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MOLECULAR CHARACTERIZATION OF POLYOLEFINS

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ABSTRACT

The results of a round-robin test carried out by IUPAC Working Party IV.2.2 on Molecular Characterization of Commercial Polymers with two grades of polypropylene with narrow (“controlled rheology” PP) and broad molar mass distribution (MMD) are summarized. The interlaboratory agreement for M_w expressed by the relative standard deviation, $\sigma(\%)$, is ± 6 for PP with broad MMD ($M_w/M_n = 5.7$) and is better than for the controlled rheology grade [$\sigma(\%) = \pm 11.7$, $M_w/M_n = 2.55$]. This finding is explained by the influence of peak broadening in size exclusion chromatography (SEC). The measured MMDs are discussed with respect to the frequency dependence of the complex shear modulus and to differentiation between the respective grades by process control data from injection molding. A comparison of procedures for the determination of MMD and distribution of short-chain branching in polyethylene of medium and high density (PE-MD and PE-HD) with an alternative sequence of fractionation is presented. The direct extraction procedure by Holtrup, which is fractionating according to molar mass followed by analytical temperature rising elution fractionation (TREF), gives the most detailed results within a considerably shorter time than a Holtrup fractionation followed by preparative TREF; both procedures give a much more detailed result than fractionation by preparative TREF followed by SEC. The contour diagrams ($\text{CH}_3/1000\text{C}$ vs $\log M$) of two PE-HD blow-molding grades with the same density values ($\rho = 0.954$) and melt flow index ($\text{MFI } 190/2.16 = 0.20 \text{ dg/min}$) are interpreted with respect to their good but distinguishable environmental stress-cracking resistance.

INTRODUCTION

Early in his career, H. F. Mark's research dealt with molecular characterization of macromolecules in dilute solution, e.g., with viscometry [1] and with chromatographic fractionation [2]. The importance of this field of polymer science for the development of plastics was recognized by Mark in the contribution "Basic Science in the Literature of Plastics," written in 1952 [3], when plastics exhibited their highest rate of growth in history:

Considering basic science in the general field of plastics there are essentially three divisions—synthesis, molecular structure, and structure and properties of bulk polymers.

In this paper the state of the art for the determination of the molar mass distribution (MMD) of isotactic propylene (PP) homopolymer, and of the distribution of molar mass and short-chain branching of ethylene- α -olefin copolymers of medium and high density (PE-MD and PE-HD) is presented. Furthermore, the relationship of these structural data to rheological properties, to polymer processing, especially injection molding, and to environmental stress cracking resistance (ESCR) will be discussed. Since 1952 the classic field of molecular characterization of plastics in dilute solution has experienced two very important innovations: the inventions of high density polyethylene and of isotactic polypropylene, the most important polymers, at least with respect to their volume of production, and size exclusion chromatography (SEC), most important as a method for determination of polydispersity by its ubiquity in industrial laboratories. In the meantime, the molecular characterization of polyolefins is routinely carried out by chemists as a service for polymer engineers.

MOLAR MASS DISTRIBUTION OF POLYPROPYLENE

Isotactic polypropylene (PP) is here considered as linear homopolymer ("simple polymer"), disregarding the complication of syndiotactic defects.

High temperature SEC of PP requires careful preparation of sample solutions which was to be optimized at the beginning of the Austrian Joint Research Project S33, "Influence of Molecular Structure and Processing Parameters on the Properties of Moulded Plastic Parts" [4, 5]. As a good compromise between incomplete dissolution, which leads to suspended gel particles, and thermooxidative degradation, the following conditions were chosen with 1,2,4-trichlorobenzene as solvent: 170°C for 60 minutes under nitrogen and with 1 wt% 2,6-di-*tert*-butyl-4-methylphenol (BHT) to prevent oxidation. After having reached satisfactory reproducibility of MMD determination in our own laboratory, a round-robin test was proposed within the IUPAC Working Party IV.2.2 on Molecular Characterization of Commercial Polymers. In this round-robin test, 12 industrial laboratories, 2 university departments, and 1 department of a national academy of science have been cooperating for about 5 years to establish two PP standards as generally available calibration samples [6]. The commercial grade samples studied in these project are specified in Table 1. Test samples of Daplen PT55 are available from the authors.

