

Characterization of molecular heterogeneities of LLDPE by multiple crystallization–dissolution steps

C. Vandermiers, J.-F. Moulin, P. Damman, M. Dosière*

Laboratoire de Physico-Chimie des Polymères, Université de Mons-Hainaut, 20, Place du Parc, Mons, B-7000 Belgium

Received 20 October 1998; accepted 25 January 1999

Abstract

This article demonstrates that a fractionation technique, based on molecular segregation during the crystallization from the melt and dissolution of the crystals, allows a complete characterization of the molecular heterogeneity in the comonomer distribution of linear low density polyethylene. An ethylene–1-hexene copolymer with a bimodal short chain branching distribution has been fractionated by multiple step crystallizations followed by selective dissolutions in tetrachloroethylene. The relative amount of each component of the distribution in each fraction was determined from the melting curves of isothermally crystallized fractions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer fractionation; LLDPE; Molecular heterogeneities

1. Introduction

Linear low density polyethylenes (LLDPE) are copolymers of ethylene and α -olefins such as 1-butene, 1-hexene, and 1-octene. Their properties are strongly affected by the degree and the distribution of short chain branching due to the incorporation of the α -olefins in the polymeric chains [1]. These copolymers are synthesized either with Ziegler–Natta (Z–N) [2] or metallocene [3] catalysts. The polymers obtained from the Z–N process are usually characterized by a molecular heterogeneity resulting from a very different distribution of comonomer units along the polymer chains [4]. As the thermomechanical properties of the polymer are strongly affected by its structural characteristics, the control of the comonomer distribution is a touchstone in the polymer industry. The short chain branching content and its distribution are usually determined by fractionation procedures involving the combination of a successive solvent fractionation (SSF) and temperature rising elution fractionation (TREF) [1,5,6]. However, a complete analysis by this technique is time consuming. The development of new techniques to characterize and estimate the heterogeneity of LLDPEs is therefore of great interest. As previously reported by Alamo et al. [7], an adequate thermal treatment based on successive isothermal crystallizations of blends of linear and branched PE at decreasing temperatures induces a

molecular segregation in the crystals, in terms of short chain branching. Nevertheless, except for the preliminary work of Adisson et al. [8], the effect of multiple step isothermal crystallizations on commercial LLDPE polymers has never been fully investigated.

In this article, we report the results obtained by fractionation of a 1-hexene LLDPE by a method based on selective dissolutions at various temperatures of isothermally crystallized samples. The experimental set-up used for fractionation is described elsewhere. The influence of the thermal treatment was established by comparing the resulting fractions with those obtained after fractionation of a quenched sample. The results obtained by SSF on the same LLDPE sample are also used as comparison.

2. Experimental

2.1. Materials

An ethylene–1-hexene copolymer, synthesized by a Phillips process (Cr catalyst) with a density of 0.933 g/cm³, is used. The average degree of short chain branching amounts to eight side branches per 1000 carbon atoms. The weight average molecular weight and the polydispersity are 220 000 and 15, respectively.

2.2. Multiple steps crystallization and selective dissolution

Prior to fractionation, the LLDPE samples are either

* Corresponding author. Tel.: +32-6537-3351; fax: +32-6537-3354.

E-mail address: dosiere@umh.ac.be (M. Dosière).

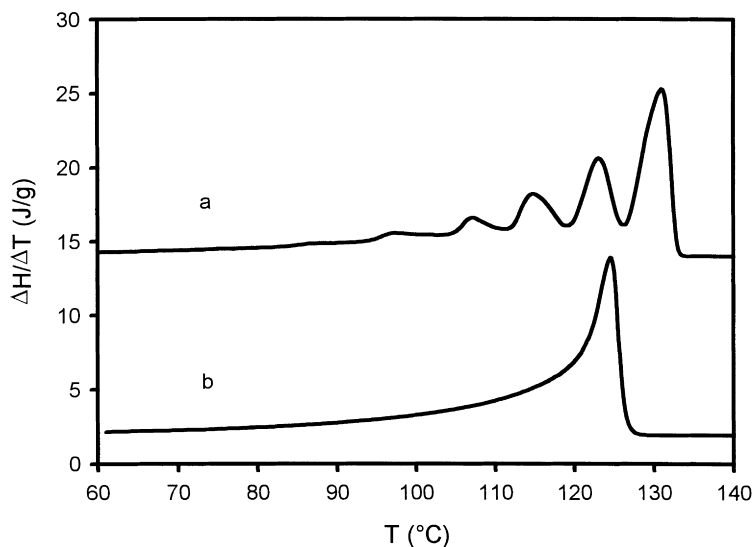


Fig. 1. DSC melting curves of the (a) isothermally crystallized and, (b) quenched samples.

