Comparison of different methods for the investigation of the short-chain branching distribution of LLDPE

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Abstract

The aim of this paper is the comparison of three different methods for the investigation of the short-chain branching distribution of linear low-density polyethylene and the analysis of the composition of polyolefin blends. The three methods to be compared are analytical temperature rising elution fractionation (TREF), the commercialized Crystaf® technique, and a method based on differential scanning calorimetry with a special sample preparation procedure.

This paper also discusses the specific advantages and disadvantages of each method by comparing the results for selected Ziegler–Natta and metallocene LLDPE (ZN-LLDPE and mLLDPE, respectively) and a model blend of LLDPE, HDPE and PP. As is demonstrated for these materials the three analytical methods yield comparable results with respect to the comonomer distribution of LLDPE. For the investigation of polyolefin blends the combination of the three methods is found to be recommendable, especially if polymers with high degrees of supercooling like polypropylene are involved. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature rising elution fractionation; Crystaf; DSC

1. Introduction

The investigation of the short-chain branching structure of linear low-density polyethylene (LLDPE) has gained importance in the last decade. This is because of the increasing importance of LLDPE in the packaging industry as LLDPE has outstanding mechanical properties. These properties are a result of the short-chain branched molecular structure and its distribution. In contrast, the flow properties and the processing behavior are mainly influenced by the molecular mass distribution. Besides the molecular mass and its distribution, however, short-chain branches affect, e.g. the film blowing process as a consequence of their influence on the solidification of the blown film at the frost line. This is because of the crystallization kinetics of LLDPE being dependent upon the short-chain branching distribution. Therefore, the short-chain branching distribution also plays an important role with respect to the processing behavior of LLDPE.

Linear low-density polyethylenes are copolymers of ethylene and α-olefins. For polymerization different types of catalysts are used like Ziegler–Natta or metallocene. The short-chain branching distribution, often also denoted as chemical composition distribution, is a result of the structure and the active centers of the catalyst itself and the polymerization conditions [1]. Generally, metallocene catalysts yield a more homogeneous short-chain branching distribution than Ziegler–Natta catalysts.

As the degree and distribution of the comonomer affect the material properties there is a need to analyze the chemical composition distribution of LLDPE. A well-established method is the analytical temperature rising elution fractionation technique (TREF). As TREF is time-consuming a newly developed method (Crystaf®) analyzes the distribution of short-chain branching only during the crystallization procedure which is performed similarly to TREF. Both techniques involve a special chromatographic-like experimental setup not available in every laboratory. On the other hand, simple calorimetric measurements of the melting behavior (DSC) can also be used to obtain information about the short-chain branching distribution of LLDPE. To achieve a high resolution the samples need a special preparation, however, which is chosen to be similar to the two techniques mentioned earlier.

To our knowledge these three methods have never been compared in literature. The aim of this paper is therefore to discuss the specific advantages and disadvantages of each

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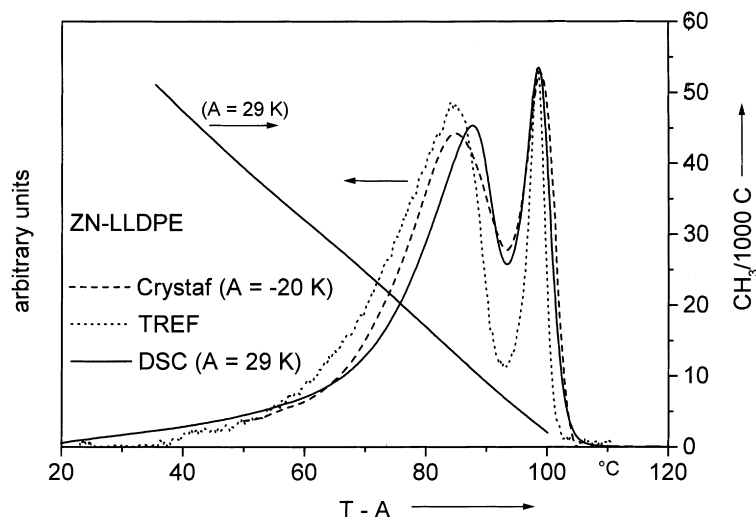   *E-mail address:* gabriel@ww.uni-erlangen.de (C. Gabriel).

