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A New Route for Evaluating Short Chain Branching Distribution of High Density Polyethylene by Measuring Crystallizability of Molar Mass Fractions

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A bimodal high density polyethylene (HDPE) has been successfully fractionated by analytical size exclusion chromatography into molar mass fractions with M_w's ranging from 3.6 kg/mol to 8 000 kg/mol, and subsequently deposited on germanium disks using the Lab Connections Transform method. After removal of the fractions from the disks, having masses in between 10 µg – 150 µg, differential scanning calorimetry has been successful in measuring the (re)crystallization and melting behavior of these fractions. Comparing the crystallization and melting peak temperatures of the fractions with those of narrow molar mass linear polyethylenes points to the HDPE being linear below and short chain branched above 100 kg/mol respectively. This value coincides roughly with the 'split' between the molar mass distributions resulting from the first and the second polymerization reactor – confirming the addition of 1-butene in the second reactor.

Keywords: linear polyethylene (LPE); bimodal high-density polyethylene (HDPE) PE100; short chain branching (SCB); size exclusion chromatography (SEC); High Performance DSC (HPer DSC); Lab Connections (LC) Transform.

1. INTRODUCTION

One of the challenging issues in the characterization of pipes, as used for transporting of water and gas, is the determination of the Short Chain Branching Distribution (SCBD) across the Molar Mass Distribution (MMD). Many publications stress the existence of a link between the way of distribution and the long-term (tens of years) properties. However, because of the very low amount of SCB present in the pipes produced, at the moment only IR is able to give correct and quick answers. However, the result is the average SCB content. Therefore, to obtain information on a possible SCBDistribution per fraction, alternative methods have to be explored, and in this publication such a method is reported based on the strong influence of SCB on crystallizability.

Normally, in order to be able to study a property like SCB as function of MM, a fractionation is performed by using techniques on a preparative scale, like solvent-gradient solution separation [2]; direct extraction (DE) or Holtrup method [3 – 7]; or preparative size exclusion chromatography (PSEC) [8]. This enables e.g. measuring the SC) content of the fractions by IR or NMR, resulting in information about the average SCB per fraction [2, 5, 6, 8, 9].

In case of possible heterogeneity of the SCBD, the preferred way to get a detailed insight in the molecular structure is performing crossfractionation, at best by starting a fractionation according to MM and subsequent fractionation according to crystallizability, followed by characterization of the cross fractions, each of them narrow with respect to MMD and SCB. Crystallizability as a discrimination parameter is used because crystallization and dissolution are known to be influenced very much by the SCBD. Typical techniques to be applied are crystallization analysis fractionation (CRYSTAF) [10] and fractionation by dissolution subsequent to crystallization [4, 5, 8], as is also the case in Temperature rising elution fractionation (TREF) [2, 11]. Obviously, one then has to find a way for calibration of the SCB content, like by applying NMR to Preparative TREF (PTREF) [12] and CRYSTAF (PCRYSTAF) [13] fractions.

It has to be remarked that the benefit of crystallizability as tool to get information about SCBD is hampered by the fact that – even during crystallization from a solution – cocrystallization of chains will occur, by which simultaneous crystallization of chains having a not-too-different chain microstructure can occur and therefore a split according to SCB cannot be realized fully.

In the present study, a new way of (cross)characterization of a polymer is reported using the capabilities of HPer DSC [1] in the combination of ASEC – Lab Connections (LC) Transform – HPer DSC [19]. It starts with a fractionation according to MM –which is anyhow the best (unequivocal) way of starting as has been demonstrated for the HDPE Hizex 7000 F [4, 8] – followed by a study of the crystallization and melting behavior of the MM fractions obtained by HPer DSC instead of a subsequent (physical) crystallizability fractionation. Evaluation of the results will also provide information about possible heterogeneity of the SCBD per MM fraction, even though, the

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interpretation will be hampered by the occurrence of cocrystallization, the influence of entanglements etc.