quenched from the melt or isothermally crystallized at different temperatures. The determination of temperatures and times of crystallization is described later. To prevent the degradation of the material, the polymer is melted at 150°C during 5 min under nitrogen atmosphere. The selective dissolution is performed by immersing polymeric films, a few hundred microns thick, in tetrachloroethylene under stirring at the chosen dissolution temperature. After 2 h, the insoluble part of the polymer is removed and the solution (containing the soluble part of the polymer) is collected. The LLDPE fraction is finally recovered after solvent evaporation. The same procedure is then repeated at higher dissolution temperatures.

2.3. Successive solution fractionation (SSF)

A standard oil bath thermostated glass reactor (2 l) fitted with a tap, a condenser, a stirrer and a nitrogen purge inlet is used for fractionation. First, a dilute solution of polymer (i.e. 0.5% w/w) is prepared with a poor solvent (cyclohexanone) at high temperature. The temperature is then lowered to a value assigned as T_{extract} . At this temperature a liquid–liquid phase separation occurs and the polymer rich phase contains most of the high molecular weight chains. The low molecular weight chains remain in the lean phase. These two phases are separated by hot filtration. The fraction is precipitated from the filtrate by addition of cold acetone, washed overnight with acetone in a Soxhlet apparatus and carefully weighed after drying at 70°C in a vacuum oven. The insoluble part of the sample is used for further fractionation at a temperature slightly higher than T_{extract} . The extraction temperatures are 90, 100, 110, 115, 120, 125 and 130°C. Two extractions are performed at each temperature, except at 100°C. Before each fractionation step a small amount of antioxidant is added to the solution to avoid the degradation of the polymer.

2.4. Differential thermal analysis

Thermal analysis is carried out with a Perkin–Elmer Pyris 1 differential scanning calorimeter. Samples of about 5 mg in aluminium pans are submitted to heating–cooling cycles. A first heating–cooling cycle at 20°C/min up to complete melting at 150°C is realized to erase the thermal history of the samples. The second cycle is recorded at a rate of 5°C/min from 30 to 150°C.

2.5. Infrared spectroscopy

The FTIR spectra are recorded from 4000 to 400 cm^{-1} with a Bruker IFS 113V spectrometer. A minimum of 32 scans are added with a resolution of 0.5 cm^{-1} . The degree of short chain branching was determined by using the methyl group absorption band [9] at 1378 cm^{-1} . For the Z–N copolymer, a vinyl, vinylene or vinylidene group absorbing at 908, 965 or 888 cm^{-1} is present at one end of the polymeric chain [10] as a result of the termination mechanism of the polymerization reaction (β -elimination). As shown later, the number average molecular weight of the fractions is determined by combining the integrated absorbances of the three different end groups.

2.6. Size exclusion chromatography

The molecular weight distributions of the fractions are determined by high temperature size exclusion chromatography (SEC) on a Waters 150C chromatograph fitted with four μ -styragel columns using 1,2,4-trichlorobenzene as the solvent. Polystyrene standards are used for calibration.

3. Results and discussion

As shown previously [11,12], LLDPE copolymers

Table 1

Endotherm	T_m (°C)	Relative contribution (%)
1	130.8	30.9
2	123.2	20.5
3	114.7	16.3
4	107.2	10.7
5	97.0	9.3
6	86.4	5.9

synthesized with Z–N catalysts usually exhibit a bimodal distribution of short chain branching (τ). In fact, two molecular species can be deduced from the TREF curves: (i) unbranched or weakly branched molecules corresponding to the narrow component of the distribution and high elution temperatures; (ii) highly branched molecules giving the broad component of the distribution observed at low elution temperatures. This bimodal distribution is usually attributed to: (i) the rate of diffusion of the comonomer towards the catalytic site: for high molecular weight polymer, the sterical hindrance of the polymer coil prevents the comonomer from reaching the site of the catalyst; (ii) the termination process by an α -olefin which is favoured in the Z–N synthesis.

