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Determination of the Distribution of Molar Mass and Comonomer Content of Medium Density Polyethylene: Comparison of Procedures with Alternative Sequence of Fractionation

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A polyethylene copolymer of medium density, synthesized from ethene and 1-hexene has been characterized according to its molar mass M distribution and comonomer mass content w_0 by means of Holtrup fractionation, size exclusion chromatography coupled with low-angle laser light scattering (SEC/LALLS), and preparative and analytical temperature rising elution fractionation (TREF).

The sequence of these analytical methods has been varied systematically, and the results obtained are represented by contour diagrams in the plot w_0 vs. $\log M$.

Preparative TREF with SEC/LALLS measurements on the respective fractions (conventional Procedure) leads to poor resolution of the distribution of M and w_0 . Better results were obtained by applying a Holtrup fractionation (including SEC/LALLS) with subsequent preparative TREF fractionation of the Holtrup fractions. Replacing the preparative TREF fractionation by analytical TREF gave more detailed information of the comonomer content, which resulted in a refined contour diagram in the plot of w_0 vs. $\log M$.

KEY WORDS Polyethylene copolymer, molar mass distribution (MMD), short-chain branching (SCB), temperature rising elution fractionation (TREF), direct extraction fractionation, SEC/LALLS

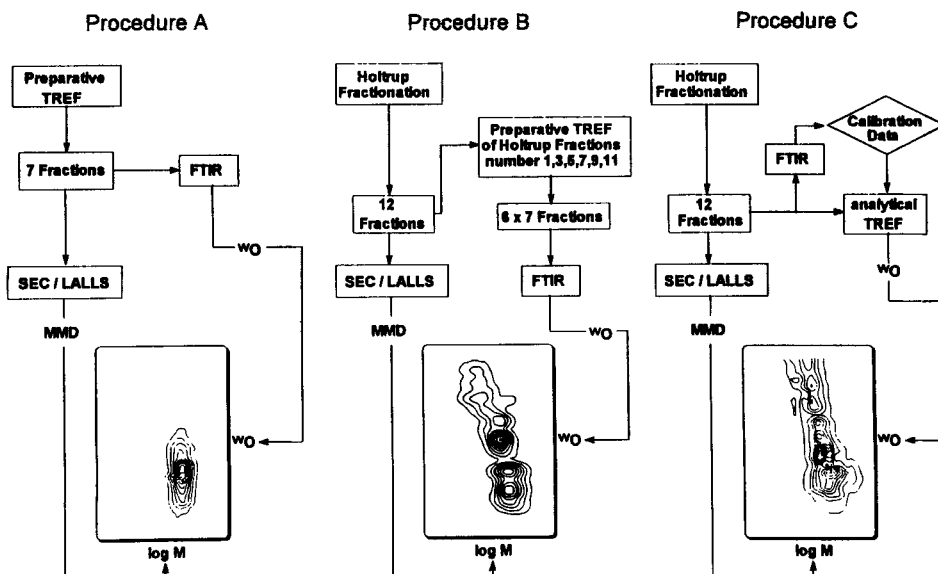
Dedicated to Professor Dr. Josef Schurz on the occasion of his 70th birthday

INTRODUCTION

Molecular characterization of linear polyethylene (LLDPE, MDPE, HDPE), that is, copolymers of ethylene with α -olefins, for example, 1-butene, 1-hexene or 1-octene, requires fractionation according to molar mass and comonomer content (branching index: $\text{CH}_3/1000\text{C}$) [1, 2].

A widely used technique to separate polyolefins according to molar mass is fractionation by the direct extraction method of Holtrup [3]. The most effective and

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SCHEME 1 Block diagram of various Procedures (A–C) used to determine the distribution of molar mass and comonomer content of the MDPE sample.

convenient method of determining the distribution of comonomer content in linear polyethylene is a stepwise or continuous temperature rising elution fractionation (TREF). The application of this technique to polyethylene resins has been reported by Shirayama et al. [4, 5] and Wild et al. [6].

In this paper, a commercial linear ethylene-1-hexene copolymer ($\rho = 0.935 \text{ g} \cdot \text{mL}^{-1}$, $\text{MFI} = 0.15 \text{ dg} \cdot \text{min}^{-1}$ (190°C ; 21.2 N)) is characterized according to its distribution of molar mass and comonomer content by means of Holtrup fractionation, SEC/LALLS, and both preparative (stepwise) and analytical (continuous) TREF. The sequence of these techniques is varied systematically as can be seen from Scheme 1.

Procedure A starts with preparative TREF followed by SEC/LALLS analysis. This procedure represents the conventional approach. According to *Procedure B* the copolymer is first fractionated by means of Holtrup fractionation (including SEC/LALLS measurement on the respective fractions) according to its molar mass and then by preparative TREF according to its composition. *Procedure C* also starts with a Holtrup fractionation (including SEC/LALLS) but in contrast to *Procedure B* is then followed by analytical TREF.