Fig. 1. Comparison of the short-chain branching distribution of ZN-LLDPE as obtained by TREF, Crystaf and DSC. A calibration curve for the DSC-data is plotted on the right axis [12].

method by comparing the results for selected Ziegler–Natta and metallocene LLDPE (ZN-LLDPE and mLLDPE, respectively) and a model blend of mLLDPE, mHDPE and PP.

2. Experimental

2.1. Analytical temperature rising elution fractionation

Analytical temperature rising elution fractionation (TREF), a method being well established in the literature [1–9], separates the molecules of different degrees of short-chain branching macroscopically according to differences in crystallizability of the polymer chains. The fractionation procedure of TREF involves a slow crystallization step (cooling rate equal to 2–15 K/h) of the polymeric solution onto an inert support and a subsequent elution process in which the concentration of the polymeric solution is detected by an on-line IR-spectrometer. During the elution procedure the temperature of the solvent which is used to dissolve and therefore separate the differently branched chains is continuously increased (heating rate 50–100 K/h). At low temperatures molecules of high short-chain branching degrees are dissolved and subsequently detected by IR. With increasing elution temperature the less highly branched chains are separated. The concentration of the polymeric solution is then plotted as a function of the elution temperature, thus giving the short-chain branching distribution. TREF can be calibrated using preparative fractions of polyethylenes having well defined short-chain branching contents. A linear correlation between the elution temperature and the degree of short-chain branching is thus established for molecular masses exceeding 10^4 g/mol [3]. For a more detailed description of TREF and the theory of separation the reader is referred to literature, especially to

the reviews of Wild [8] and Glöckner [9]. The TREF-apparatus used in this publication is a self-developed equipment, which is located in the BASF laboratory.

2.2. Crystaf®

The analysis of the comonomer distribution by Crystaf[®1] is performed in a single step during the crystallization procedure of the polymeric solution [10]. The typical cooling rate is 12 K/h. The stirred solution is sampled at well-defined temperatures. These samples of the polymeric solution containing the non-crystallized fractions, only, are analyzed by an IR-spectrometer with respect to their concentration. As the specimens are taken during the crystallization step the information about the short-chain branching distribution is obtained in a cumulative way. By differentiation the directly measured cumulative distribution can be converted into a distribution curve that is similar to TREF-data. Besides the fast collection of data another advantage of Crystaf is that the soluble or noncrystallizable fraction can be determined quantitatively.

2.3. Solution crystallization with subsequent DSC-analysis

In order to gain information about the distribution of short-chain branching the melting behavior of LLDPE can be studied using thermal analysis. To achieve a high resolution in comparison to samples that are crystallized from the molten state a special sample preparation technique is applied. Wild et al. [11] proposed that samples should be slowly crystallized in a dilute solution, precipitated in methanol and dried under vacuum. The dried samples are then analyzed in DSC by measuring the heat flow as a function of temperature at constant heating rate. Molecules of

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[1] Crystaf is the trade name of an equipment manufactured by Polymer Char, P.O. Box 176, E-46980 Paterna, Spain.

different branching degrees will melt at different temperatures and it is therefore possible to obtain information about the short-chain branching distribution of LLDPE. The results from thermal analysis can also be converted to the degree of short-chain branching using calibration curves that are given in the literature [11–13].

The details of the sample preparation technique we have chosen are as follows: solutions of LLDPE in a suitable solvent (1,2,4-TCB, concentration 10 g/l) are cooled down in an oil bath from 150°C to room temperature at a slow cooling rate of 0.1 K/min. At ambient temperature the samples are precipitated in methanol and dried under vacuum for at least 12 h to evaporate the solvent. Subsequently the melting endotherms of the samples are determined in a differential scanning calorimeter (DSC) at a constant heating rate of 10 K/min.

To qualitatively compare the DSC-results with the other two analytical methods, as for example, in Fig. 1 only the excess heat flow of the melting peaks of the DSC-curve is displayed, i.e. the contribution of the baseline is subtracted. The heating scans in DSC have to be started at temperatures much below room temperature to obtain a reliable baseline.