TABLE 1. Polypropylene Grades Studied in Austrian Joint Research Project S33 and in a Round-Robin Test (r.r.t.) of IUPAC Working Party IV.2.2

Grade	Producer	Project
Moplen S30S: MFI (230/2.16) = 4 dg/min with broad MMD (used for blow molding, deep drawing, and ropes)	Himont, Italy	r.r.t.
Daplen KS10: MFI (230/2.16) = 8 dg/min with broad MMD (used for injection molding)	PCD Polymere, Schwechat-Linz, Austria	S33
Daplen PT55: MFI (230/2.16) = 19 dg/min with narrow MMD) "controlled rheology" (used for injection molding with deep flow and non-wovens)	PCD Polymere, Schwechat-Linz, Austria	r.r.t. and S33

Table 2 summarizes the results of high temperature SEC of the respective IUPAC round-robin tests with Moplen S30S. Eliminating the results of those 7 laboratories which applied rougher conditions of sample dissolution than 4 hours at 150°C or 1 hour at 170°C, the value of the relative standard deviation for M_w could be reduced to $\sigma(\%) = \pm 6$ with respect to the mean value (considering 31

TABLE 2. Results of the Round-Robin Test (14 laboratories) with Moplen S30S. Statistical parameters: \bar{x} = arithmetic mean, σ = standard deviation, and $\sigma(\%)$ = relative standard deviation. M_w = weight-average molar mass, M_n = number-average molar mass

Number of reported runs	Statistical parameter	M_w , kg/mol	M_n , kg/mol	M_w/M_n
43 (14 laboratories)	\bar{x}	426	77.4	5.53
	σ	76	12	0.74
	$\sigma(\%)$	17.8	15.5	13.4
31 (7 laboratories)	\bar{x}	467	83.7	5.70
	σ	28	8.2	0.58
	$\sigma(\%)$	6.0	9.8	10.1

independent SEC runs of 7 laboratories). For M_n , $\sigma(\%) = \pm 9.8$; for M_w/M_n , $\sigma(\%) = \pm 10.1$ was found.

A considerable larger scattering of the respective molar mass averages was found with the controlled rheology grade Daplen PT55 (cf. Table 3). Despite the fact that this grade dissolves faster and is not prone to form gel particles, a considerably larger scattering of data was observed, especially for M_w , than in case of Moplen S30S, even after elimination of the "rougher" laboratories.

The scattering of the average values of molar mass in this first round-robin test for high temperature SEC in the case of Moplen S30S is about twice as large as in a round robin test of SEC at room temperature which served as a basis for the new DIN 55672 standard [7]. With respect to M_w , the scattering in this round-robin test with PP was only half as large as in a similar Japanese test with radically polymerized polystyrene in tetrahydrofuran as the eluent at 25–45°C [8]. It is quite remarkable that even in the case of "benign" polystyrene, carefully applied modern SEC leads to a scattering of M_n and M_w of the same order of magnitude as the classic methods of membrane osmometry and light scattering in a first round-robin test with radically polymerized polystyrene which was reported by Frank and Mark over forty years ago [9].

Figure 1 shows the MMD determined in the round-robin test for Moplen S30S by seven different laboratories. The MMD is given as differential mass distribution $w(\log M)$ obtained without correction for peak broadening: The chosen scale of $w(\log M)$ fulfills the condition $\int w(\log M) d \log M = 1$. These results show large differences, especially at very low and very high molar mass.

Also in the case of Daplen PT55, considerable differences are observed between the MMDs reported by different laboratories (cf. Fig. 2). In the case of this grade with its narrower distribution ($M_w/M_n = 2.55$), it is essential to correct for the peak broadening effect. This correction was carried out by a special procedure for simultaneous calibration of separation and peak broadening in SEC coupled with low angle laser light scattering (LALLS) [10–12] combined with the procedure

TABLE 3. Results of the Round-Robin Test (12 laboratories) with Daplen PT55. Statistical parameters: x = arithmetic mean, σ = standard deviation, and $\sigma(\%)$ = relative standard deviation. M_w = weight-average molar mass, M_n = number-average molar mass