The results of these various procedures are presented in the form of two-dimensional contour maps showing comonomer and molar mass distribution. In this way, a comparative judgement on the efficiency of these procedures can be given.

EXPERIMENTAL

Materials

The polymer investigated was a polyethylene copolymer of medium density (MDPE) synthesized from ethene and 1-hexene with the aid of a chrome catalyst. The

MDPE with a density of $\rho = 0.935 \text{ g} \cdot \text{mL}^{-1}$ and a melt flow index of $\text{MFI} = 0.15 \text{ dg} \cdot \text{min}^{-1}$ (190°C ; 21.2 N) was kindly supplied by PCD GmbH (Linz, Austria).

The solvents, 1,2,4-trichlorobenzene, *p*-xylene, and diethylene glycol monoethyl ether (DEME, systematic IUPAC name: 3,6-dioxaoctanol), "pro synthesis" grade, were purchased from Merck (Darmstadt, Germany).

The nitrogen supplied from a pressure cylinder had a purity of 99.999 vol% ($\text{O}_2 \leq 3 \text{ ppm}$, $\text{H}_2\text{O} \leq 5 \text{ ppm}$, $\text{C}_n\text{H}_m \leq 0.2 \text{ ppm}$) and was further purified by a molecular sieve (Oxisorb[®] cartridge, Merrer-Griesheim, Frankfurt, Germany).

Methods

Preparative fractionation: The principle of the direct extraction procedure developed by Holtrup (Holtrup fractionation) and the apparatus used are described in detail [3, 7]. The fractionation was carried out at 150°C with *p*-xylene as a solvent and DEME as a nonsolvent. To avoid polymer degradation, $0.5 \text{ g} \cdot \text{L}^{-1}$ 2,6-di-*tert*-butyl-(4-methylphenol) (BHT) were added to the solvent and the solution flushed continuously with nitrogen.

The following values of the volume content of *p*-xylene have been used to obtain 12 Holtrup fractions with different molar masses: 35, 40, 50, 54, 56, 60, 62, 64, 66, and 68%.

SEC/LALLS-coupling: The molar mass and its distribution of the respective copolymer and its various fractions were determined by means of size exclusion chromatography (SEC) coupled with a low-angle laser light scattering (LALLS). The self-assembled SEC/LALLS apparatus consisted of an HPLC pump L-510 (Waters, Milford, USA), a sixport-injection valve 7010 (Rheodyne) with a $305\text{-}\mu\text{L}$ sample loop, a LALLS-photometer KMX-6 (633 nm) (Chromatrix, Sunnyvale, USA), and an infrared (IR) detector (DuPont Instruments Company, Wilmington, USA) set at wavelength of $3.42 \mu\text{m}$ and used as a concentration detector. The commercially available IR cell was modified by two Infrasil[®] windows each with a thickness of 2 mm (Hellma, Freiburg, Germany) and a Teflon spacer (thickness: 1 mm). A combination of 3 linear columns were used from Toyo Soda Mfg. Co. Ltd. (Tokyo, Japan): TSK-Gel GMH6-HT, $13\text{-}\mu\text{m}$ particle size, $300 \text{ mm} \times 7.5 \text{ mm}$ i.d., estimate exclusion limit $4 \cdot 10^8 \text{ g/mol}$ and from Merck (Darmstadt, Germany): LiChrogel PS40000 and PS4, $10\text{-}\mu\text{m}$ particle size, $250 \text{ mm} \times 7 \text{ mm}$ i.d., exclusion limit $5 \cdot 10^4\text{--}1 \cdot 10^7 \text{ g/mol}$ (PS40000) and $100\text{--}5 \cdot 10^3 \text{ g/mol}$ (PS4).

The measurements were performed at 135°C with 1,2,4-trichlorobenzene serving as eluent. The optimal elution rate has been found in the range of $0.5 \text{ mL} \cdot \text{min}^{-1}$. The polymeric solutions were prepared by dissolving between 10 and 25 mg of the copolymer in 25 mL 1,2,4-trichlorobenzene at 160°C within 45 minutes. The solvent contained $0.5 \text{ g} \cdot \text{L}^{-1}$ BHT and was flushed with nitrogen for 15 minutes.

The value of the refractive index increment was assumed to be $-0.104 \text{ mL} \cdot \text{g}^{-1}$, irrespective of the comonomer content [8]. A computer-aided evaluation was carried out according to the method described by Huber and Billiani [9]; the data were not corrected for peak broadening.

TREF: The TREF system consisted of an isocratic HPLC pump FR-30 (Knauer, Berlin, Germany) and the IR detector described above set to $3.42 \mu\text{m}$. Two

stainless-steel columns of different size were used for preparative and analytical TREF fractionation. The preparative column had a length of 400 mm and an inner diameter of 76 mm. For analytical fractionation, a column with a length of 250 mm and an inner diameter 8 mm was used. Both columns were filled with non-porous glass beads having an approximate size of 0.15 mm (BHD Chemicals Ltd., Poole, England). The columns were thermostated in an oil bath, the temperature controlled by a Haake E8 thermostat in combination with a programmable temperature control regulator PG20 (Haake, Karlsruhe, Germany).

