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Determination of the Crystallinity of Polyethylene/α-Olefin Copolymers by Thermal Analysis: Relationship of the Heat of Fusion of 100% Polyethylene Crystal and the Density

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ABSTRACT: The heat of fusion measured with differential scanning calorimetry (DSC) is typically divided by a constant value of the heat of fusion of 100% polyethylene (PE) crystal (ΔH^{o}_{m}) for the estimation of the fraction crystallinity of PE copolymers, regardless of the density [i.e., the short-chain branching (SCB) concentration]. In this work, values of ΔH^{o}_{m} of about 288 J/g were determined with a combined DSC and X-ray diffraction (XRD) method for a series of PE copolymers containing SCB from 0 to 50 Br/1000 C (density = 0.965–0.865 g/cc). There was no systematic change in ΔH^{o}_{m} observed across this density range. This result supports the suitability of determining the fraction crystallinity of PE of any density by the simple division of the observed heat of fusion determined by DSC by a constant value of ΔH^{o}_{m}. This DSC method yielded values of PE crystallinity in good agreement with corresponding values determined by XRD for a series of PE copolymers. The determination of ΔH^{o}_{m} involved a small precision error for higher density (lower SCB) PEs, but the precision error increased for lower density (i.e., higher SCB) PEs. This was due to the difficulty in measuring the heat of fusion for lower density PEs, which exhibited low values of the heat of fusion and melted only slightly above room temperature, and due to the difficulty of measuring lower values of crystallinity by XRD. The crystal thickness measured by small-angle X-ray scattering for this series of PE copolymers decreased exponentially from about 280 to 6 Å. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 1637–1643, 2002
Keywords: crystallinity; differential scanning calorimetry (DSC); polyethylene (PE); density

INTRODUCTION

The melting and crystallization of polyethylene (PE) copolymers, modified with α-olefins such as 1-butene, 1-hexene, and 1-octene, are processes of prime importance for these commercially significant polymers. These polymers in their commercial applications in the plastics industry crystallize only partially to form semicrystalline solids. An important variable of interest for research and commercial purposes is the fraction crystallinity.

The determination of the fraction crystallinity is commonly done with measurements of the density, X-ray diffraction (XRD), and thermal properties. Density measurements are often complicated by voids, inorganic contaminants, or additives in the specimens. The XRD measurements are complicated by the need for a noncrystalline PE, which is used to obtain an amorphous-halo

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XRD pattern. This amorphous halo must be subtracted from the XRD pattern of the sample of interest to estimate fraction crystallinity. The determination of fraction crystallinity by differential scanning calorimetry (DSC) is an attractive alternative because of the ease of obtaining this measurement.

The heat of fusion of 100% PE crystal (ΔH_m^o) has been determined by a variety of techniques. For example, a careful study arrived at a value of 293 J/g, which is similar to generally accepted values.[1] A value of ΔH_m^o = 288 J/g has been used in our laboratory.[2] A straightforward method to determine the fraction crystallinity of PE has been described in which the heat of fusion of the sample of interest is simply divided by the heat of fusion of the perfect crystal of PE, that is, ΔH_m^o.[3]

This method is fairly uniformly agreed to be accurate for PEs of reasonably high crystallinity, such as PE without significant short-chain branching (SCB). However, there has been the contention that the determination of the crystallinity of copolymers with the use of a constant value of ΔH_m^o is not valid for copolymers.[4] As the SCB increases, it is necessary to determine the heat of fusion of 1 g of pure crystals of such branched PE copolymers. Of course, if the heat of fusion of the pure crystal of such PE copolymers varies significantly from 288 J/g, then the simple method previously described for determining the fraction crystallinity would be invalid. Specifically, the question at hand is whether there is a functional dependence of ΔH_m^o on the comonomer concentration (i.e., SCB) in PE copolymers. Here, ΔH_m^o is redefined as the heat of fusion of 100% PE crystals with various concentrations of SCB, not only zero SCB, as it is ordinarily defined.

The results of various investigations concerning the inclusion of side branches in the PE crystals of copolymers with propene, 1-butene, 1-hexene, and 1-octene indicated that the concentration of side-branch inclusion in the crystal phase decreased in the following order: methyl > ethyl > butyl > hexyl.[5–8] These studies typically indicated a small concentration of side-branch inclusion in the crystals of 1-butene copolymers and a very small concentration of inclusion in the crystals of 1-hexene and 1-octene copolymers. If the inclusion is small, this might indicate that the crystals of PE copolymers with various SCBs have the same heat of fusion per gram as crystals of unbranched PE. A further effect of the concentration of side branches excluded to the basal planes of the crystals (with lamellar crystals assumed) on ΔH_m^o might also be significant.