Number of reported runs	Statistical parameter	M_w , kg/mol	M_n , kg/mol	M_w/M_n
38 (12 laboratories)	x	206	61.4	3.42
	σ	28	8.2	0.59
	$\sigma(\%)$	13.6	13.4	17.3
30 (7 laboratories)	x	213	62.2	3.51
	σ	25	7.3	0.58
	$\sigma(\%)$	11.7	11.7	16.5

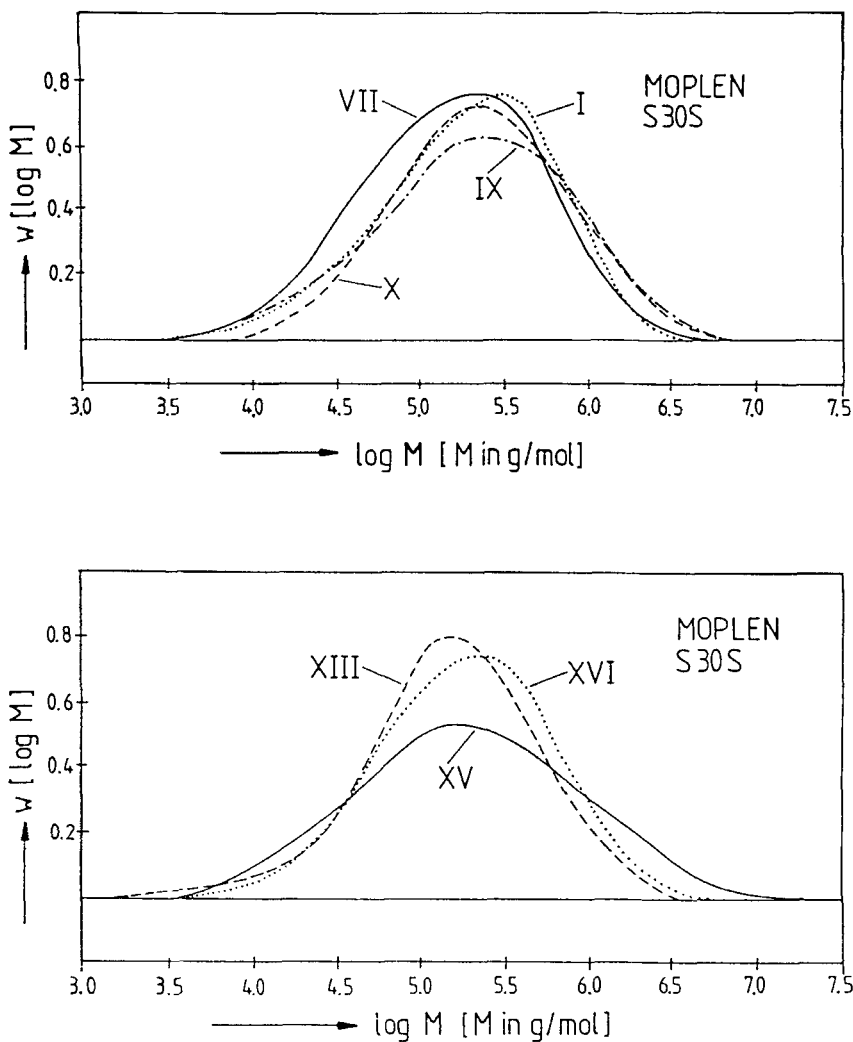


FIG. 1. Differential mass distribution of molar mass, $w(\log M)$, reported by various laboratories (I-XV) for Moplen S30S.

of Ishige et al. [13], Method II. The effect of this correction depends on the quality of the column set (cf. Table 4). For comparable values of the peak elution volume V_R and of the slope of the calibration function $\log M(V_R)$, the quality of the column set can be assessed by the variance σ^2 of the peak broadening function which can usually be approximated by a Gaussian. Applying the respective correction, nearly the same value of the polydispersity M_w/M_n was found for Daplen PT55 when using different column sets (cf. Table 4). The effect of the peak correction procedure in the case of column set 1 is shown in Fig. 3.