3.1. Determination of the times and temperatures of crystallization

As shown previously by Alamo et al. [7], the co-crystallization between linear and branched macromolecules (hydrogenated polybutadiene) is observed only when the blends are quenched from the melt. Isothermal crystallizations above 120°C for more than 110 min induces a segregation of both molecular species in the melt which finally yields separate crystals of linear and branched molecules. Consequently, the temperature and time of

crystallization for the first step are chosen as 121°C and 210 min, respectively. It is assumed that most of the linear or weakly branched macromolecules will have crystallized during this step. Nevertheless, under some conditions, co-crystallization between branched molecules can be observed and this prevents an efficient fractionation. The other crystallisation temperatures are chosen to observe the highest number and the best resolved melting endotherms in the melting curve of the sample. For the 1-hexene LLDPE used throughout this work, the crystallization temperatures are 121, 115, 109, 102, 95, 85 and 75°C, and the crystallization time is 210 min. The DSC melting curves of quenched and isothermally crystallized samples are shown in Fig. 1. The multiple step crystallisation (MSC) induces a molecular segregation in the melt as indicated by the six well resolved melting endotherms. The melting temperatures of the crystals and the relative contribution of each endotherm are reported in Table 1. As shown by several authors [1,5,13], the degree of short chain branching strongly affects the crystallization of polymers. By using the MSC thermal treatment, the growth of crystals with different thickness is observed, the thinner and the thicker lamellar crystals corresponding to highly branched and linear unbranched molecules, respectively. The different endotherms can thus be related to different molecular species from the Thomson–Gibbs equation relating the melting temperature and the crystal thickness. The high temperature endotherm corresponds to unbranched or weakly branched molecules, the low temperature endotherms being associated to branched molecular species.

3.2. Fractionation of the LLDPE copolymers

Quenched and isothermally crystallized LLDPE samples

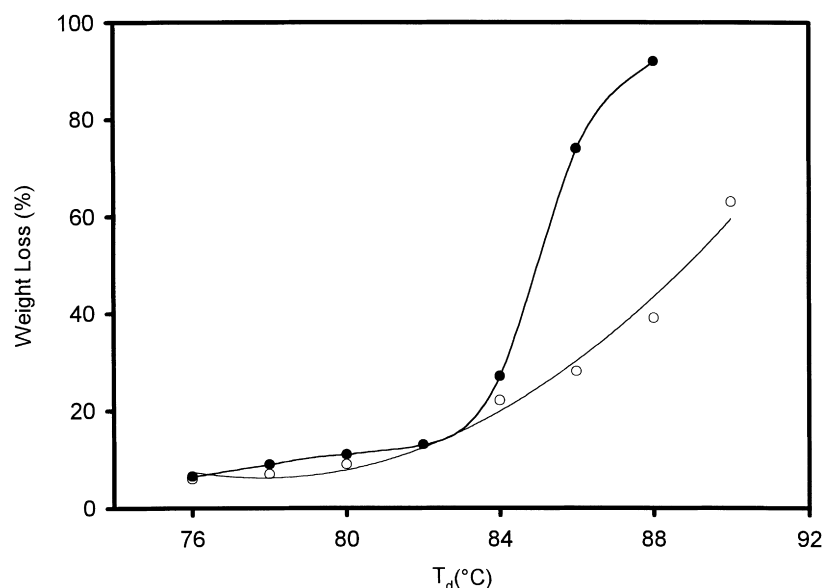


Fig. 2. Weight loss versus dissolution temperature for the quenched sample (●) and isothermally crystallized sample (○).

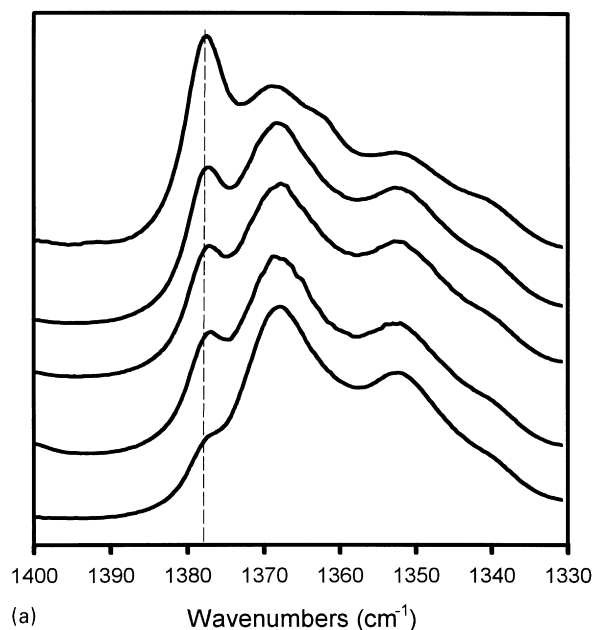
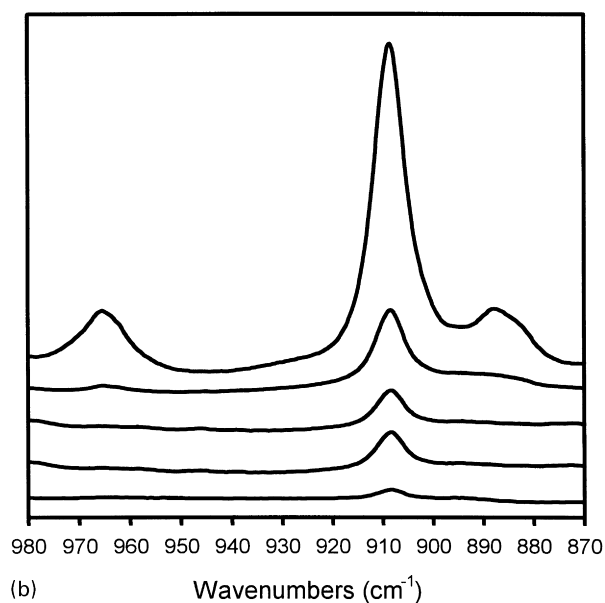
(a) Wavenumbers (cm⁻¹)(b) Wavenumbers (cm⁻¹)