This study was performed to determine ΔH_m^o of PE as a function of SCB (or density). The intent of this work was to compare the values of ΔH_m^o determined across the density range studied to the value used in our laboratory of 288 J/g. It was not the intent of this work to redetermine ΔH_m^o, the heat of fusion for 100% crystalline PE homopolymer. This investigation was expected to indicate the suitability of determining the fraction crystallinity of PE and PE copolymers with various SCBs by the simple division of the observed heat of fusion by a constant value of ΔH_m^o.

EXPERIMENTAL

Materials

The polymers used in this study are described in Table 1. The samples were all commercial polymers made with catalyst types presented in Table 1.

DSC

The thermal analysis was performed on a PerkinElmer DSC-4 that was under nitrogen and was equipped with MC2 thermal analysis software. Indium metal was used as a calibration standard. Sample sizes of about 4 mg were used throughout this study for an increased DSC signal-to-noise ratio. Specimens prepared as described in the Crystallization Procedure section were measured at the first melting with no additional treatment. Samples were cooled to 0 °C, held for 1 min, and heated to 150 °C at 10 °C/min for the recording of the melting endotherm. All DSC endotherms were baseline-corrected. Extended liquid baselines (or approximations thereof) were used to determine the heat of fusion (ΔH_m; see the Appendix). No significant heat of melting was observed below 20 °C. Therefore, values of ΔH_m did not include significant contributions from the melting of the material that crystallized during the cooling step of the DSC test.

Temperature Rising Elution Fractionation (TREF)

The analytical temperature rising elution fractionation (A-TREF) procedure that we followed has been described in detail previously.[9,10] A-TREF was used to obtain analytical elution temperature fractograms, which were deconvoluted

Table 1. Characteristics of the PE Copolymers

Sample	Comonomer	Catalyst Type	MI (g/10 min)[a]	Density (g/cc)	NMR (Br/1000 C)	M_w (g/mol)	M_w/M_n	TREF Breadth (Br/1000 C)[b]
M-1	C4	Metallocene	10	0.865	84.6	63,300	2.26	0.5[c]
M-2	C4	Metallocene	0.8	0.880	51.4	136,900	2.35	2.8
M-3	C4	Metallocene	2.2	0.888	43.9	97,600	2.09	3.4
M-4	C4	Metallocene	3.5	0.900	30.7	80,900	2.22	5.1
M-5	C4	Metallocene	4.5	0.905	25.3	75,300	2.51	4.7
M-6	C4	Metallocene	1.2	0.910	18.5	107,600	2.18	2.4
Z-1	C6	Ziegler	0.057	0.938	3.2	251,000	21.1	3.9
Z-2	C4	Ziegler	0.055	0.949	1.4	259,000	26.5	1.5
Z-3	—	Ziegler	0.7	0.965	0	126,000	7.40	—

[a] ASTM Standard D 1238.
[b] Breadth of the SCB distribution at half-height obtained by A-TREF.
[c] This polymer was soluble in trichlorobenzene at room temperature.

into SCB distributions by calibration, as described previously.[9] Measurements were made on commercial pellet samples of each polymer. The breadth of the composition distribution of each polymer sample in the A-TREF test is presented in Table 1. The breadth of the composition distribution was represented by the breadth at half-height of the A-TREF peak in branches per 1000 total carbon atoms (see the Appendix).

Nuclear Magnetic Resonance (NMR) Spectroscopy

The SCB of the PE/α-olefin copolymers was determined by ^{13}C NMR on a Varian Unity-300 NMR operating at 75 MHz at 125 °C in trichlorobenzene/benzene-d_6 (20% v/v) with a 90° flip angle, an acquisition time of 1.5 s, and a pulse delay of 10 s. The SCB concentration was calculated by a previously described method[11] and was expressed as branches per 1000 total carbon atoms. Measurements were made on commercial pellet samples of each polymer.

Crystallization Procedure

We crystallized all the polymers by compression molding thin films (~50 μm), holding these films at 150 °C in an oven for 10 min, and cooling them at 4.8 °C/min to 30 °C. These specimens were directly melted in the differential scanning calorimeter.