2. EXPERIMENTAL PART

In the research a bimodal HDPE, type PE100 (PE100 stands for material of the highest-pressure standard), has been studied. It was produced in two reactors [20 – 22] using a Z-N (Ziegler-Natta) catalyst/cocatalyst in a slurry process, with hexane as solvent. In the first reactor, no SCB is incorporated into the macromolecules; in the second reactor 1-butene was added, resulting in 3.3 CH_3/1000C in total for side chain branches as measured by NMR.

The HDPE PE100 (PE100 hereafter) sample (pellets) has been analyzed using a PL (Polymer Laboratories) 220 chromatograph equipped with five polystyrene columns and an RI-detector at a flow rate of 1 ml/min. The specification of the columns was SDV-gel 2, 3, 5, 6, 7 (column dimensions 8.0 mm × 300 mm). These columns are not optimal for the high MM region. The eluent was 1,2,4-trichlorobenzene, stabilized with BHT. Guard column: SDV-gel 10 μm (8.0 mm × 50 mm). The measurement temperature was 140 °C.

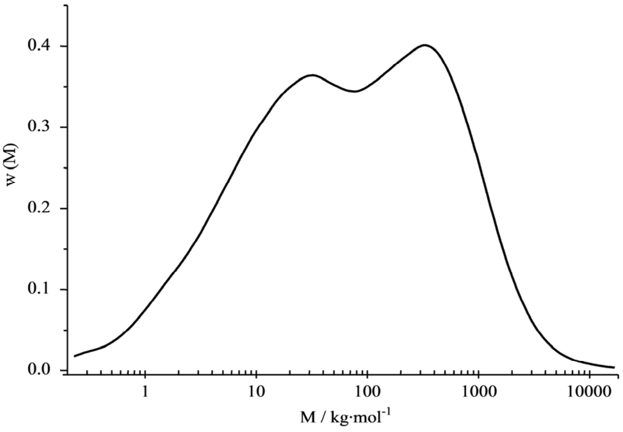

Fig. 1. ASEC curve of PE100, PS-based calibration, recalculated to PE

The values of the molar masses for the PE100 whole polymer and its fractions, see Table 1, are PE-based; they were calculated using the Mark-Houwink equation based on a PS-calibration using narrow MM standards. The factor between M(PE) and M(PS) is taken as 1.3. The ASEC curve, Fig. 1, shows the characteristic bimodal behavior for the MMD. The 'split' – the local minimum indicating the overlap region between the Low MM and High MM components of the bimodal MMD – is situated just around 100 kg/mol.

The M_v's, the viscosity-average MM values, of the LPEs in Table 1 have been taken from [8].

By the ASEC columns all additives, pigments, nucleants and stabilizers are removed. Because of lack of stabilizers in the fractions, some degradation could occur. Actually, the fractions of the bimodal PE100, as combined from different depositions on different disks, are yellowish /brownish. Still it is not expected that appreciable degradation occurs, because a few molecules can cause such discoloring, while the subsequent HPer DSC measurements are performed under a Neon/Helium gas mixture.

2.1. Molar mass fractionation and collection of fractions

Fig. 2 schematically shows the route followed: fractionation of the PE100 according to MM by ASEC; subsequent deposition of the fractions on a rotating disk using a LC Transform set up [23], and finally off-line HPer DSC on the fractions.

The elution rate of the ASEC was 1 ml/min; the rotation speed of the (germanium) disk was 10°/min, so 10° corresponds to 1 ml, see Table 1.

Normally 600 μg to 800 μg of a whole polymer on a disk is the maximum amount to be deposited. However, the PE100 is much more difficult to deposit: spraying of the low MM fractions is not precise, material gets lost sideways of the disk; high MM fractions do crystallize at the nozzle. That is why 200 μg per deposition on a disk is about the maximum for polyethylenes at the moment.

Because the ASEC procedure will influence crystallization and melting behavior, and for optimal comparison with the fractions, also the PE100 / whole sample was run through the SEC – LC Transform – HPer DSC combination twice. The two separate depositions, each of 200 μg, on one disk (two spots) have been collected using an aluminum foil and subsequently measured as a whole. Thus, in total, 323 μg has been collected and measured, see Table 1. Obviously, 77 μg has been lost throughout the fractionation and working up, especially during spraying on the disk and may be also during mechanical removal by scraping.