Fig. 3. FTIR spectra recorded for fractions recovered by selective dissolutions of the quenched sample: (a) methyl group absorption band (1378 cm⁻¹) and, (b) end groups absorption bands: vinylidene (888 cm⁻¹) vinyl (908 cm⁻¹), and vinylene (965 cm⁻¹).

are then fractionated by selective dissolutions. To determine the dissolution temperatures, the weight loss of both the quenched and the MSC samples are measured for different extraction temperatures (Fig. 2). Systematically, higher dissolution temperatures are observed for the MSC samples. This observation can obviously be related to the growth of thicker crystals induced by the thermal treatment. The dissolution temperatures are finally determined from the weight loss curve in order to obtain a sufficient amount of the fraction for further investigations.

The same copolymer is also fractionated by successive

Table 2

Sample	$\langle M_n \rangle$	$\langle M_w \rangle$	P
1-hexene LLDPE	15 733	2 38 244	15.1
Selective dissolution			
Quenched sample:			
Fraction 83°C	2441	16 151	6.6
Fraction 85°C	14 583	53 653	3.7
Fraction 86°C	21 087	74 171	3.5
Fraction 87°C	22 903	1 09 124	4.8
insoluble fraction	46 559	4 90 330	10.5
MSC treated sample:			
Fraction 84°C	2931	28 841	9.8
Fraction 86°C	11 291	42 132	3.7
Fraction 88°C	15 450	62 172	4
Fraction 90°C	21 749	122 872	5.6
Insoluble fraction 90°C	34 260	3 56 959	10.4
Successive solution fractionation			
Fraction 90°C/1	2571	7970	3.1
Fraction 90°C/2	4948	12 370	2.5
Fraction 100°C	8758	15 765	1.8
Fraction 110°C/1	17 456	27 930	1.6
Fraction 110°C/2	21 741	47 830	2.2
Fraction 115°C/1	44 542	57 905	1.3
Fraction 115°C/2	46 643	65 300	1.4
Fraction 120°C/1	33 418	83 545	2.5
Fraction 120°C/2	42 050	92 510	2.2
Fraction 125°C/1	75 910	1 44 230	1.9
Fraction 125°C/2	36 250	1 45 000	4
Fraction 130°C/1	1 09 286	2 29 500	2.1
Fraction 130°C/2		3 00 600	
Insoluble fraction 130°C	3 58 333	6 45 000	1.8

solution fractionation. This method based on a liquid–liquid phase separation is usually used to fractionate polymers with respect to molecular weight [14]. It leads to very low polydispersity fractions and minimizes the time that low molecular weight species are kept at high temperature. This is important because low molecular weight molecules are more branched and therefore more prone to degradation than the high molecular weight linear macromolecules.

3.3. Characterization of the LLDPE fractions

All the fractions obtained from the SSF method and the selective dissolution of the quenched and the MSC copolymer were first characterized by FTIR spectroscopy and SEC. Fig. 3 shows the infra-red spectra of the fractions obtained by selective dissolution of the quenched sample. FTIR spectroscopy can be used to determine the degree of short chain branching [9] (τ) and the number average molecular weight [10] ($\langle M_n \rangle$). Fig. 3(a) and (b) show the methyl group absorption band at 1378 cm⁻¹ related to short chain branching and the absorption bands corresponding to the end groups, respectively. During the copolymer synthesis, the termination occurs by β -elimination either from an ethylene or 1-hexene monomer then giving vinyl, vinylene or vinylidene chain ends. These groups possess absorption bands observed in the IR spectra at 908, 965 and 888 cm⁻¹, respectively. The integrated absorbances of the chain ends IR bands are