Wide-Angle XRD

The diffraction patterns were obtained with a Siemens D-500 XRD system equipped with a TX-500 texture goniometer and a Phillips diffractometer. Both cameras operated in reflection geometry. The diffraction experiments were performed with a nickel-filtered Cu Kα radiation source for the Siemens camera and with a graphite monochromator for the Phillips instrument. Both instruments were operated at 30 mA and 40 kV. Specimens prepared as described in the Crystallization Procedure section were measured directly with no additional treatment. Neither XRD instrument was equipped with a hot stage, so it was necessary to use a close-to-amorphous sample of highly branched PE (sample M-1 in Table 1) for subtraction of the amorphous patterns from the semicrystalline patterns. The amorphous and semicrystalline runs were corrected for Compton scattering by the subtraction of a flat background observed at the highest angle. The amorphous curve was then subtracted by being scaled to fit the amorphous halo under the semicrystalline curve with automated software developed at the University of Cincinnati. From integrals of $I\mathbf{q}^2$ versus $\mathbf{q}$ (where I is the scattering intensity and $\mathbf{q}$ is the scattering vector), the volume fraction crystallinity was determined. This approach was reproducible (with a new sample and a new amorphous reference) to within about ±2%. The accuracy of the result can be determined by comparison with results from a density gradient column, and it was found to agree within the error involved in this technique, about ±5%.

Small-Angle X-Ray Scattering (SAXS)

SAXS measurements were made with a two-dimensional detector and focusing optics that pro-

duced pinhole monochromatic X rays with wavelengths of $\lambda = 1.54$ Å. All SAXS data were corrected for the detector sensitivity, dark current, and empty cell. Specimens prepared as described in the Crystallization Procedure section were measured directly with no additional treatment. The two-dimensional pattern was radially averaged to produce an azimuthal plot of the scattered intensity versus $\mathbf{q} = 4\pi/\lambda \sin(\theta/2)$, where θ is the scattering angle. A Lorentzian correction was applied to the data and the lamellar correlation distance; that is, the long period was determined from the mean $\mathbf{q}^*$ value for a Gaussian fit to the resulting Lorentzian corrected peak, $I\mathbf{q}^2$ versus $\mathbf{q}$. The long period is given by $L = 2\pi/\mathbf{q}^*$. The lamellar thickness, ℓ_c, was estimated with the degree of crystallinity, ϕ_c, from the XRD pattern, determined as described later, and with a two-phase model assumed, so that $\ell_c = L\,\phi_c$. It is recognized that crystals, especially at the lower densities, may not be lamellar; however, lamellar crystals were assumed for comparison.

RESULTS AND DISCUSSION

This study employed a series of PEs with a range of SCB (and density) as presented in Table 1. The metallocene catalyst polymers with lower densities had narrow molecular weight and copolymer composition distributions, as indicated by the polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] and TREF breadth (see the Appendix) in Table 1. The higher density polymers had broader molecular weight distributions, but the composition distributions were narrow. The polymers were all prepared for analysis in the same way, that is, by thin films being compression-molded, held at 150 °C in an oven for 10 min, and cooled at 4.8 °C/min to 30 °C. The DSC melting endotherms, XRD, and SAXS of these specimens were collected. In the DSC testing, extended liquid baselines (see the Appendix) were used to determine ΔH_m. No significant heat of melting was observed below 20 °C. Therefore, values of ΔH_m did not include a significant contribution from the material that crystallized during the cooling step during the DSC test.

The DSC data for these polymers are presented in Table 2. A systematic broadening of the melting endotherm and a shifting of the melting temperature (T_m) to a lower temperature were observed as the density decreased.

Table 2. DSC T_m, ΔH_m, and Crystallinity (X_{tal})

	DSC		
Sample	T_m (°C)	ΔH_m (J/g)	X_{tal} (%)[a]
M-1	47.6	10.6	3.7
M-2	60.0	33.9	11.8
M-3	69.0	59.6	20.7
M-4	86.9	84.6	29.3
M-5	99.3	95.0	33.0
M-6	107.6	109.9	38.2
Z-1	130.3	166.7	57.9
Z-2	128.4	185.6	64.4
Z-3	135.9	233.0	80.9

[a] Observed heat of fusion divided by 288 J/g.

The reported T_m was the peak melting temperature. The crystallinity of the polymers was calculated by the division of the observed heat of fusion by 288 J/g. The XRD calculated fraction crystallinities are presented in Table 3. The DSC and XRD crystallinities are plotted against each other in Figure 1. There is good agreement between the crystallinities determined by the two methods.