The fractions of PE100 were obtained by combining material from various depositions on various disks: 3 disks of 200 μg each and 1 disk of 300 μg, so 900 μg starting mass in total. In the end, 621 μg in total has been collected and measured, see Table 1. Thus, an appreciable amount of material, 279 μg, has been lost during the procedure. Obviously, this is one of the items to be improved [24].

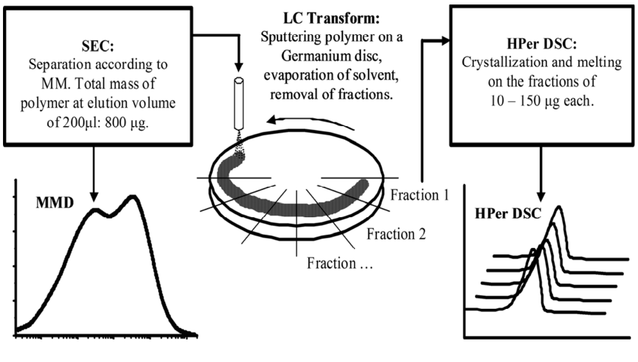

Fig. 2. The ASEC - LC Transform - HPer DSC combination

Since the amount of starting material for ASEC (at the moment typically 800 μg of polymer) has decreased over the years (20 years ago it was typically 5 mg), at the start of this study it was anticipated that the recently developed HPer DSC [1] could be of help, because HPer DSC improves the sensitivity of the measurement by its capability to realize higher cooling and heating rates (±500 °C/min maximum).

Table 1. Molecular characteristics of the LPEs and of the HDPE PE100 and its fractions; and the HPer DSC sample masses used

HDPE PE100	ASEC Elution volume (ml)	LC Angle (°)	ASEC M_n (kg/mol)	ASEC M_w (kg/mol)	ASEC M_z (kg/mol)	HPer DSC Sample mass (mg)
Whole polymer [a]			7.1	343	2 400	0.323
Fractions						
F1	<27	<70	7 600	8 000	8 500	0.012
F2	27–29	70–90	2 600	2 800	3 400	0.041
F3	29–31	90–110	880	975	1 080	0.081
F4	31–33	110–130	310	340	370	0.136
F5	33–35	130–150	118	126	136	0.143
F6	35–38	150–180	38	44	50	0.152
F7	38–41	180–210	11	13 000	14	0.026
F8	>41	>210	3.0	3.6	4.0	0.030
Total mass of fractions						0.621

LPEs	Viscosity based molar mass M_v (kg/mol)	HPer DSC Sample mass (mg)
SNPA 1B-I	13.6	0.930
SNPA 2B-I	32.2	1.310
SNPA 3B-I	65	0.990
NBS SRM 1484	119.6	1.070
SNPA 5A	218	0.817
SNPA 7A	730	1.095

[a] Also ran through the SEC – LC Transform – HPer DSC combination.

2.2. HPer DSC measurements

The HPer DSC measurements have been done with a PerkinElmer PYRIS Diamond DSC, equipped with a Cryofill liquid nitrogen cooling system. A Neon/Helium gas mixture (90/10 %-vol), flow rate ~(20 – 30) ml/min has been used as purge gas, enabling measurements in between –180 °C and 580 °C, with a dry nitrogen air shield.

Temperature calibration was performed using adamantine, benzophenone, indium and tin at a scan rate in heating (S_h) of 10 °C/min with 1 mg samples. The heat flow rate was calibrated using 1 mg samples of indium and tin at the same heating rate of $S_h = 10$ °C/min.

The temperature program for the HPer DSC measurements on the LPEs and on PE100 and its fractions was as follows: melting at 180 °C for 3 minutes; cooling at a scan rate (S_c) of 5 °C/min or $S_c = 150$ °C/min to 0 °C; holding at 0 °C for 5 minutes; heating at a scan rate of $S_h = 5$ °C/min or $S_h = 150$ °C/min to 180 °C in case cooling was done at $S_c = 5$ °C/min or $S_c = 150$ °C/min respectively.