The TREF columns were filled at 140°C by applying pressurized nitrogen with the aid of a storage tank in which the polymeric solutions have been prethermostated. The mass of polymer that was injected into the columns was in the range of 2.5 g for preparative and 6–8 mg for analytical fractionation. The solutions contained 0.5 g · L⁻¹ BHT and were flushed with nitrogen for 15 minutes. The columns were sealed and cooled to 25°C with a rate of 0.02°C/min.

For the elution process, the HPLC pump was connected to the system. Preparative TREF fractions were obtained at 40, 64, 74, 84, 90, 95, and 100°C by heating the column with a rate of 0.08°C/min. At each of the given steps, the temperature was kept constant for about 90 minutes, and the polymer dissolved was eluted with a flow rate of 1 mL · min⁻¹ [10].

The analytical TREF column was heated continuously at a rate of 0.25°C/min. The concentration of the polymer eluted was detected by the IR detector and recorded with a strip-chart recorder. The optimal flow rate for the analytical TREF was found to be 1 mL · min⁻¹.

FTIR: Infrared spectrum measurements were carried out with a Fourier-Transform-Infrared-Spectrometer (FTIR) Model 1600 (Perkin-Elmer, Norwalk, USA). The samples were compressed between two aluminium plates at 120°C with a pressure of 2 bars to give a film of 150 μm thickness. By use of the compensation method of Willbourn [11], the branching parameter (CH₃/1000 C) was calculated according to Equation (1):

$$\text{CH}_3/1000 \text{ C} = A_{1378}/d \cdot 0.85 \quad (1)$$

where A_{1378} : absorbance at 1378 cm⁻¹ (CH₃ bending), and d : film thickness. The comonomer mass content $w_0/\%$ was calculated according to Equation (2):

$$w_0 = \frac{n \cdot (\text{CH}_3/1000 \text{ C})}{10} \quad (2)$$

where n : number of C-atoms of the comonomer ($n = 6$ in the case of 1-hexene).

Calculation of contour maps: The two dimensional contour maps were made with the aid of the computer program, "Surfer V4.15" (Golden Software Inc., Golden, Colorado, USA), at the Institut fuer Markscheidewesen, Montanuniversitaet Leoben. The contour maps represent the distribution of molar mass (x-axis) and comonomer mass content (y-axis). The height $z = w(\log M, w_0)$ is normalized

according to Equation (3):

$$\iint w(\log M, w_0) d \log M \cdot dw_0 = 1 \quad (3)$$

The minimum contour (cf., Figures 1, 4, 7, and 8) specifies the smallest z -values and the contour interval is the number of data units between contour lines. For comparative reasons the same contour levels have been chosen in Figures 1, 4, 7, and 8.

RESULTS AND DISCUSSION

Procedure A

The principle of *Procedure A* is shown in Scheme 1. The MDPE sample was subjected to preparative TREF to give seven fractions of different comonomer content. By means of infrared analysis, the branching parameter of each fraction, $\text{CH}_3/1000 \text{ C}$, was determined. From this parameter, the comonomer mass content w_0 was calculated according to Equation (2), neglecting terminal H_3C -groups and short-chain branches formed by side reactions during the polymerization. Subsequently, the molar mass distribution of each of the seven TREF fractions was determined by SEC/LALLS and the polydispersity $\text{PD} = M_w/M_n$ was calculated from these data summarized in Table I. Also given in Table I are the yields of the preparative TREF fractionation obtained at different elution temperatures ϑ_E . The last two rows of Table I give the weight-average and number-average molar masses calculated from the yield and the corresponding molar mass of each fraction; these values agree quite well with those of the unfractionated sample.

TABLE I

Yield, comonomer mass content w_0 , molar mass averages (M_w, M_n), and polydispersity ($\text{PD} = M_w/M_n$) of preparative TREF fractions of the MDPE sample, obtained at the elution temperature ϑ_E .