The value of $M_w/M_n = 3.52$ calculated from the uncorrected MMD in Fig. 3 closely agrees with the value reported in Table 3; this finding clearly demonstrates

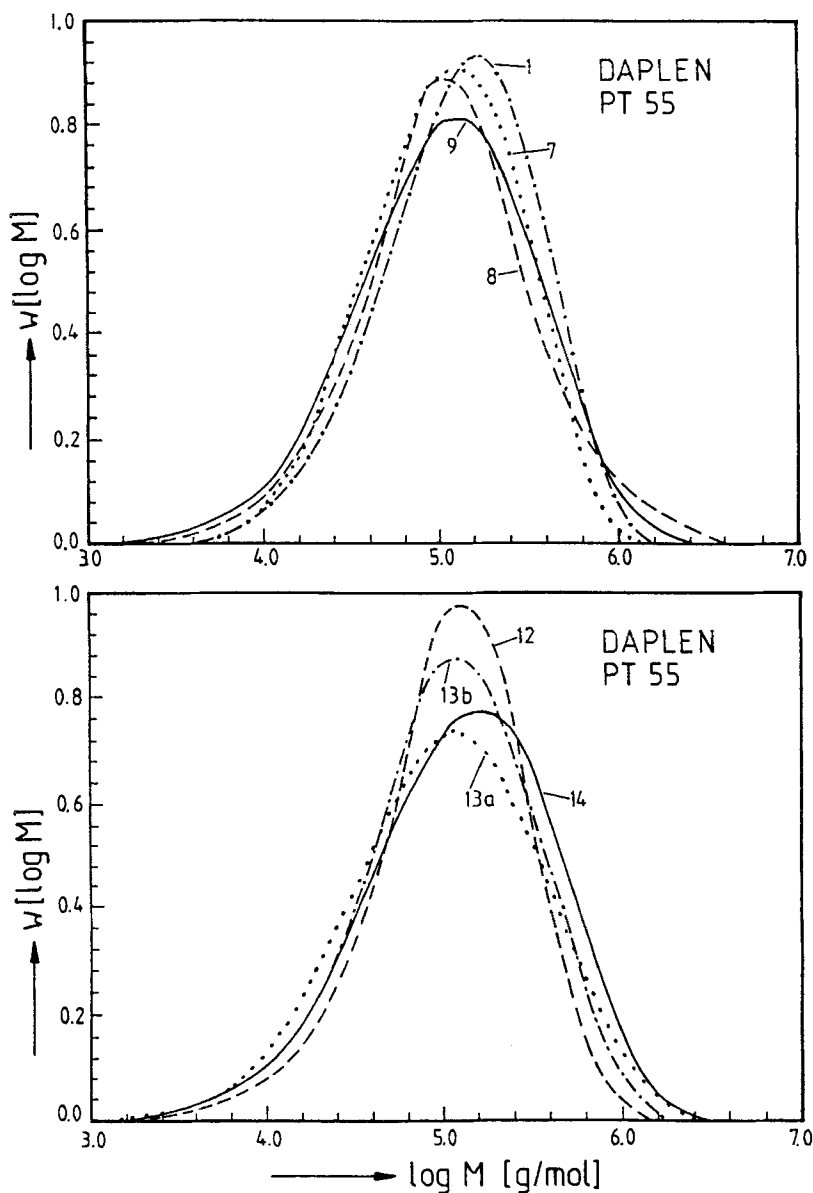


FIG. 2. Differential mass distribution of molar mass, $w(\log M)$, reported by various laboratories (1-14) for Daplen PT55.

that in SEC of samples with M_w/M_n smaller than 3-4, correction for peak broadening is usually necessary [14].

In high-temperature SEC using polystyrene-divinylbenzene column packings with an average particle size of 5-10 μm and 1,2,4-trichlorobenzene at 135°C as eluent, the dependence of the variance of the peak broadening parameter σ on the

TABLE 4. Corrections for Peak Broadening in High Temperature SEC of Daplen PT55

Column set number	V_R , mL	Peak broadening σ^2 , mL ²	Corrections		Corrected M_w/M_n	Uncorrected M_w/M_n
			ΔM_w , %	ΔM_n , %		
1	20	0.20	-11	+18	2.64	3.52
3	16.5	0.050-0.15	-8.3	0.0	2.53	2.85
4	19.5	0.029	-4.8	0.0	2.57	2.71

elution volume was found different for narrow fractions of polypropylene and for anionically polymerized polystyrene standards. Under these experimental conditions, correction for peak broadening in SEC of PP therefore requires calibration of the peak broadening with narrow fractions of PP for each column set. Furthermore, this calibration must be repeated whenever a change in the quality of the column set is realized. It would be very attractive if SEC columns which exhibit long-term stability at high temperature and a universal dependence of peak broadening on elution volume were available.