The ΔH_m^o value of each polymer in Table 3 was calculated by the division of the observed heat of fusion by the XRD fraction crystallinity, and these are also presented in Table 3. The value of ΔH_m^o is plotted against SCB in Figure 2. It may be seen in Table 3 and Figure 2 that values of ΔH_m^o very close to 288 J/g were obtained for the higher density (low SCB) polymers. Furthermore, the values of ΔH_m^o are clustered around 288 J/g for the lower density (high SCB) polymers. The determination of ΔH_m^o had higher intrinsic error for the higher SCB polymers because of the difficulty of measuring relatively lower values of ΔH_m for polymers melting only slightly above room temperature and because of the difficulty of measuring lower values of crystallinity by XRD. This may be seen in the increasing standard deviation of the determinations of ΔH_m^o as SCB increases in Figure 2 and Table 3.

The arbitrary line drawn at $\Delta H_m^o = 288$ J/g in Figure 2 shows the remarkable recovery of this value of ΔH_m^o for polymers ranging from 0 to 50 Br/1000 C. This result supports the suitability of the simple procedure of determining fraction crystallinity by the division of the observed ΔH_m by 288 J/g for PEs of any density. This value of ΔH_m^o is in good agreement with literature values ob-

Table 3. XRD Crystallinity (X_{tal}), Calculated ΔH°_{m}, and ℓ_c from SAXS

Sample	XRD X_{tal} (%)	ΔH_m (J/g)	ΔH^{o}_{m} (J/g)[a]	Standard Deviation (J/g)[b]	SAXS ℓ_c (Å)
M-1	—[c]	10.6	—	—	5.8
M-2	12.1	33.9	280.5	±82	18.7
M-3	25.0	59.6	238.3	±51	28.8
M-4	30.7	84.6	275.4	±49	44.3
M-5	39.2	95.0	242.4	±27	50.8
M-6	45.0	109.9	244.3	±8.0	65.2
Z-1	59.0	166.7	282.6	±16	166.7
Z-2	67.7	185.6	274.2	±21	162.3
Z-3	83.0	233.0	280.7	±7.5	279.1

Overall Average of ΔH^{o}_{m}	Standard Deviation of ΔH°_{m}
264.8	±19.4

[a] Observed heat of fusion divided by the fraction of crystallinity determined by XRD.
[b] Three replicates.
[c] Not determined.

tained from measurements for highly crystalline PEs, which range from about 288 to 293 J/g.[1,2] The actual average value of ΔH^{o}_{m} determined for the whole density range included in Table 3 was 264.8 ± 19.4 J/g for PEs ranging in density from 0.965 to 0.880 (SCB = 0–51.4 Br/1000 C). However, as stated, it was not the intent of this work to redetermine ΔH^{o}_{m}. It appears that for typical, modern DSC instrumentation, values of crystallinity are not readily accessible that are more accurate than those obtained by the procedure described herein. This is especially due to the inherent error in the measurement of ΔH_m, an error that increases as density decreases. It should be noted that the accuracy of the crystallinity determined by DSC measurements is based on the crystallinity determined by XRD measurements.

ℓ_c values of the polymers (see Table 3) are plotted against SCB in Figure 3. ℓ_c decreases exponentially with increasing SCB. Although the thickness of the lamellae decreased over such a large range, as well as the perfection of the crystals,[8] the heat of fusion to melt 1 g of crystals remained constant at about 288 J/g. It was assumed that crystals in polymers across the entire density range were lamellar. However, it is recognized that crystals, especially at the lower densities, may not be lamellar, but for simplicity and comparison all SAXS data were treated with the

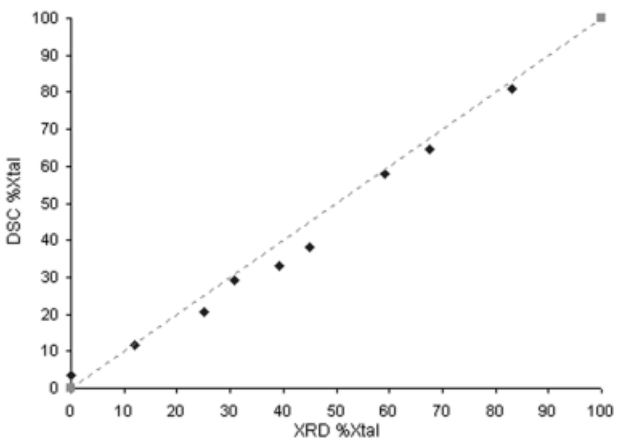

Figure 1. Correlation of the percentage of crystallinity (X_{tal}) determined by XRD and DSC.