3. Results and discussion

For the comparison of the three different methods two typical linear low-density polyethylenes are chosen.[2] One is a Ziegler–Natta LLDPE with 1-octene as a comonomer (ZN-LLDPE). The ZN-LLDPE is polymerized in solution at temperatures between 100 and 200°C and a pressure of 100 bar. The second LLDPE is a metallocene LLDPE with 1-butene as comonomer (mLLDPE). The densities of the two LLDPE are 0.9195 and 0.900 g/cm³, respectively. The two LLDPE are typical film grades with weight average molecular masses in the range of 100 kg/mol and a polydispersity of $M_{\mathrm{w}}/M_{\mathrm{n}} = 3$ for the ZN-LLDPE [14] and 1.9 in the case of mLLDPE [15]. In order to investigate the resolution and to demonstrate the effects of supercooling of the different analytical methods a model blend of three polyolefins is also investigated. It comprises the short-chain branched metallocene mLLDPE, a linear high-density metallocene polyethylene homopolymer (HDPE) and a high isotactic ZN-polypropylene (PP).

3.1. Comparison between analytical TREF, DSC and Crystaf®

With respect to the chemical composition distribution of the ZN-LLDPE a bimodal distribution is expected. Such a bimodal distribution reflects the heterogeneity of the incorporation of the comonomer into the growing polyethylene backbone during polymerization. As a result ZN-LLDPE in

general can be regarded as blends of highly short-chain branched and more or less linear chains. This composition distribution is, e.g. reflected in the bimodality of the temperature dependent concentration profile of the TREF-peak.

In order to compare the experimental results obtained by the three methods the DSC- and the Crystaf-curve of the ZN-LLDPE were shifted along the temperature axis to be superimposed with the TREF-peak at a temperature of 98°C. The height of the peaks at 98°C was chosen to be the same, therefore the y-axis is represented in arbitrary units.

As is obvious from Fig. 1 the different experimental methods agree very well in a qualitative way. The distribution curves have similar shapes and give a good picture of the short-chain branching distribution of the Ziegler–Natta LLDPE. The lower elution temperatures of TREF in comparison to the melting temperatures of the DSC-curve are because of the depression of the melting temperature by the solvent used in TREF. The degree of the depression of melting temperature can be calculated from the Flory–Huggins theory. The supercooling effect during crystallization is responsible for the temperature shift of the Crystaf results to even lower values.

The reason for the good agreement is the fact that the crystallization step is basically the same for the three methods. The crystallization step is the important procedure for the separation of the different molecules [8]. Differences in the method of the subsequent detection of the branching structure like, e.g. the elution procedure in TREF or the measurement of the heat flow in DSC do therefore not play a major role.

To test whether recrystallization phenomena occur during the heating scan in the DSC various heating rates between 2 and 30 K/min were also chosen (not shown in this publication). With an increase in heating rate the melting peaks of the Ziegler–Natta LLDPE shifted to higher temperatures as expected. A slight decrease in the difference of the melting temperatures of the two peaks of about 2 K was also observed. Smaller heating rates than 10 K/min resulted in a slightly better resolution of the two melting peaks, the overall shape of the melting range did not change much within this range of heating rates. Higher heating rates lowered the resolution considerably. As a standard heating rate a value of 10 K/min is therefore chosen which seems to be an optimum value with respect to resolution and required time of the experiments. It is nearly impossible that recrystallization takes place in TREF because of the macroscopic separation of the molecules in the elution step. From the good agreement with the measurement of the heat flow in DSC it follows that recrystallization phenomena do also not impair the DSC-measurements at the chosen heating rate of 10 K/min. The extremely low cooling rate in the crystallization step is another reason why recrystallization is not likely to occur in the subsequent heating scan.

It can be concluded that the results of analytical TREF and Crystaf as well as those of the DSC-method applied to

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[2] The LLDPE chosen for this publication are identical to the ones investigated rheologically in former publications: ZN-LLDPE is identical to LLDPE 1 in Ref. [14]; and mLLDPE is the same as mLLDPE 4 in Ref. [15].
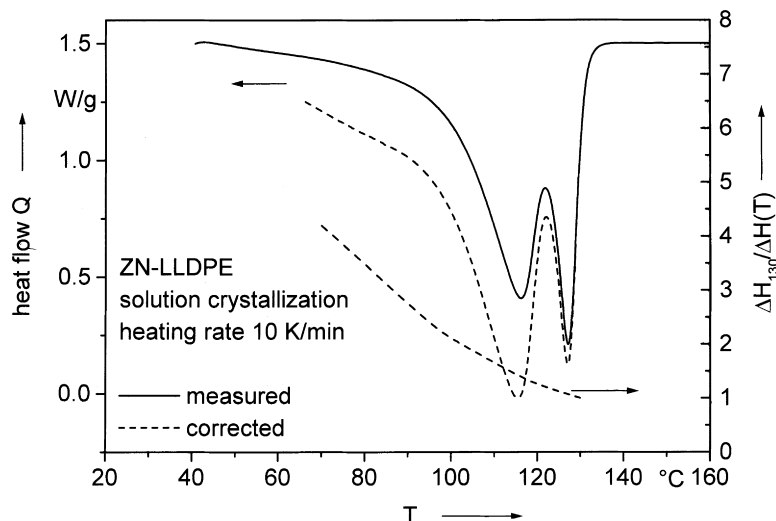
Fig. 2. Correction of the DSC curve of ZN-LLDPE for the heat of fusion.

samples that were slowly crystallized in solution agree very well in a qualitative way.