For a judgment on these problems with the enhancement of precision in SEC, the high precision of other methods which are also very sensitive to changes of molar mass must be taken into account. As an example, the dependence of the complex shear modulus of polymer melts on the frequency shall be considered. This dependence can be calculated from MMD according to Schausberger et al. [15, 16]. Assuming only a very small change in the high molar mass tail of the differential MMD, this calculation leads to a measurable change of the expected shape of the corresponding functions $G'(\omega)$ and $G''(\omega)$. Actually, the points of the curves for

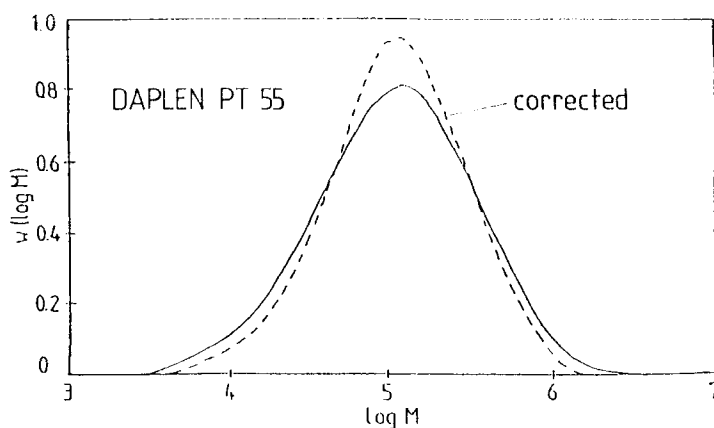


FIG. 3. Differential mass distribution of molar mass, $w(\log M)$, measured for Daplen PT55 with column set 1: (—) uncorrected and (---) corrected for peak broadening.

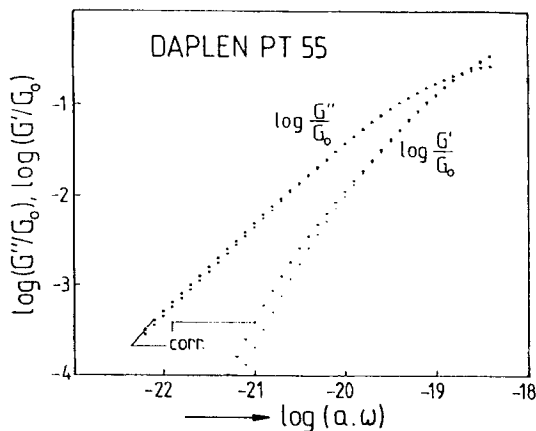


FIG. 4. Frequency dependence of the real and imaginary shear modulus, $\log G'(a\omega)/G_0$ and $\log G''(a\omega/G_0)$, calculated by Schausberger [17] for Daplen PT55. The points indicated by "corr." were calculated from the hatched area for the MMD histogram in Fig. 5.

$G'(\omega)$ and $G''(\omega)$ designated by "corr." in Fig. 4 were measured by Schausberger [17] on Daplen PT55, and exactly the same curves were calculated from the MMD of Daplen PT55 shown in Fig. 5 by adding a very small hatched area to the high molar mass tail (shown in Fig. 5 with tenfold magnification). For comparison, two curves with a detectable shift to higher frequency at low values of $G''(\omega)$ and $G'(\omega)$, respectively, are shown in Fig. 4. They were calculated for the molar mass distribution of Daplen PT55 without addition of the hatched area (cf. Fig. 5). This hatched area is too small to be detected in SEC; the sensitivity of SEC in the high molar mass range can, however, be improved considerably by the use of a low angle laser light scattering (LALLS) detector [18].

