°C	θ_m 44°C	θ_m 36°C	θ_m 26°C
	E	nBA							
#1	65.7	34.3	0.15	2.88	5.23	2.96	5.28	1.85	4.66
#2	66.1	33.9	1.16	4.90	5.48	6.25	3.73	1.94	5.48

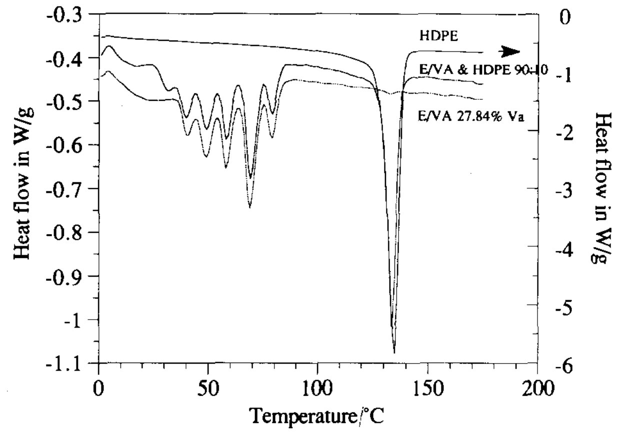

Fig. 15. Profiles of DSC-fractionated E/VA, HDPE and the blend of the two in 90/10 ratio.

Fig. 15. Melt-blended 90/10 (w/w) ratio of E/VA (72.2/27.8 wt%) and homopolymer HDPE can be well separated by DSC fractionation. The source of the ethylene in the blend is clearly illustrated by the melting points of the ethylene segment lengths. The fraction profile of the blend is the combination of the E/VA copolymer and HDPE. ^{13}C NMR of a solution blend of the same composition cannot distinguish the source of ethylene runs longer than three units.

4. Conclusions

We have a powerful fractionation technique for examining the distribution of ethylene block lengths and distinguishing the structural subtleties of ethylene copolymers. The technique uses differential scanning calorimetry (DSC) to recrystallize ethylene copolymers from above their melting temperatures with controlled stepwise cooling. The fraction profiles of the recrystallized specimens are recorded in the subsequent dynamic scans.

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