TREF fraction	$\vartheta_E, ^\circ\text{C}$	yield, %	$w_0, \%$	$M_w, \text{g} \cdot \text{mol}^{-1}$	$M_n, \text{g} \cdot \text{mol}^{-1}$	PD
1	40	4.8	3.45	110 000	39 300	2.80
2	64	12.8	2.91	122 000	39 400	3.10
3	74	19.6	2.54	100 000	47 600	2.10
4	84	27.2	2.42	98 000	30 600	3.20
5	90	16.4	2.18	114 000	34 500	3.30
6	95	13.2	1.88	121 000	43 200	2.80
7	100	5.6	1.63	98 000	39 200	2.50
\sum yield, %		99.6				
not fractionated				126 900	26 100	4.86
$\sum w_i \cdot M_{w_i}$				107 500		
$\left(\sum \frac{w_i}{M_{n_i}} \right)^{-1}$					37 200	

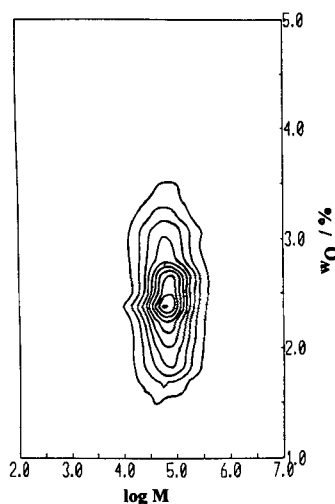


FIGURE 1 Contour map of the distribution of molar mass M and comonomer mass content w_0 of the MDPE sample determined by preparative TREF followed by SEC/LALLS; minimum contour: 0.1, contour interval: 0.1.

It is obvious that preparative TREF fractionates the polymer according to its comonomer mass content, which lies between 3.45% for the fraction with the lowest elution temperature of $\vartheta_E = 40^\circ\text{C}$ and 1.63% for the last fraction eluted at $\vartheta_E = 100^\circ\text{C}$. A fractionation according to molar mass could not be observed, the values of M_w of the fractions are in the range between 98 000 and 122 000 $\text{g} \cdot \text{mol}^{-1}$ with polydispersity (PD) between 2.10 and 3.30.

The contour map obtained by *Procedure A* is given in Figure 1. The contour height is defined by Equation (3). As can be seen from Figure 1, only one maximum in the region of $M \approx 90\,000 \text{ g} \cdot \text{mol}^{-1}$ and $w_0 \approx 2.4\%$ was obtained.

Procedure B

According to *Procedure B* (cf. Scheme 1), the polymer sample was first subjected to a Holtrup fractionation leading to 12 fractions of different molar masses that were characterized by means of SEC/LALLS. The results are collected in Table II. The PD lies between 1.23 and 1.58 for Holtrup fractions number 1—9 as expected for fractionated products. The last three fractions have a higher PD in the range of 2.15 and 3.47. The weight- and number-averages of molar mass increase continuously with all fractions considered, for example, from $M_w = 11\,700 \text{ g} \cdot \text{mol}^{-1}$ for Holtrup fraction 1 up to $M_w = 380\,900 \text{ g} \cdot \text{mol}^{-1}$ for fraction number 11, except for the last fraction, which had a lower M_w of $290\,200 \text{ g} \cdot \text{mol}^{-1}$. The resulting molar mass distribution curves are shown in Figure 2. The yield of each fraction obtained according to the method of Holtrup is also shown in Table II. The calculation of the number- and weight-average from the yield and the molar mass averages of each fraction shows a good agreement with those of the unfractionated sample as documented in the lowest two rows of Table II.

Holtrup fractions number 1, 3, 5, 7, 9, and 11 have been subjected to preparative TREF, each to give seven sub-fractions. The resulting 42 TREF fractions have

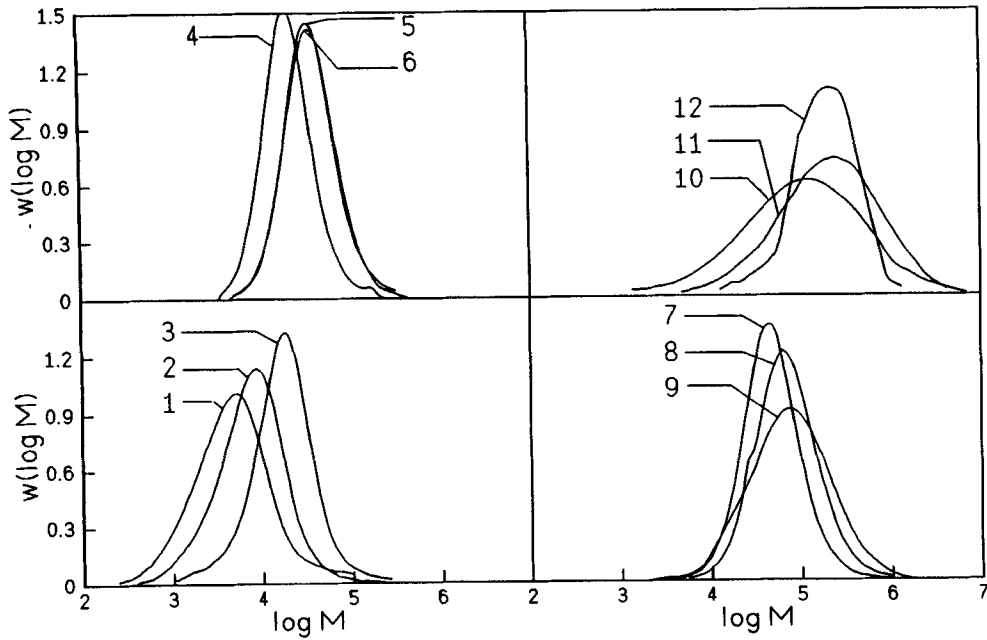


FIGURE 2 Molar mass distribution curves of Holtrup fractions number 1-12 (see Table II) of the MDPE sample.