One drawback of the DSC-method is the fact that the distribution curve cannot directly be converted into a weight percentage of the components of different branching structures. This is possible for the TREF-analysis, because the distribution curve directly reflects the concentration at a given elution temperature. In TREF the relative amount of differently branched fractions can be calculated from the peak areas. In DSC the heat flow depends on the amount of the material melting at a certain temperature as well as on the temperature-dependent specific heat capacity. The temperature-dependence of the specific heat capacity c_p in the melting regime of LLDPE leads to an increase in the heat of fusion with decreasing comonomer content [11]. Wild et al. determined the heat of fusion for a series of preparative fractions of a 1-butene LLDPE as a function of their melting temperature. Taking the ratio of the heat of fusion at a temperature of 130°C for a linear fraction (ΔH_{130}) and the temperature-dependent heat of fusion ($\Delta H(T)$) the DSC curve can be converted into a weight-dependent distribution curve (e.g. Wild et al. [11]). The temperature-dependent function $\Delta H_{130}/\Delta H(T)$ is shown on the right axis in Fig. 2. With the data obtained by Wild et al. [11] the DSC curve of ZN-LLDPE is converted into such a weight dependent curve in a temperature range between 60

and 130°C (Fig. 2). From the area of the corrected melting peaks the relative amount of linear and short-chain branched fractions can be calculated. By comparing the peak areas of the raw data and the corrected heat flow it is obvious that the relative amount of the short-chain branched fraction is underestimated in the raw data of DSC. It is also obvious that such a correction does not very much influence the area of the melting peak at higher temperatures, which represents the more or less linear fraction.

Nevertheless, this effect does not seem to be very important at least for obtaining a qualitative insight into the branching distribution of LLDPE. The correction of the DSC-data for the heat of fusion in principle allows for the quantification of the relative amount of linear and short-chain branched fractions. As the heat of fusion for highly branched fractions is not well known below a melting temperature of 60°C these data obtained by DSC and TREF are not compared.

The correction of the heat flow does not have much influence on the position of the melting peaks. From calibration curves established in literature it is possible to calculate short-chain branching degrees from the temperature positions of the maxima of the melting peaks of the DSC data. With the calibration data supplied by Wild et al. [11], which are plotted on the right axis in Fig. 1, the following values were obtained for ZN-LLDPE and the metallocene LLDPE that is investigated in Fig. 4. From the comparison of calibration curves for different types of comonomer no systematic tendency can be found. In Table 1 we did therefore not distinguish between the different comonomers of ZN-LLDPE and mLLDPE. A calibration curve for TREF-data is, for example, published by Mirabella and Ford [4]. For Crystaf the calibration curve published by Monrabal for 1-octene LLDPE fractions [10] is used for the comparison.

A good agreement between the branching degrees of the highly branched fraction of ZN-LLDPE is found for the three methods. A similar agreement is also found for the short-chain

Table 1
Comparison between short-chain branching degrees (CH$_3$/1000°C) of ZN-LLDPE and mLLDPE obtained by TREF, Crystaf and DSC

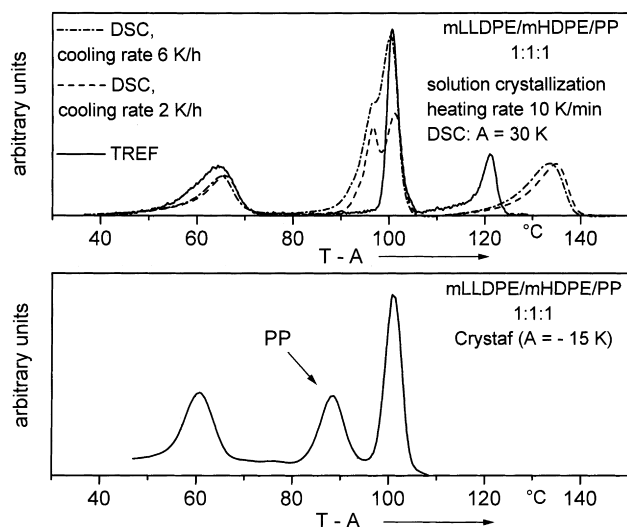|	Peak 1 (low comonomer content)			Peak 2 (high comonomer content)		
	DSC	TREF	Crystaf	DSC	TREF	Crystaf
ZN-LLDPE	2	1	4	10	10	12
mLLDPE	–	–	–	24	22	–