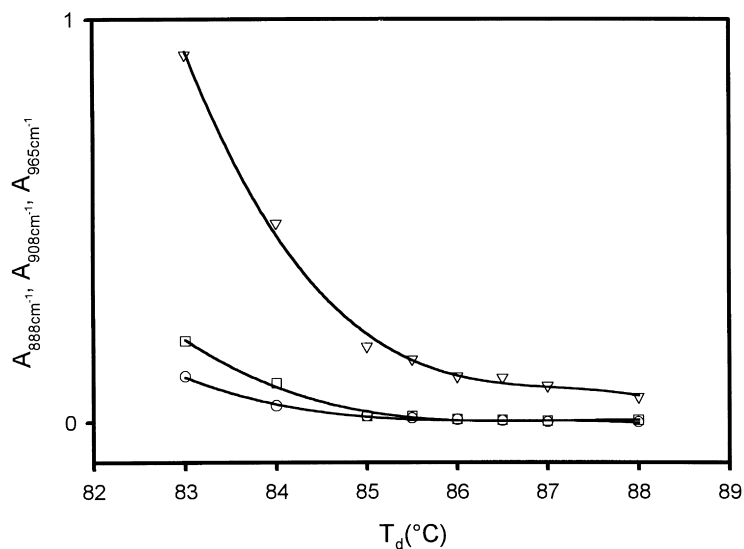


Fig. 4. Integrated absorbance (A) of the infra-red bands characteristic of the different end groups versus dissolution temperature (T_d): vinylidene (O), vinyl (∇) and vinyene (\square).

plotted versus the dissolution temperature in Fig. 4. The decrease of these absorbances at higher dissolution temperatures corresponds to the increase in the molecular weight. In addition, the vinyene and vinylidene IR bands (965 and 888 cm^{-1}) vanish at dissolution temperatures above 85°C . As we will see later, this observation can be related to the

rapid decrease of the degree of branching (τ) with increasing $\langle M_n \rangle$. To determine the correlation between the IR absorbances and the molecular weight of the fractions, their size exclusion chromatograms are recorded. The results are listed in Table 2. For the three fractionations, the number average molecular weight ($\langle M_n \rangle$) increases with the dissolution

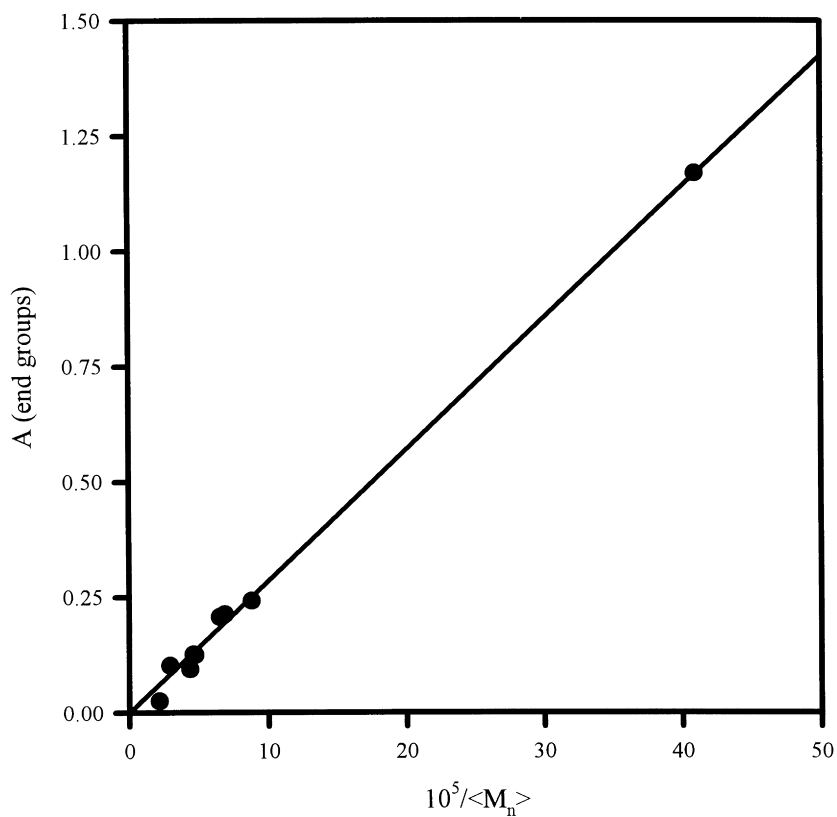


Fig. 5. Normalized sum of the integrated absorbances of IR peaks characteristic of the end groups versus the inverse of the number average molecular weight ($\langle M_n \rangle$).