TABLE II

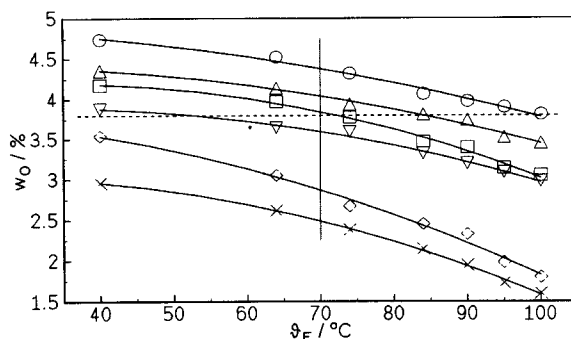
Yield, molar mass averages (M_w , M_n) and polydispersity ($PD = M_w/M_n$) of the fractions obtained from direct extraction according to Holtrup.

Holtrup fraction	yield, %	M_w , $g \cdot mol^{-1}$	M_n , $g \cdot mol^{-1}$	PD
1	7.64	11 700	7 900	1.48
2	8.28	17 200	11 900	1.45
3	4.74	23 800	15 300	1.56
4	6.96	28 500	23 100	1.23
5	10.20	46 900	31 100	1.51
6	10.90	46 300	37 400	1.24
7	13.40	63 900	49 900	1.28
8	14.96	88 300	63 900	1.38
9	16.44	123 000	78 000	1.58
10	3.08	344 500	99 300	3.47
11	1.60	380 900	177 000	2.15
12	0.42	290 200	90 600	3.20
Σ yield, %	98.62			
not fractionated		126 900	26 100	4.86
$\Sigma w_i \cdot M_{w_i}$		110 300		
$\left(\Sigma \frac{w_i}{M_{n_i}} \right)^{-1}$			27 400	

TABLE III

Comonomer mass content (w_0 , %) of TREF fractions 1–7 of Holtrup fractions number 1, 3, 5, 7, 9, 11.

Holtrup	TREF						
	1	2	3	4	5	6	7
1	4.74	4.52	4.32	4.07	3.98	3.91	3.82
3	4.36	4.14	3.94	3.81	3.74	3.52	3.45
5	4.18	3.98	3.78	3.47	3.40	3.14	3.05
7	3.89	3.65	3.59	3.32	3.20	3.09	2.98
9	3.54	3.05	2.67	2.45	2.33	1.98	1.80
11	2.96	2.62	2.38	2.14	1.94	1.73	1.60

FIGURE 3 Comonomer mass content w_0 of Holtrup fractions number 1(\circ), 3(Δ), 5(\square), 7(∇), 9(\diamond) and 11(\times), sub-fractionated by preparative TREF.

been characterized according to their comonomer content by means of FTIR. The results are collected in Table III. The horizontal rows show the comonomer content of the TREF fractions 1–7 obtained from the Holtrup fractions mentioned above. As expected, the comonomer content decreases with increasing TREF fraction numbers. In Figure 3, these comonomer contents are plotted as a function of the elution temperature. The data points can be fitted by a function of $w_0 = a_0 + a_1 \cdot \vartheta_E + a_2 \cdot \vartheta_E^2$. The constants a_0 , a_1 , a_2 , and the regression coefficient r of these curves are given in Table IV.

It can be seen from Figure 3 (cf. Table II), that a molar mass dependence of the elution temperature of TREF exists. For a certain comonomer mass content (e.g., $w_0 = 3.8\%$; see dashed line in Figure 3), the elution temperature decreases with increasing molar mass. This means fractions with different molar masses eluted at the same temperature (e.g., $\vartheta_E = 70^\circ\text{C}$; see vertical line in Figure 3) contain less

TABLE IV

Constants a_0 , a_1 , a_2 , and regression coefficient r of curves in Figure 3 fitted by the function $w_0 = a_0 + a_1 \cdot \vartheta_E + a_2 \cdot \vartheta_E^2$ (see text).

Fraction	a_0	a_1	a_2	r
1	4.921	$6.929 \cdot 10^{-4}$	$-1.207 \cdot 10^{-4}$	0.9395
3	4.330	$6.914 \cdot 10^{-3}$	$-1.572 \cdot 10^{-4}$	0.9818
5	3.864	$1.891 \cdot 10^{-2}$	$-2.736 \cdot 10^{-4}$	0.9457
7	3.728	$1.154 \cdot 10^{-2}$	$-1.918 \cdot 10^{-4}$	0.9619
9	3.828	$1.142 \cdot 10^{-3}$	$-2.119 \cdot 10^{-4}$	0.9998
11	2.908	$1.087 \cdot 10^{-2}$	$-2.413 \cdot 10^{-4}$	0.9794

TABLE V

Molar mass averages (M_w , M_n) and polydispersity ($PD = M_w/M_n$) of preparative TREF fractions of Holtrup fraction number 7.