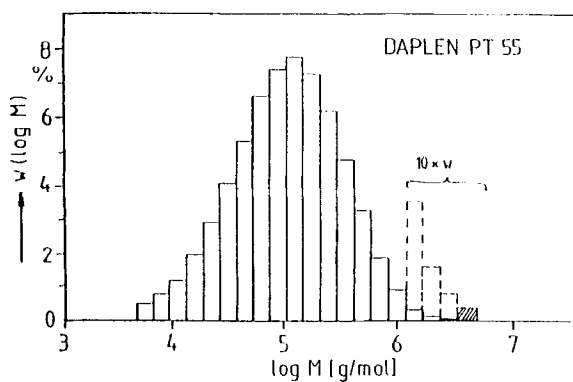


FIG. 5. Histogram of the MMD of Daplen PT55 as used for calculation of the frequency dependence of the complex shear modulus (cf. Fig. 4). Addition of the hatched area (given with a tenfold magnification) leads to the curves designated by "corr." in Fig. 4.

The strong dependence of rheological properties on MMD allows the diagnosis of batch to batch changes by the acquisition of suitable process data in modern processing machines with well controlled melt and mold temperatures. Figure 6 shows the change of hydraulic pressure during mold filling in injection molding of Daplen KS10 and Daplen PT55 under identical process conditions, especially at constant translational screw velocity during injection [19] and the MMD determined for the respective PP grades by SEC coupled with LALLS [5].

In view of the steady progress of process control and data acquisition in polymer processing machines, it is a real challenge to improve the methods for direct measurement of MMD. In the case of polypropylene, interlaboratory reproducibility is not yet satisfactory but could be improved by validation of polypropylene standards with rather low polydispersity; this optimistic judgment is based on the much higher reproducibility of successive SEC runs in the same laboratory. In such series of experiments, minor changes in the high molar mass tail of Daplen KS10 could be detected during injection molding without packing [20].

DISTRIBUTION OF MOLAR MASS AND SHORT-CHAIN BRANCHING IN ETHYLENE- α -OLEFIN COPOLYMERS OF MEDIUM AND HIGH DENSITY AND ITS INFLUENCE ON ENVIRONMENTAL STRESS CRACKING RESISTANCE

The influence of the average molar mass, of branching, and of crosslinking by high energy radiation on the environmental stress-cracking resistance (ESCR) of PE-HD and PE-LD was studied by Hittmair, Mark, and Ullmann as early as 1958;

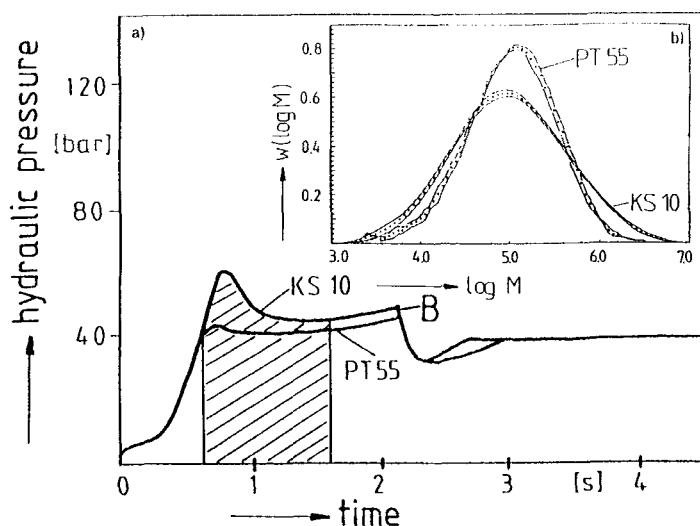


FIG. 6. (a) Hydraulic pressure as a function of time during mold-filling under identical conditions in injection molding of Daplen PT55 and Daplen KS10. "B" indicates the changeover from injection to packing. (b) MMD of Daplen PT55 and Daplen KS10 measured in six consecutive runs. The full line widths give the standard deviations.

their very concise report on the basic correlation between molecular structure and ESCR [21] is still considered to be valid. Later, the view of these authors was refined by the statement that PE-HD with very high density and modulus will exhibit sufficient ESCR if the α -olefin copolymer units are preferably built-in in the high molar mass fraction [22].