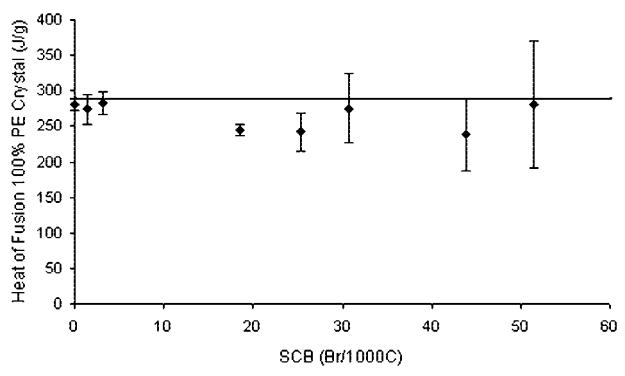

Figure 2. Heat of fusion of 100% PE crystal versus SCB of PEs.

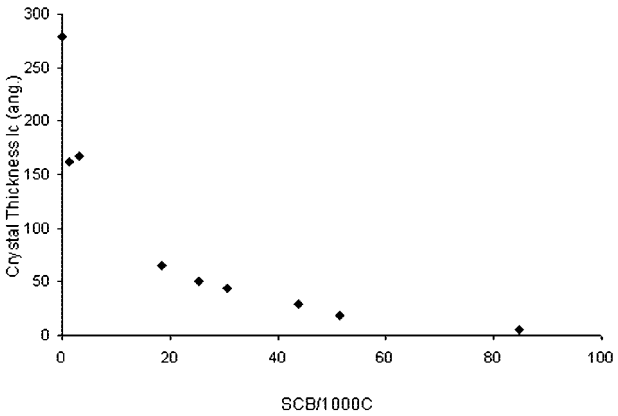

Figure 3. Crystal thickness determined by SAXS versus SCB of PEs.

same assumption that the crystal morphology was lamellar.

Some results relevant to this study merit mention. The peak melting temperature and heat of fusion were correlated with SCB in a study of A-TREF calibration.[12] A correlation between crystallinity and ethylene content in linear low-density PE copolymers was reported.[13] A study of the crystallinity of ethylene/α-olefin copolymers included data on the melting of these copolymers.[14] Recalculation of these data permitted the determination of ΔH^{o}_{m} over a range of SCB for 1-butene and 1-octene copolymers with ethylene. The values of ΔH^{o}_{m} were clustered around 288 J/g and exhibited no functional dependence on SCB, as in this study. The average value of ΔH^{o}_{m} obtained by recalculation of the data was 289.1 $\pm$ 49.9 J/g for nine copolymers ranging in SCB from 8.5 to 38.8 Br/1000 C. The data in that study produced results similar to those of this study over a smaller range of SCB and with higher precision error.

CONCLUSIONS

The determination of the fraction crystallinity by DSC by the simple division of the observed heat of fusion by a constant value of ΔH^{o}_{m} yielded sufficiently accurate crystallinity in comparison with that determined by XRD for a series of PE copolymers containing SCB from 0 to 50 Br/1000 C. These results indicate that crystallinity can be estimated by this method for PEs with narrow composition distributions. Likewise, this same method should be applicable to PEs with broad composition distributions because interactions such as cocrystallization would not appear to compromise the implications of these results.

A value of ΔH^{o}_{m} around 288 J/g was determined for this series of PE copolymers over the entire density range. No functional dependence of ΔH^{o}_{m} on polymer density was observed. This value is in good agreement with literature values for highly crystalline PE. The determination of ΔH^{o}_{m} involved a small error for higher density (lower SCB) PEs, but the error increased for lower density (i.e., higher SCB) PEs. This was due to the difficulty of measuring ΔH_{m} for lower density PEs, which exhibited lower values of ΔH_{m} and melted only slightly above room temperature, and due to the difficulty of measuring lower values of crystallinity by XRD.

ℓ_c for this series of PE copolymers decreased exponentially from about 280 to 6 Å. Although the thickness and presumably the perfection[8] of the crystals changed over such a large range, the heat of fusion to melt 1 g of crystals was shown to remain constant at about 288 J/g.