For the sample containment, 19.1 mg ±0.1 mg aluminum foils [1] were used to have an appropriate area for deposition and wrapping of the debris from wiping the knife used to scrape the material from the disk.

In the present research, the sample masses have been chosen to be within 1.0 mg ±0.3 mg, see Table 1 for the LPEs. In case it is not possible to make a choice – like for most of the ASEC fractions where the yield is limited, see Table 1 – corrections for the influence of sample mass have been made as based on [25]. The data reported in [8] have been obtained on (the same) LPEs, having sample masses within 0.800 mg ±0.025 mg.

All HPer DSC curves presented in this report have been corrected [25] for cooling and heating rates, using extrapolated onset temperatures of indium by way of the specific 'black box' formula mirroring around 0°C/min. The crystallization peak temperatures, shown in Fig. 4, have in addition been corrected for sample mass and scan rate using the specific 'black box' formula for indium given in [25].

3. RESULTS AND DISCUSSION

3.1. LPEs

HPer DSC results for the crystallization peak temperatures, T_c, of the LPEs by cooling at 5 °C/min, see Fig. 4, show that with increasing MM, crystallization of LPEs takes place at decreasing temperatures, and then levels off to more or less constant temperatures. This confirms earlier experiments on many more LPEs [8] where in addition at very low MM (narrow MM LPEs up to 20 kg/mol were studied while literature data on paraffins was added) first an increase of the crystallization temperature with increasing MM is seen.

Such increase of the crystallization peak temperatures with increasing MM is what one usually expects; it parallels the well-known increase of the melting peak temperatures with increasing MM. The subsequent decrease and leveling off of the crystallization peak temperatures with increasing MM is not widely known. The maximum is caused by an increasing influence of entanglements, hindering crystallization, while the leveling off is understood by the fact that at high MM the segments in long chains crystallize independently of each other: they also become fixed at various places in the same and in different crystallites. As a result, the length of the chain itself is not the key factor anymore.

The decrease and leveling off of the crystallization temperatures with increasing MM is not paralleled by a same behavior of the melting temperatures due to the fact that during heating, subsequent to crystallization, extensive reorganization takes place, resulting in an increase of the perfection and/or of the dimensions of the crystallites. This reorganization causes the melting peak temperatures (T_m) to increase with increasing MM, resulting in the well-known $T_m(M)$ relationship which has been reported in literature for long, see [8] for discussion and for relevant references.

It is striking that the new results for the crystallization peak temperatures shown in Fig. 4 (using the Diamond DSC and the Pyris 1 DSC) at 5 °C/min match within 1 °C with the DSC-2 values measured in the late seventies [8], though the equipment and conditions used are quite different.

As the reproducibility is excellent, the measurements done on the LPEs obviously are very useful for comparison with results on short-chain branched samples: the idea is that the data on the LPEs function as reference values, providing the influence of MM on crystallization. Any remaining difference between T_c's of HDPE and LPE is then ascribed to the influence of SCB. Besides the data for crystallization shown here, in the same way also the data for melting will be used.

One has to realize that it is not implicated that the way of crystallization and melting of LPEs and short chain branched polyethylenes is the same: the short chain branches and the ethylene sequences in between them have a crucial and different influence on crystallization compared to segments of linear chains.

Thus, results have been obtained using two simple thermal histories: the combinations of cooling/heating at 5/5 °C/min and of 150/150 °C/min. In case of double melting peaks, occurring for some samples measured at 5 °C/min, the lowest-temperature peak values have been used as these reflect melting without recrystallization.

The HPer DSC heat flow rate measurements done at 150 °C/min after cooling at the same rate (not shown here) appear to have, for all samples, just one melting peak. Obviously, recrystallization is hindered effectively by the higher heating rate.