Fig. 3. Comparison of the three methods for a model blend of mLLDPE/mHDPE/PP.

branching degree of mLLDPE. The agreement is worse, however, for the short-chain branching degree of the less branched fraction of ZN-LLDPE.

These findings underline the usefulness of the simple DSC-method for the investigation of the degree of short-chain branching of LLDPE.

3.2. Investigation of model blends

From the comparison of the distributions of short-chain branching obtained by the different methods it could be concluded that they give a good qualitative agreement (Fig. 1). In order to test the performance of the methods with a more difficult system the model blend of three poly-olefin components is investigated (Fig. 3). For the blend of mLLDPE, mHDPE and PP three distinct peaks are expected reflecting the differences in crystallizability of the three components. The TREF-data, which are regarded as a reference for this model blend, indeed exhibited an excellent separation of the three components in the concentration profile of the elution diagram. The elution temperature increases in the order of mLLDPE, mHDPE and PP (Fig. 3).

The DSC-experiments were performed with two different preceding cooling rates during the sample preparation procedure (2 and 6 K/h). To compare the DSC-data with TREF the DSC-curves were shifted by 30 K to superimpose the HDPE-peaks at 100°C. Also for the DSC-data three distinct melting peaks are observed, which means that a complete separation of the three components is obtained. The mHDPE- and the mLLDPE-component have got similar positions on the temperature axis for the shifted DSC-results (at a cooling rate of 6 K/h) and the TREF-data. A similar agreement between the two methods was already reported for ZN-LLDPE (Fig. 1). The PP-peaks, however, are separated on the temperature axis by 13 K. The DSC-peak is found at a higher temperature than that from TREF.

For Crystaf the shift of the PP peak is even larger than for TREF, which is a result of the high degree of supercooling of polypropylene. The maximum of the PP peak is detected at a shifted temperature of $T - A = 89°C$, it is therefore located in between the peaks of mLLDPE ($T - A = 61°C$) and mHDPE ($T - A = 100°C$) (lower part of Fig. 3). As the tacticity of polypropylene influences the crystallization temperature especially the combination of the three methods allows for the exact determination of the composition of a polyolefin blends from the differences in the degree of supercooling. This is for example important in the case of LLDPE/PP-blends for which the crystallization temperatures of the two components might overlap and are therefore not distinguishable in Crystaf[®].

As was already mentioned the DSC-experiments were performed with samples that had been prepared using two different cooling rates. The differences in the shape of the melting peaks of the HDPE-component are obvious from Fig. 3. The smaller the cooling rate during sample preparation the more pronounced is the bimodality of the melting peak. Wild et al. [11] also found a slight shoulder for a similar model blend, but he only investigated samples prepared with a fixed cooling rate. As our experiments demonstrate the appearance of the shoulder strongly depends on the cooling rate during sample preparation. At a cooling rate of 2 K/h the shoulder develops into a double peak. This observation can be explained by a cocrystallization of mLLDPE and HDPE that is more likely to occur for a smaller cooling rate. In addition, the relatively high concentration of the solutions in our experiments might be another reason for the observed cocrystallization. Nevertheless, in the experiments of Wild et al. such a splitting of the HDPE peak was found at a concentration of the solution that was ten times smaller than in our case. From this result the conclusion can be drawn that the cooling rate during sample preparation is the important parameter for the cocrystallization to occur in the DSC-experiments. The influence of the preceding cooling rate on the mLLDPE- and the PP-peak can be regarded to lie within the accuracy of the measurements.

As Monrabal [10] pointed out cocrystallization can also occur in Crystaf at higher concentrations and slow crystallization rates. The absence of cocrystallization in TREF was demonstrated by Wild [8] using a three component blend of polyethylenes of narrow short-chain branching distribution.

It is obvious from our results that the DSC-method using the special sample preparation technique is suitable for the investigation of the composition of polyolefin blends.