TREF fraction	M_w , $g \cdot mol^{-1}$	M_n , $g \cdot mol^{-1}$	PD
1	50 400	36 300	1.39
2	60 900	46 100	1.32
3	59 500	45 800	1.30
4	58 400	45 700	1.28
5	62 500	46 700	1.34
6	60 300	49 000	1.23
7	57 000	44 000	1.30

branching with increasing molar mass. A possible explanation for this phenomenon might be found by regarding the crystallization behavior of the copolymer. The crystallization process of molecules with shorter chains, i.e., lower molar mass, is less hindered and may lead to crystallites with higher melting point and corresponding higher temperatures of elution in TREF. However, it could be clearly revealed by SEC/LALLS measurements of preparative TREF fractions that TREF does not separate according to molar mass (cf. Tables I and V).

Cross fractionation according to *Procedure B* leads to a contour map, which is shown in Figure 4. For the evaluation of these data, it was assumed that each sub-fraction obtained by preparative TREF of one Holtrup fraction has the same molar mass distribution.

The contour diagram obtained by *Procedure A* (cf. Figure 1) clearly reveals the advantage of a Holtrup fractionation with subsequent preparative TREF compared with a conventional TREF fractionation. Although no remarkable extension in the range of molar mass could be obtained, *Procedure B* leads to an improved accessibility in the range of comonomer content. The comonomer mass content w_0

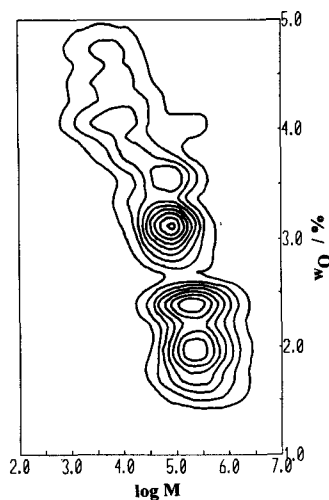


FIGURE 4 Contour map of the distribution of molar mass M and comonomer mass content w_0 of the MDPE sample determined by Holtrup fractionation (including SEC/LALLS) followed by preparative TREF; minimum contour: 0.1, contour interval: 0.1.

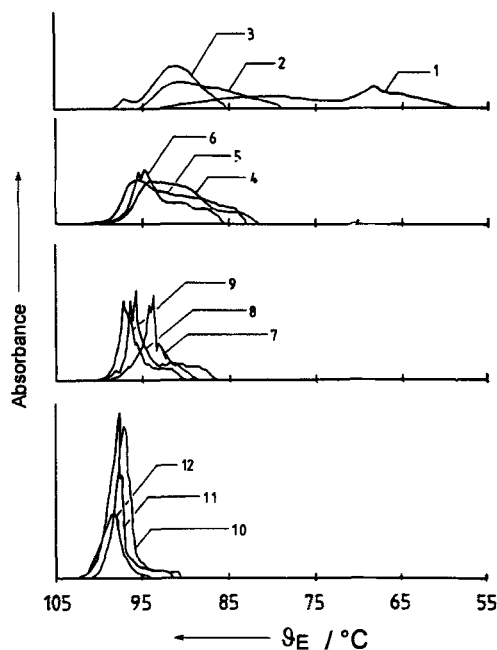


FIGURE 5 Analytical TREF curves of Holtrup fractions number 1-12.

derived by *Procedure A* lies between 1.6% and 3.5% (cf. Table I and Figure 1); in *Procedure B* the upper limit of w_0 could be extended to 4.7%. Furthermore, a more structured contour map is shown with four maxima (cf. Figure 3), in contrast to only one in Figure 1.

Procedure C

The main difference between *Procedure C* and *Procedure B* is the substitution of preparative TREF by analytical TREF (cf. Scheme 1). Whereas preparative TREF runs are extremely time-consuming and a large number of fractions need to be filtered off, weighed, and examined according to their comonomer content by infrared analysis, the analytical TREF procedure saves time, is easily performed due to reduced sample and column size, and the eluted polymer can be monitored as a function of temperature.

The analytical TREF curves of Holtrup fractions number 1-12 are presented in Figure 5. The fractions number 1, 2, 4, and 5 have a very broad and nonsymmetric distribution of the elution temperature. In contrast, fractions number 3 and 6-12 show a well-pronounced maximum and a more symmetric distribution.

For calibration of the analytical TREF column, with respect to the dependence of the comonomer mass content w_0 on the elution temperature ϑ_E , the comonomer contents of the Holtrup fractions number 1-12 have been determined by means of infrared analysis. The derived comonomer mass contents w_0 are summarized in Table VI. The elution temperatures at the peak maximum of the analytical TREF (cf. Figure 5) are also collected in Table VI.