In the meantime, the procedures for fractionation of linear ethylene- α -olefin copolymers have been greatly improved. As semicrystalline polymers, these copolymers can be fractionated according to molar mass in a poor solvent (e.g., a mixture of ethylene glycol monoethylether and xylene) at 130°C by elution fractionation according to Holtrup [23] with a gradually increasing content of xylene. In the good solvent xylene, such a copolymer can be fractionated according to the extent of short-chain branching by a gradual increase of temperature (*Temperature Rising Elution Fractionation* = TREF) [24]. The quality of xylene as a solvent for polyethylene was studied by Muthana and Mark in 1949 [25].

The detailed distribution of molar mass and short-chain branching in ethylene- α -olefin copolymers can be determined by a combination of Holtrup fractionation and TREF [26]. The results of this analysis can be presented in contour diagrams, e.g., using the plot form of $\log M$ vs $\text{CH}_3/1000\text{C}$ ($\text{CH}_3/1000\text{C}$ = number of methyl groups per 1000 carbon atoms as a measure for short-chain branching), with contour lines to describe the density of the mass content, $w(\log M, \text{H}_3\text{C}/1000\text{C})$, which is normalized to fulfill the condition

$$\int w(\log M, \text{H}_3\text{C}/1000\text{C}) d \log M d(\text{CH}_3/1000\text{C}) = 1$$

These fractionation procedures require considerable time. Therefore, it was interesting to evaluate the performance of three different procedures with alternative sequence of fractionation with respect to structural resolution and consumption of time.

The results of this evaluation are summarized in Fig. 7 [27]. Figure 7 shows that Procedure A, which is predominantly applied in industrial laboratories, results in a much lower resolution with respect to the $\text{CH}_3/1000\text{C}$ coordinate but requires less time than Procedures B and C. Procedure B is very time-consuming but offers the advantage of detecting and taking into account the dependence of TREF on MMD [27, 28]. Procedure C shows an even better resolution with respect to branching ($\text{H}_3\text{C}/1000\text{C}$), and is considerably less time-consuming than Procedure B. However, the calibration of the analytical TREF used in Procedure C via the TREF-peak elution temperature of the Holtrup fractions covers only a limited range of $\text{H}_3\text{C}/1000\text{C}$. For the example given in Fig. 7, an ethylene-1-hexene copolymer with $\rho = 0.935 \text{ g/cm}^3$, this calibration covers only the range $3 < \text{CH}_3/1000\text{C} < 7$; in the range of $\text{CH}_3/1000\text{C} > 7$, a linear extrapolation was used in accordance with the results of Wild et al. [25].

Figure 8 shows such contour diagrams of two PE-HD blow molding grades with the same density and melt flow index but different ESCR. These contour diagrams were determined by Procedure B with the restriction of preparative TREF to Holtrup fractions 1, 5, and 9 [28]. Table 5 summarizes the characteristic data of these grades with exceptionally high ESCR.

As shown in Fig. 8, Grades I and II (cf. Table 5) show very similar contour diagrams. The comonomer content of Grade I is about 20% higher, and this higher