NOTE ADDED IN PROOF

In a previous publication we presented a theoretical treatment for the correction of the enthalpy of fusion for the case of finite crystal thickness (B. Crist and F. M. Mirabella, J. Polym. Sci.: Part B: Polym. Phys. *37*, 3131 (1999)). Lamellar crystal morphology was assumed in that treatment and resulted in

$$\Delta H^{\ell}_{v} = \Delta H_{v}\,[T_{m}/T^{\circ}_{m}]$$

where ΔHv is the enthalpy of fusion per unit volume of infinitely thick lamella melting at T°_{m} (=418.7°C) and ΔH^{ℓ}_{v} is the enthalpy of fusion per unit volume of lamella of thickness ℓ melting at T_{m}. Application of this correction to the data in this paper results in reductions in enthalpy of fusion due to finite ℓ ranging from 2.4% for sample Z-3 to 21.5% for sample M-2. This correction may only be appropriate for samples that exhibit lamellar crystal morphology. Nevertheless, the theoretically predicted reduction in enthalpy of fusion is too small to detect, due to the precision error of the measurements (see Table 3 in text). This supports the conclusions of this paper. That is, more accurate values of crystallinity are not accessible from modern DSC instrumentation than those obtained by simply dividing the ob-

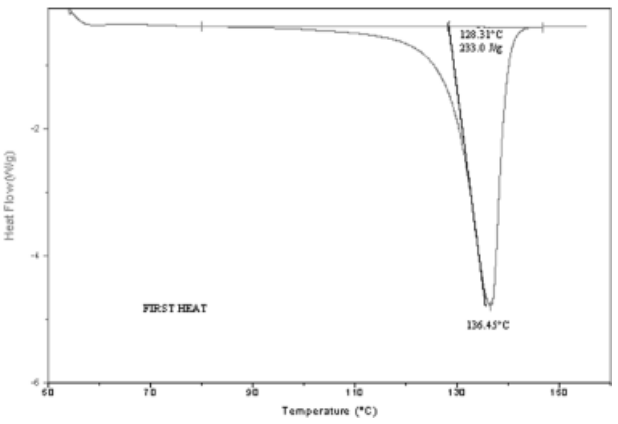

Figure A1. DSC endotherm of Z-3.

served heat of fusion by a constant value of the heat of fusion of 100% crystalline PE.

APPENDIX

The baseline drawing procedure is demonstrated for sample Z-3 (density = 0.965) in Figure A1. The extension of the baseline from the high-temperature side of the endotherm produces a good approximation of the total ΔH_m. This baseline is called an extended liquid baseline because the baseline is extended from the side of the endotherm representing molten material. As the densities of the polymers decrease, this procedure becomes more dubious, and a best estimate of the baseline is made as demonstrated for sample M-2 (density = 0.880) in Figure A2.

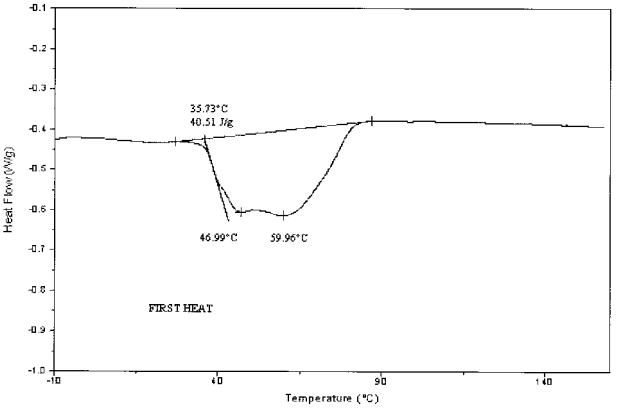

Figure A2. DSC endotherm of M-2.

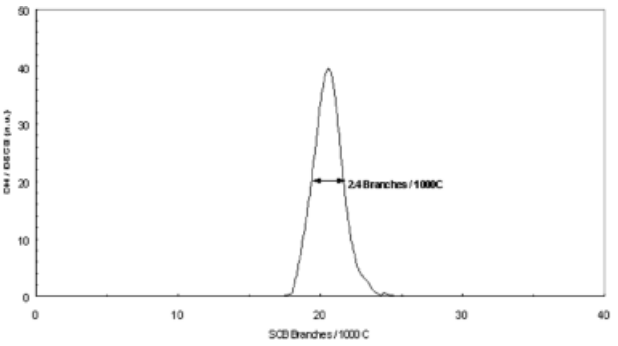

Figure A3. A-TREF SCB distribution of M-6.

The breadth of the composition distribution of the polymers was represented by the breadth at half-height of the A-TREF peak in branches per 1000 total carbon atoms, as demonstrated for sample M-6 in Figure A3.

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