3.2. Short chain branched PE100 and its fractions

As an example of the measurements performed, Fig. 3 presents the heating curves at 5 °C/min, after cooling at 5 °C/min for PE100. Noise is noticeable, though it is not hampering the evaluation. However, it is seen that for fractions F2, F3 and F8 determination of the peak maxima becomes tricky. At 150 °C/min (not shown here) however, no noise is discernible while the evaluation of the peaks of fractions F2, F3 and F8 poses no problem at all, confirming that the increased sensitivity because of the higher heating rate is of great benefit.

In both cases fraction F1 does not give an interpretable curve. Most probably, this is mainly caused by the high molar mass of 8000 kg/mol which hinders crystallization appreciably and less by the small heat flow rate as caused by the low sample mass of 12 µg. The data, obtained in cooling and heating at 5/5 °C/min and 150/150 °C/min respectively for the LPEs and PE100 fractions, have been compared, and Fig. 4 presents an example for the scan rates of 5/5 °C/min. All data were corrected for the sample mass and scan rate (see Experimental).

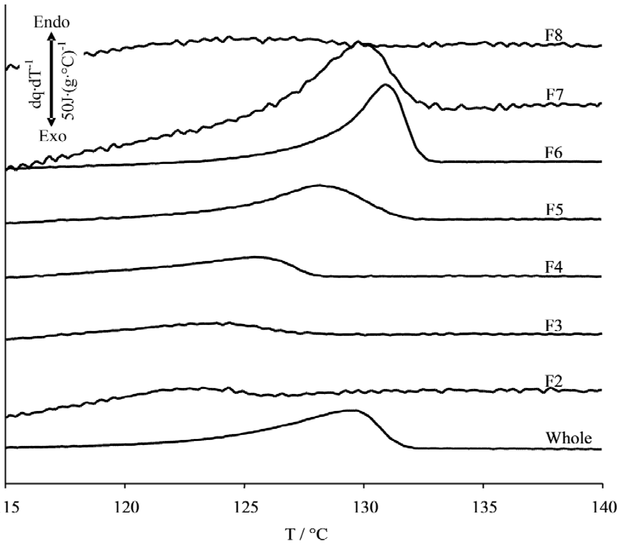

Fig. 3. HPer DSC curves at a scan rate in heating (S_h) of 5 °C/min after crystallization at the same rate showing the molar mass dependence of melting of PE100 whole polymer and its fractions

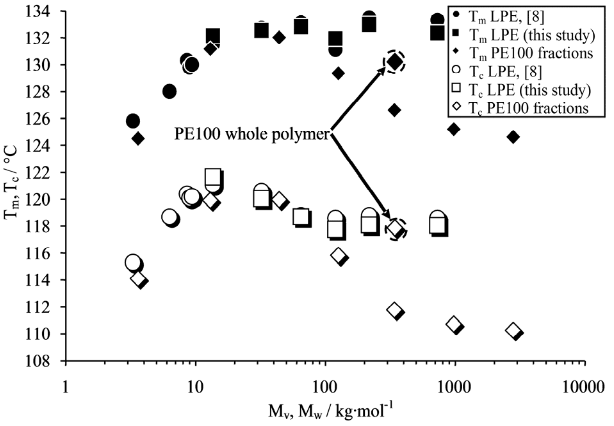

Fig. 4. T_c and T_m as function of molar mass from HPer DSC cuves at scan rates of 5/5 °C/min in cooling/2nd heating respectively, for LPEs and for PE100 whole polymer and its fractions

From Fig. 4, it is evident that for low MM, up to roughly 100 kg/mol (which value roughly coincides with the split between the MMDs resulting from the polymerizations in the 1st and 2nd the reactor), the data of the LPEs and of the PE100 fractions do not differ significantly. Therefore, up to that MM the chain structure of PE100 is concluded to be linear.

Above 100 kg/mol the differences between the peak temperature values for LPE and for the PE100 increase with increasing MM, for both crystallization and melting. These differences point to the presence of SCB at higher MM. The same behavior is found for the 5/5 °C/min combination and the 150/150 °C/min combination. Origin and nature of SCBD along MMD of the HDPE PE100 materials are explained in more detail in the next section.