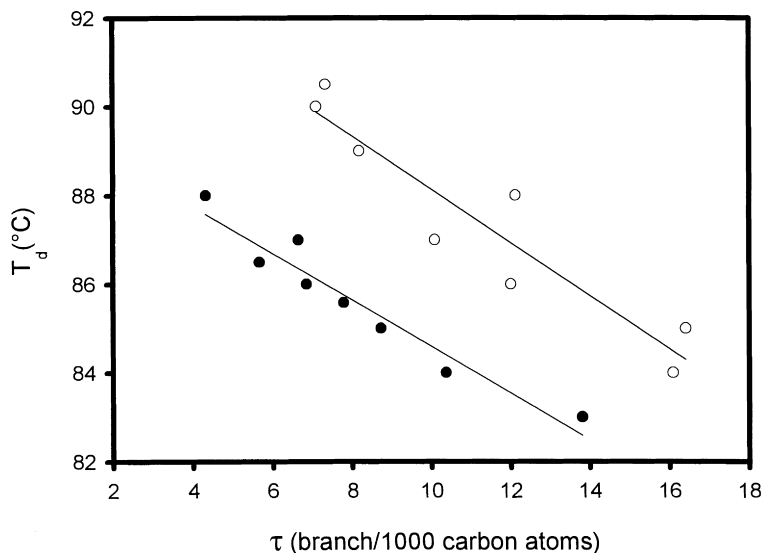


Fig. 6. Evolution of the dissolution temperature (T_d) with the degree of short chain branching, quenched sample (●) and isothermally crystallized sample (○).

temperature. By combining SEC and FTIR spectroscopy results, a calibration curve can be determined and facilitates the ability to estimate $\langle M_n \rangle$ values directly from the FTIR spectra (Fig. 5). The analysis of the IR band at 1378 cm^{-1} does not allow to separate the contributions of the methyl end groups and the methyl groups of the side branches. The number of methyl end groups can however be calculated from the values of $\langle M_n \rangle$ and therefore subtracted from the total number to obtain the number of side branches. The calibration is performed with a Z–N homopolymer, by plotting the integrated absorbance of the IR band at 1378 cm^{-1} against the number of methyl molecules calculated from $\langle M_n \rangle$.

The relation between the dissolution temperature and the degree of short chain branching (τ) is given in Fig. 6. We

note that these curves are similar to the elution temperature versus τ plots obtained from TREF experiments. For both quenched and MSC samples, the dissolution temperature linearly decreases with increasing degree of short chain branching. However, the crystallization of the samples obviously has important implications in the dissolution behaviour of the copolymer. In fact, higher dissolution temperatures are systematically observed for the MSC copolymer compared to the quenched sample. This increase can be related to the isothermal crystallization of the MSC copolymer at high temperatures which induces a molecular segregation in the melt. Therefore, the crystals grown from this segregated melt have larger lamellar thicknesses than that obtained for the quenched

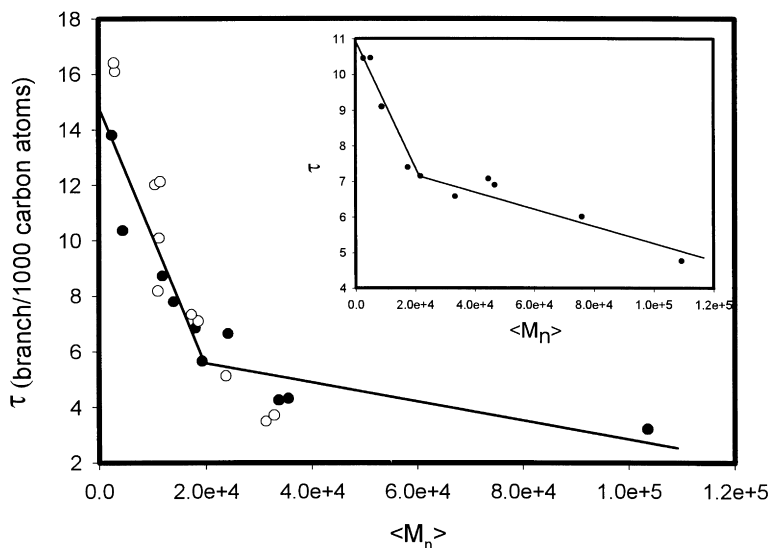


Fig. 7. Plot of the degree of short chain branching (τ) versus the number average molecular weight ($\langle M_n \rangle$) for the fractions obtained from selective dissolutions (quenched sample (●) and isothermally crystallized sample (○)). The inset shows the plot of τ versus $\langle M_n \rangle$ for the fractions obtained by SSF.