TABLE VI

Comonomer mass content w_0 (see text) and peak elution temperature ϑ_E in the analytical TREF of Holtrup fractions number 1–12 determined by infrared analysis and analytical TREF.

Holtrup fraction	ϑ_E , °C	w_0 , %
1	—*)	4.21
2	—*)	4.04
3	92.4	3.88
4	—*)	3.75
5	—*)	3.55
6	93.9	3.48
7	93.8	3.40
8	95.6	2.97
9	96.9	2.55
10	97.6	2.37
11	98.3	2.20
12	98.9	2.05

*) No pronounced maximum in IR absorbance (cf. Figure 4), neglected for calibration of analytical TREF column.

According to Wild et al. [6], a distinct linear correlation between comonomer content and elution temperature is valid for all types of linear ethylene copolymers. Figure 6 shows the calibration curve of the analytical TREF column derived by plotting the comonomer content as a function of elution temperature for the peak maximum. Only Holtrup fractions with a well-pronounced maximum in the analytical TREF have been taken into account. The linear relationship of the graph in Figure 6 is expressed by the function $w_0 = a_0 + a_1 \cdot \vartheta_E$.

The fitted constants are $a_0 = 30.05$ and $a_1 = -0.2835$ (regression coefficient $r = 0.98$). In view of the stated molar mass dependence of TREF found by *Procedure B*, it must be emphasized that this calibration curve (cf. Figure 6) is not expected to be a universal function for ethylene- α -olefin copolymers, but may be only valid for the respective sample. The analytical TREF curves have been normalized, integrated and, with the aid of the calibration function mentioned above, the total comonomer mass content of each Holtrup fraction was determined. To evaluate the analytical TREF curves of Holtrup fractions number 1 and 2, the calibration curve given in Figure 6 had to be extrapolated into regions below

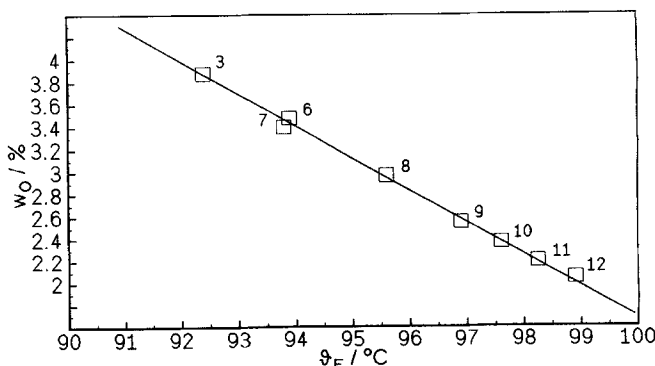


FIGURE 6 Calibration curve of the analytical TREF column obtained from Holtrup fractions number 3 and 6–12.