3.3. The SCBD along the MMD

Despite bimodal HDPEs are being in use for quite a while now, few information about characteristic SCBDs across the MMD is published up to now in open literature, most probably because of its sensitivity with respect to industrial proprietary. Nevertheless, based on the scarce information available, it is possible to arrive at a simplified but realistic understanding.

As remarked in [20]: "bimodal production technologies include different combinations of all the main low pressure polymerisation processes and reactor types". However, the desired SCBD along the bimodal MMD [26] is nowadays mostly realized by using a tandem reactor process with different feeds and conditions [20, 22]. Either the low molar mass component is made in the first reactor, followed by the high molar mass component in the second one (the 'normal' mode), or the other way around (the 'reversed' mode) [20]. In the normal mode, the feed of the first reactor typically contains just ethylene and a high amount of hydrogen what leads to formation of low molar mass polyethylene (supplying the 'low MM' component of the final MMD), because the hydrogen gas leads to chain termination and produces saturated chain ends. The second reactor is typically fed with much less hydrogen and in addition with an 1-olefin comonomer, leading to a short chain branched 'high MM' component of the final MMD [20 – 22].

Therefore, is assumed that, in first order, the bimodality of the MMD and of the SCBD connected can be seen as caused by addition of two, quite different, unimodal MMDs with their respective SCBDs. Thus, the first focus is to find out possible SCB profiles across the MMD for unimodal HDPEs.

As is well known, comonomers, incorporated by active sites of the Z-N catalyst used also act as 'chain propagation stoppers' resulting in shorter macromolecules. Therefore, the SCB content typically decreases with increasing MM. This behavior is well documented for Z-N unimodal HDPEs [11] and for Z-N linear low-density PEs (LLDPE) [2, 5, 16, 27]. Following recent SEC-FTIR [12, 17], the decrease is most rapid at low MM while the SCB content shows a steady decrease with increasing MM.

In contrast to the Z-N produced unimodal HDPEs, some catalysts result in a constant SCB with MM, as in case of certain types of metallocene catalysts [12] and modified chromium oxide catalysts [12, 17].

Based on the sketched SCB profiles across the MMD of unimodal Z-N HDPEs as found in literature, an educated guess can be made for the case of bimodal Z-N HDPEs as produced using a tandem reactor processes. When the low MM component does not contain any comonomer and only the high MM component contains comonomer, then the SCB vs. MM relationship of a bimodal Z-N HDPE must have a maximum [9, 17].

In the present case, a maximum value of SCB is reached at approximately 100 kg/mol and a subsequent constant or possible decrease of SCB with increasing MM is found by Scholten et al. [6]. Liu et al. [9] reported a maximum of SCB with MM just below 100 kg/mol, from fractionation by MM and subsequent measurement of SCB by NMR for a bimodal HDPE PE100 as produced in a single gas phase reactor using engineered catalyst technology. DesLauriers et al. [17] reported a maximum just above 100 kg/mol for a Ziegler-based bimodal resin and remarked "Thus, SCB in the bimodals tends to fade away in the very highest MM chains, despite the selective blending of high SCB/high MM with low SCB/low MM". Ortin et al. [15] presented data from a cross fractionation (ATREF followed by ASEC) and a maximum of SCB(M) in between approximately 300 kg/mol and 1000 kg/mol is reported. In view of the foregoing, it is remarkable that in some articles sketches are presented showing just a continuous increase in SCB with increasing MM of bimodal Z-N HDPE [7, 21, 22]. Most probably, this is caused by not taking into account the behavior of the highest molar mass fractions. However, though unusual, a continuous increase in SCB of a bimodal whole polymer with increasing MM is feasible – for example by using single site catalysts – and has also been achieved by blending of well-chosen components [12, 28].

Our results coincide well with up-to-date understanding of SCBD of the PE100 HDPE, and illustrate the applicability of the new ASEC – LC Transform – HPer DSC method as an useful route for evaluating molecular structures, in addition to the useful-as-such and straightforward obtained information about crystallization, melting and thermal properties in general.