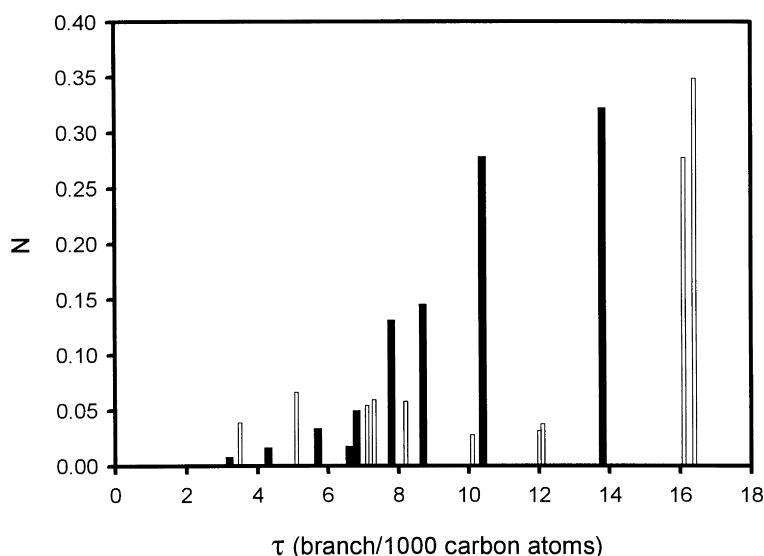


Fig. 8. Molar fraction of each molecular species (N) versus the degree of short chain branching (τ). Full and open bars refer to the fractions obtained from the quenched sample and the isothermally crystallized sample, respectively.

copolymer, as indicated by their DSC curves (see Fig. 1). Note that these observations also illustrate the heterogeneous distribution of the comonomers in the polymeric chains. The evolution of the degree of short chain branching (τ) with the number average molecular weight ($\langle M_n \rangle$) is given in Fig. 7 for the fractions obtained from selective dissolution and SSF experiments. As expected for such a Z–N LLDPE copolymer, a bimodal distribution can be deduced from the evolution of τ versus $\langle M_n \rangle$. The highly branched molecules correspond to the low molecular weight parts of the distribution which exhibit a sharp decay of τ when $\langle M_n \rangle$ increases. The high molecular weights correspond to weakly branched or unbranched macromolecules.

At this point of the work, the fractionations performed by selective dissolution of quenched and MSC copolymers show similar behaviours. However, the molar content of each molecular species (defined with respect to τ) can be calculated from the $\langle M_n \rangle$ and the weight amount of each fraction. The plot of these molar contents versus the degree of branching clearly reveals significant differences between the different fractionation procedures (Fig. 8). In fact, the fractionation by selective dissolutions of the MSC sample is more efficient in terms of short chain branching, i.e. the variation of the degree of branching is sharper than that observed for the quenched sample. Moreover, the curve obtained for MSC sample alone exhibits the bimodal behaviour characteristic of the LLDPEs.

3.4. Multiple step crystallizations of the LLDPE fractions

The efficiency of the different fractionation procedures is now investigated from the analysis of the obtained fractions. As shown earlier, the typical bimodal distribution is observed

in the τ versus $\langle M_n \rangle$ plots. Owing to the heterogeneity of the copolymer, each fraction contains a linear unbranched and a highly branched component. Therefore, a full description of the copolymer, in terms of molecular weight and short chain branching, similar to that obtained from SSF–TREF analysis, requires not only the determination of the average values of τ but also of the relative contributions of the linear and branched components [10]. The occurrence of a molecular segregation in the melt between linear and branched molecules, described earlier and in Ref. [7], allows us to perform a semi-quantitative determination of their relative contributions in each fraction. The various samples obtained from SSF and selective dissolutions fractionation are then submitted to a MSC thermal treatment in order to induce this molecular segregation. Fig. 9

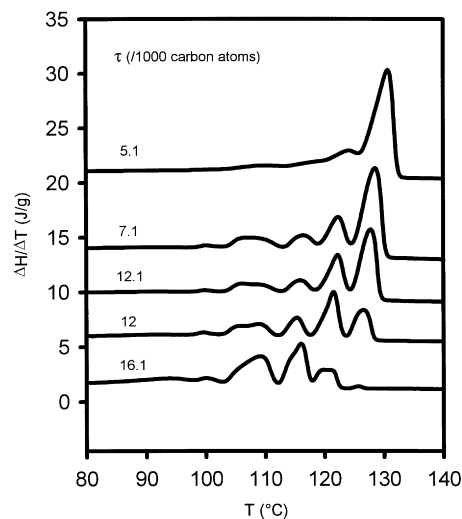


Fig. 9. Melting curves of the MSC treated fractions obtained by fractionation of the isothermally crystallized LLDPE sample.