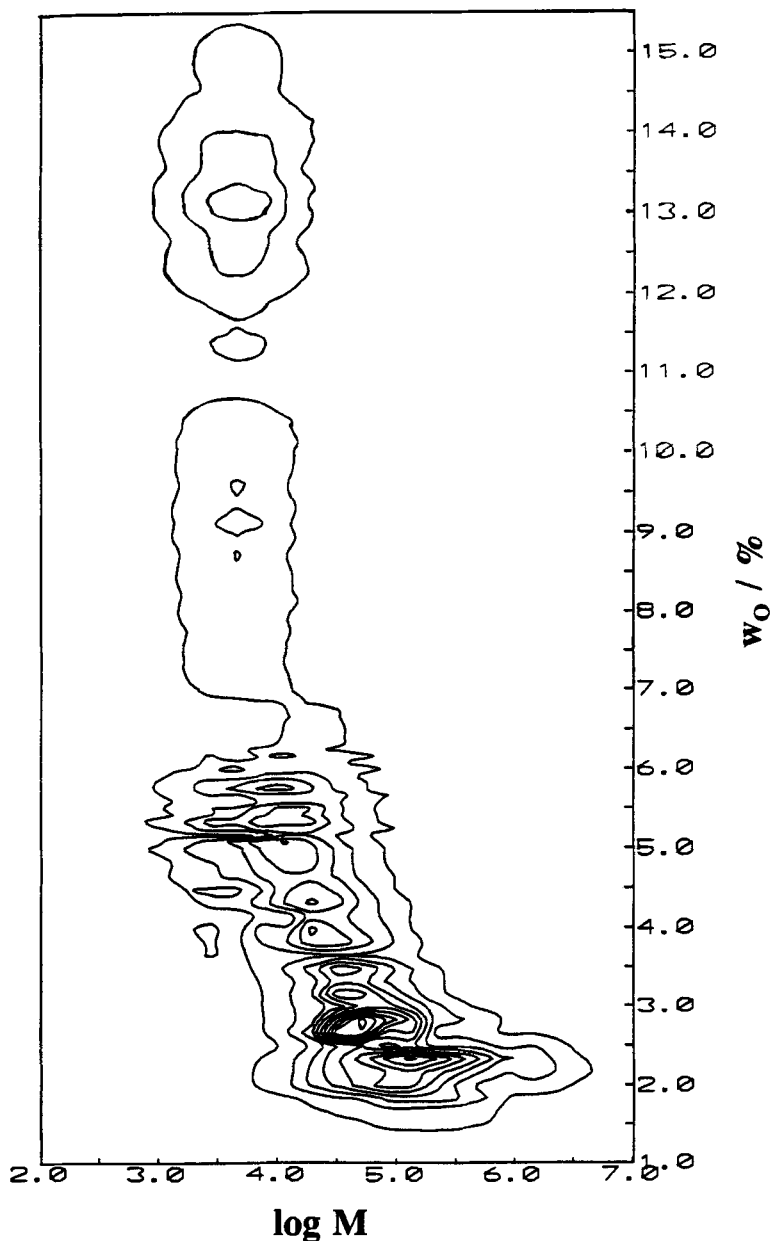


FIGURE 7 Contour map of the distribution of molar mass M and comonomer mass content w_0 of the MDPE sample determined by Holtrup fractionation (including SEC/LALLS) followed by analytical TREF; minimum contour: 0.1, contour interval: 0.1.

90°C (cf. Figure 5). This leads to an enlarged range of comonomer mass content above 5 percent. This linear extrapolation is rather inaccurate and relies on the linear correlation between comonomer content and elution temperature reported in the literature [6, 12].

It was assumed that each analytical TREF interval of one Holtrup fraction had the same molar mass distribution. The contour map obtained in this way by

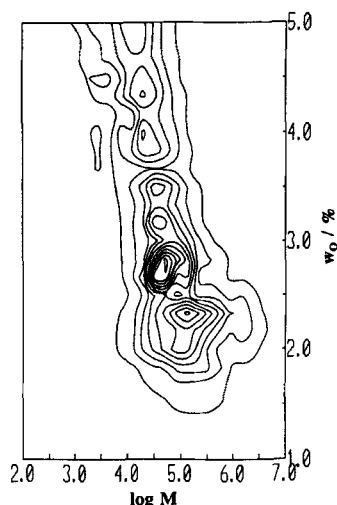


FIGURE 8 Enlarged detail of Figure 7 (see text).

Procedure C is depicted in Figure 7. As can be seen, a remarkable extension of the comonomer mass content w_0 up to 15 percent is achieved by applying analytical TREF fractionation to the Holtrup fractions, which is not accessible by the conventional *Procedure A* or the improved *Procedure B*. Figure 8 shows an enlarged detail of Figure 7. As the graduation of the scale is similar in Figures 1, 4, and 8, it clearly is revealed that more precise information on the distribution of molar mass and comonomer content can be achieved by applying a Holtrup fractionation including SEC/LALLS and a subsequent analytical TREF for the characterization of a given ethylene copolymer. A surface plot of Figure 8 is depicted in Figure 9 to give a three-dimensional impression of the comonomer and molar mass distribution within the chosen range of w_0 .

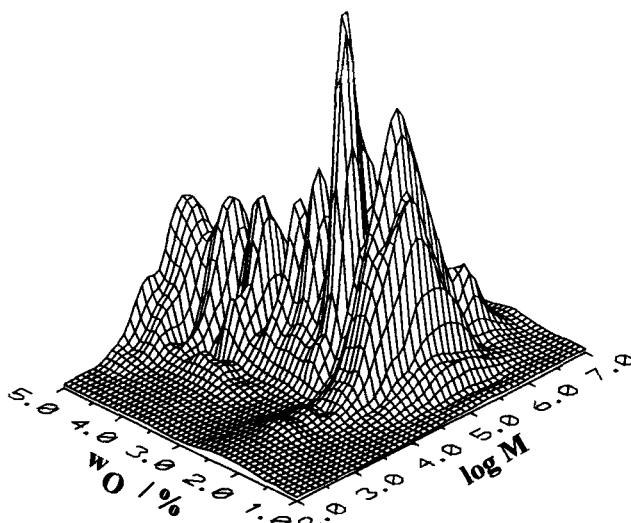


FIGURE 9 Figure 8 presented as a surface plot.

CONCLUSIONS

The characterization of a copolymer according to its molar mass and comonomer distribution by applying a Holtrup fractionation including SEC/LALLS with subsequent analytical TREF (*Procedure C*) seems to be superior to the conventional procedure with preparative TREF followed by SEC/LALLS on the TREF fractions (*Procedure A*) or a Holtrup fractionation with a subsequent preparative TREF (*Procedure B*). This could clearly be demonstrated in the case of a statistical linear copolymer of ethylene and 1-hexene of medium density.

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