CONCLUSIONS

A new method has been successfully applied to a crystallizable polymer (HDPE is taken as an example) in order to determine possible SCB across the MMD: fractionation by ASEC according to MM; depositing of the polymer on a disk using a LC Transform device; removal of MM fractions from the disk and finally measuring the crystallization and melting behavior of the fractions by HPer DSC. From comparison of the data obtained on the LPEs and on the PE100 fractions it is concluded that for MM up to approximately 100 kg/mol (roughly the MM of the split between the MMDs from the polymerizations in the 1st and the 2nd reactor) the chain structure of PE100 is linear. Above 100 kg/mol the comparison points to the presence of SCB at higher MM.

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REFERENCES

1. **Pijpers, T. F. J., Mathot, V. B. F., Goderis, B., Scherrenberg, R. L., van der Vegte, E. W.** High-Speed Calorimetry for the Study of the Kinetics of (De)vitrification, Crystallization, and Melting of Macromolecules *Macromolecules* 35(9) 2002: pp. 3601 – 3613.
2. **Hosoda, S.** Structural Distribution of Linear Low-density Polyethylenes *Polymer Journal* 20 (5) 1988: pp. 383 – 397.
3. **Holtrup, W.** The Fractionation of Polymers by Direct Extraction *Makromolekulare Chemie* 178 (8) 1977: pp. 2335 – 2349.
4. **Mathot, V. B. F., Pijpers, M. F. J.** Crystallization and Melting Behavior of Polyethylene Fractions Obtained by Various Fractionation Methods *Polymer Bulletin* 11 (3) 1984: pp. 297–304.
5. **Mathot, V. B. F.** Polycon '84, Proc. Meeting on LLDPE, Organized by PRI and SPE. Leeuwenhorst, The Netherlands, 9 – 11 May 1984, p. 1.
6. **Scholten, F. L., Rijpkema, H. J. M.** In Proc Plastics Pipes VIII, Koningshof, near Eindhoven, The Netherlands, Sept. 21 – 24, 1992; The Plastics&Rubber Institute / Institute of Materials: London, 1992.
7. **Alt, F. P., Böhm, L. L., Enderle, H.-F., Berthold, J.** Bimodal Polyethylene – Interplay of Catalyst and Process *Macromolecular Symposia* 163 2001: pp. 135 – 143.
8. **Mathot, V. B. F.** The Crystallization and Melting Region. In: Mathot, V. B. F., editor. Calorimetry and Thermal Analysis of Polymers. Munich: Hanser Publishers, 1994: pp. 231 – 299 and references therein.
9. **Liu, H.-T., Davey, C. R., Shirodkar, P. P.** Bimodal Polyethylene Products from UNIPOL Single Gas Phase Reactor Using Engineered Catalysts *Macromolecular Symposia* 195 2003: pp. 309 – 316.
10. **Monrabal, B.** In: Hosoda, S., Editor. New Trends in Polyolefin Science and Technology. Trivandrum: Research Signpost, 1996: p. 71, 119.
11. **Kim, Y.-M., Kim, C.-H., Park, J.-K., Kim, J.-W.; Min, T.-I.** Short Chain Branching Distribution and Thermal Behavior of High Density Polyethylene *Journal of Applied Polymer Science* 6 (13) 1996: pp. 2469 – 2479.
12. **DesLauriers, P. J., Rohlfing, D. C., Hsieh, E. T.** Quantifying Short Chain Branching Microstructures in Ethylene 1-olefin Copolymers Using Size Exclusion Chromatography and Fourier Transform Infrared Spectroscopy (SEC-FTIR) *Polymer* 43 (1) 2001: pp. 159 – 170.
13. **Soares, J. B. P., Abbott, R. F., Kim, J. D.** Environmental Stress Cracking Resistance of Polyethylene: the Use of CRYSTAF and SEC to Establish Structure-property Relationships *Journal of Polymer Science Part B: Polymer Physics* 38 (10) 2000: pp. 1267 – 1275.