From the data presented in Figs. 1 and 3 it could be concluded that TREF is the preferable technique for studying the short-chain branching distribution of LLDPE as the TREF-curves show the narrowest peaks and the best resolution in comparison to the other methods. The DSC-technique, however, clearly reveals a very broad melting region in the case of the metallocene LLDPE (mLLDPE) with a
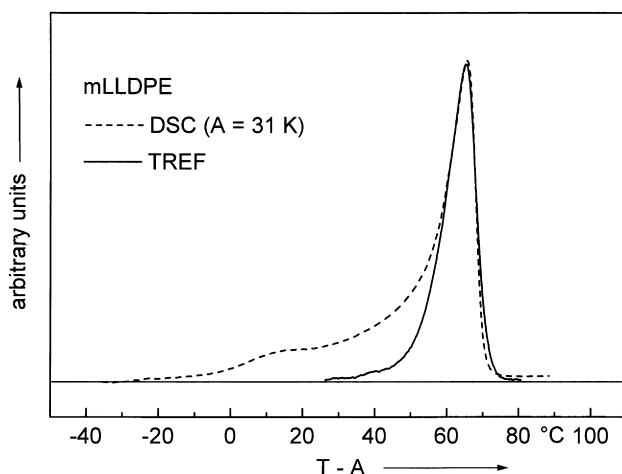
Fig. 4. Comparison of TREF and DSC for the metallocene mLLDPE.

pronounced shoulder at very low temperatures (Fig. 4). This broad melting regime reflects the fact that highly branched molecules crystallize and melt at temperatures that are close to ambient temperature. In contrast, TREF yields a much more narrow distribution curve without resolving the highly branched fraction that is detected by DSC. It has to be mentioned that the shoulder in the melting endotherm of mLLDPE can also be seen by measuring the untreated pellets. The shoulder displayed in Fig. 4 is therefore not an artifact from sample preparation.

There are two possible reasons for these differences. One reason is that in TREF 1,2,4-TCB is used as a solvent. The crystallization step can therefore not be expanded to temperatures below 20°C, because otherwise the solvent would solidify. The other reason could be that block-like structures of high and low comonomer content are present amongst the molecules of mLLDPE. It can be assumed that the different blocks crystallize separately at different temperatures. In TREF such a block-like molecule will be detected at the (higher) elution temperature of the block containing less comonomer [16], because the highly branched blocks cannot be eluted if they are still fixed to the less branched blocks. In DSC, however, the melting of differently branched blocks can be detected in the heat flow.

4. Conclusions

The aim of this paper was the comparison of three different methods for the investigation of the short-chain branching distribution of linear low-density polyethylene and for the determination of the composition of polyolefin blends. As was demonstrated for typical Ziegler–Natta and metallocene LLDPE the methods TREF, Crystaf and DSC, using a special sample preparation technique, yield comparable results. The results of the three methods are qualitatively comparable with respect to the distribution of comonomer and the branching degree of the fractions. This is especially

important because the rather simple DSC-method yields equivalent results even without correcting the measured heat flow for the temperature-dependent heat of fusion.

Several conclusions have to be drawn from the experimental results with respect to specific features of the three methods. The unique advantages of TREF are the excellent separation and the correspondingly high resolution of differently branched components in polyolefins and the possibility to directly calculate the composition of polyolefin blends from the weight dependent distribution curves. The disadvantages of TREF are the poor resolution with respect to highly branched fractions eluting at low temperatures and the time consumption of the experiments.

The advantages of TREF also apply to a great extent to Crystaf with the additional advantage of shorter analysis times. The most obvious disadvantage of Crystaf is the large effect of supercooling in the case of polypropylenes, especially if polyethylene-polypropylene blends have to be analyzed.

Besides its simplicity other advantages of the DSC-method are the good agreement with TREF- and Crystaf-results for ZN-LLDPE and the resolution of highly branched components that cannot be detected in TREF. The usefulness of DSC was also demonstrated by the investigation of a model blend of three components where a good separation comparable to TREF and Crystaf was achieved. Of practical importance is further that the melting temperatures determined by DSC can directly be correlated to mechanical properties or the processing behavior of polyolefins. The most obvious disadvantage of DSC is that the melting curves have to be transformed into weight dependent curves taking the heat of fusion into account.

For the investigation of polyolefin blends a combination of the three methods is recommendable, especially if polymers with high degrees of supercooling like polypropylene are involved.

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