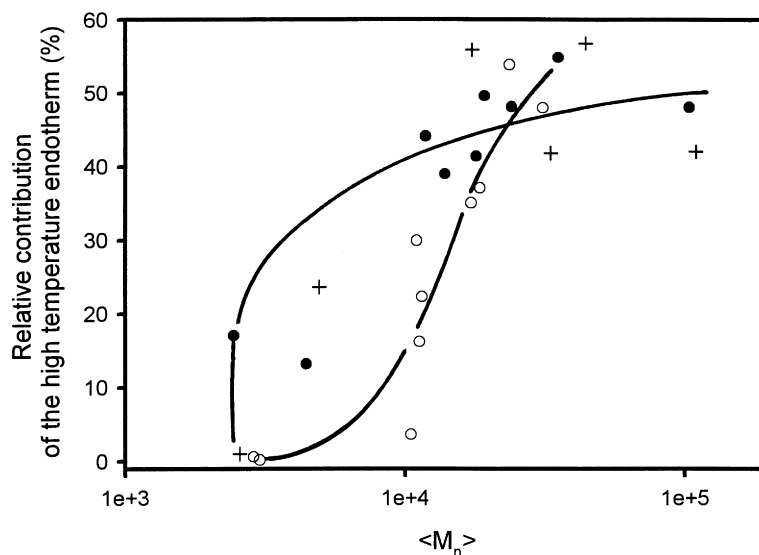


Fig. 10. Evolution of the relative contribution of the high temperature endotherm versus the number average molecular weight ($\langle M_n \rangle$) for the selective dissolution fractionation of the quenched sample (●), the isothermally crystallized sample (○) and for the SSF fractionation (+).

shows the melting curves recorded for some selected MSC treated fractions (obtained from a selective dissolution fractionation). As shown previously, the high temperature endotherms, with melting temperatures above 120°C, can be related to the melting of unbranched or weakly branched polymeric material. To compare the three fractionations of the Z–N copolymer, the evolution of the relative contribution of the high temperature endotherm is plotted against the number average molecular weight (Fig. 10). First, the fractions obtained by SSF and selective dissolution fractionation of the quenched copolymer exhibit the same tendency. The plot corresponds to a continuous evolution of the linear molecules contribution (high temperature endotherm) followed by a plateau for high molecular weight. This observation is typical of a fractionation sensitive to the molecular weight instead of the degree of short chain branching. On the contrary, the plot of the relative amount of linear molecules versus $\langle M_n \rangle$ obtained for the selective dissolution fractionation of the MSC copolymer corresponds to a discontinuous curve with a sharp increase observed for $\langle M_n \rangle$ slightly larger than 10 000. This observation is expected from the examination of the τ versus $\langle M_n \rangle$ plot (Fig. 7), i.e. the branched molecules correspond to molecular weights lower than 15 000. In addition, the fractionation of the MSC sample is also in agreement with the evolution obtained by SSF–TREF analysis for a similar LLDPE copolymer [11]. However, it should be noted that the variation of the melting enthalpy is related to a variation of crystallinity. As the molecules contained in the amorphous regions are not taken into account, only partial information is obtained. In addition, we note that the MSC–SD fractionation method described in this article was also used to characterize HDPE copolymers [15].

4. Conclusions

The study of the different fractionation procedures made by selective dissolutions or by SSF was realized. Our results clearly indicate that a fractionation procedure based on molecular segregation from the melt, consisting of the realization of multiple crystallization steps followed by selective dissolutions of the crystals appears to be an efficient, fast and easy method to characterize the heterogeneity in the comonomer distribution of a LLDPE copolymer. The combination of this fractionation procedure with the study of the melting of isothermally crystallized fractions gives a complete description of the copolymer similar to that derived from SSF–TREF analysis.

Acknowledgements

This work was supported by the European Union, the Walloon Region of Belgium in the framework of the FEDER–Objective 1 Program and the Belgian National Funds for Scientific Research (FNRS). The authors thank M.H.J. Koch for his fruitful discussions. C. Vandermiers acknowledges the European Commission for a grant. P. Damman is a Research Associate of the F.N.R.S.

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