14. **Nakano, S., Goto, Y.** Development of Automatic Cross Fractionation: Combination of Crystallizability Fractionation and Molecular Weight Fractionation *Journal of Applied Polymer Science* 26 (12) 1981: pp. 4217 – 4231.
15. **Ortin, A., Monrabal, B., Sancho-Tello, J.** Development of an Automated Cross-fractionation Apparatus (TREF-GPC) for a Full Characterization of the Bivariate Distribution of Polyolefins *Macromolecular Symposia* 257 2007: pp. 13 – 28.
16. **Tso, C. C., DesLauriers, P. J.** Comparison of Methods for Characterizing Comonomer Composition in Ethylene 1-olefin Copolymers: 3D-TREF vs. SEC-FTIR *Polymer* 45 (8) 2004: pp. 2657 – 2663.
17. **DesLauriers, P. J., McDaniel, M. P., Rohlfing, D. C., Krishnaswamy, R. K., Secora, S. J., Benham, E. A., Maeger, P. L., Wolfe, A. R., Sukhadia, A. M., Beaulieu, B.B.** A Comparative Study of Multimodal vs. Bimodal Polyethylene Pipe Resins for PE-100 Applications *Polymer Engineering and Science* 45 (9) 2005: pp. 1203 – 1213.
18. **Hiller, W., Pasch, H., Macko, T., Hofmann, M., Ganz, J., Spraul, M., Braumann, U., Streck, R., Mason, J., Van Damme, F.** On-line Coupling of High Temperature GPC and 1H NMR for the Analysis of Polymers *Journal of Magnetic Resonance* 183 (2) 2006: pp. 290 – 302.
19. **Luruli, N., Pijpers, T., Brull, R., Grumel, V., Pasch, H., Mathot, V. B. F.** Fractionation of Ethylene/1-pentene Copolymers Using a Combination of SEC-FTIR and SEC-HPer DSC *Journal of Polymer Science Part B: Polymer Physics* 45 (21) 2007: pp. 2956 – 2965.
20. **Knuuttila, H., Lehtinen, A., Nummila-Pakarinen, A.** Advanced Polyethylene Technologies – Controlled Material Properties *Advances in Polymer Science* 169 2004: pp. 13 – 27.
21. **Böhm, L. L.** The Ethylene Polymerization with Ziegler Catalysts: Fifty Years after the Discovery *Angewandte Chemie* 42 (41) 2003: pp. 5010 – 5030.
22. **Scheirs, J., Böhm, L. L., Boot, J. C., Leevers, P. S.** PE100 Resins for Pipe Applications: Continuing the Development into the 21st Century *Trends in Polymer Science* 4 (12) 1996: pp. 408 – 415.
23. **Willis, J. N., Wheeler, L.** In: Provder, T.; Barth, H. G.; Urban, M. W.; Marek, W., editors. Chromatographic Characterization of Polymers: Hyphenated and Multidimensional Techniques. Adv Chem Ser, 1995: p 247, 253.
24. **Somsen, G. W., Gooijer, C., Brinkman, U. A. T.** Liquid Chromatography-Fourier-transform Infrared Spectrometry *Journal of Chromatography A* 856 (1 – 2) 1999: pp. 213 – 242.
25. **Vanden Poel, G., Mathot, V. B. F.** High-speed/high Performance Differential Scanning Calorimetry (HPer DSC): Temperature Calibration in the Heating and Cooling Mode and Minimization of Thermal Lag *Thermochimica Acta* 446 (1 – 2) 2006: pp. 41 – 54.
26. **Krumme, A.** Crystallisation Behaviour of High Density Polyethylene Blends with Bimodal Molar Mass Distribution *Ph. D. Thesis* Tallinn University of Technology, Tallinn, January 2004: pp. 11 – 12.
27. **Defoor, F., Groeninckx, G., Schouterden, P., Van der Heijden, B.** Molecular, Thermal and Morphological Characterization of Narrowly Branched Fractions of 1-octene Linear Low-density Polyethylene. 1. Molecular and Thermal Characterization *Polymer* 33 (18) 1992: pp. 3878 – 3883.
28. **Stehling, F. C., Speed, C. S., Welborn, C. H. Jr.** US Patent Number: 5382630, Filing Date: Feb 4, 1993, Issue Date: Jan 17, 1995.

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