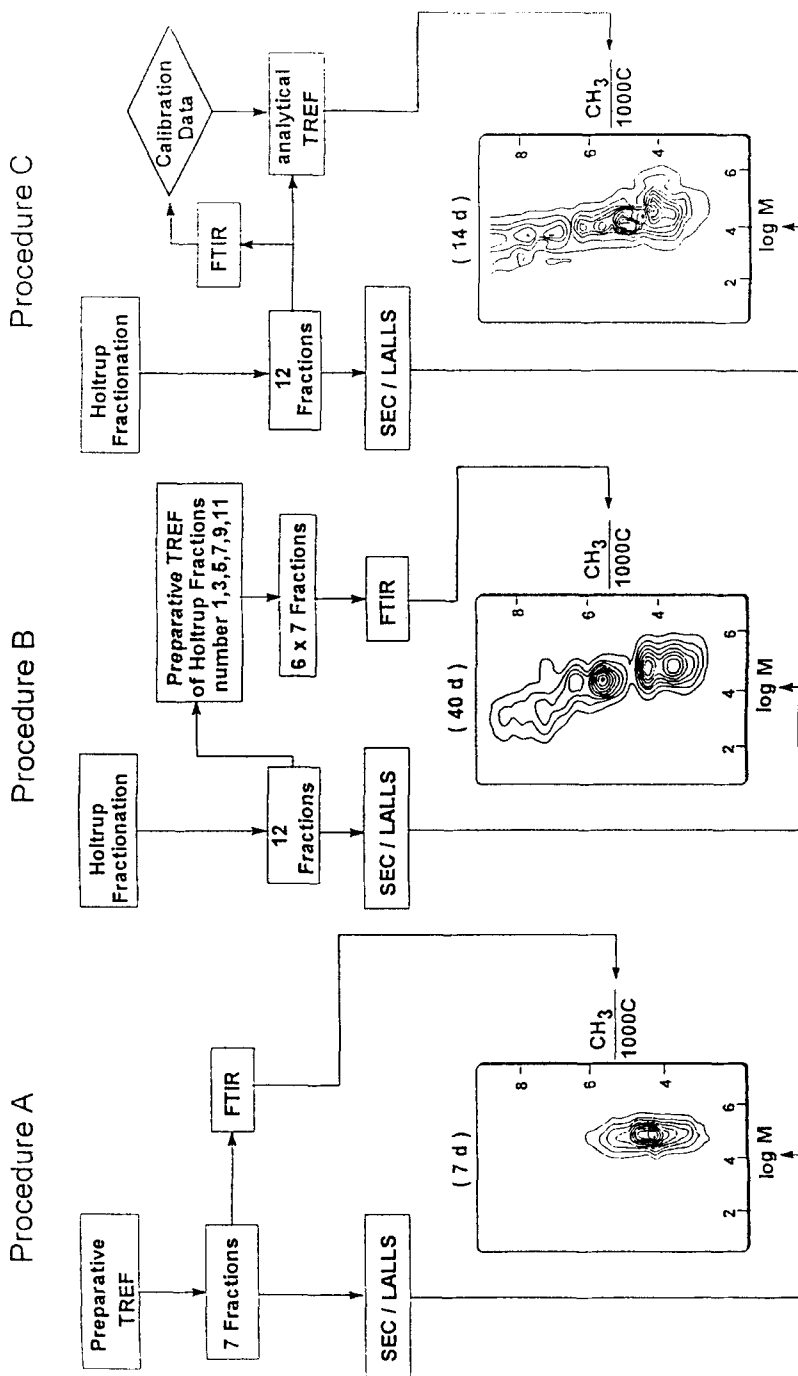


FIG. 7. Procedures with alternative sequences of fractionation for determination of the distribution of molar mass and branching of PE-MD. Consumption of time given in days (in parentheses). For the other symbols, cf. text.

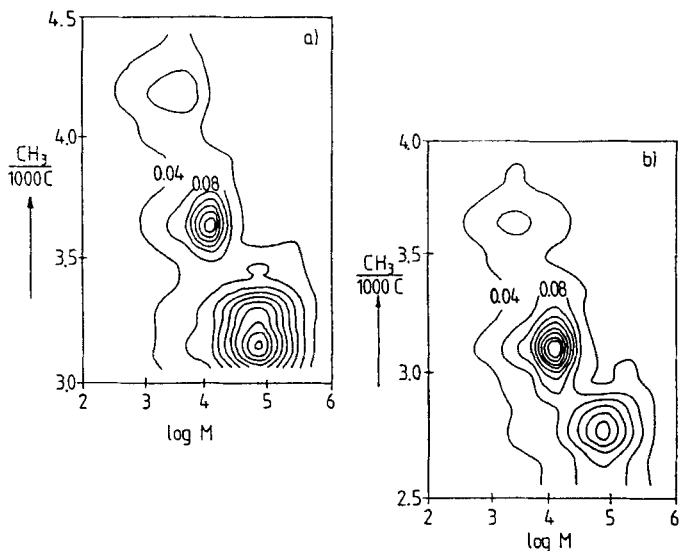


FIG. 8. Contour diagram in the plot of branching frequency $\text{H}_3\text{C}/1000\text{C}$ vs $\log M$ as determined for two grades of PE-HD (characteristic data for these grades are given in Table 5): a) Grade I, b) Grade II.

content lies to a larger extent at higher molar mass. In this example, the improvement of ESCR going from Grade I to Grade II can be interpreted to be in accordance with the assumptions of Hayes and Webster [22].

CONCLUSION

These examples, taken from work on the molecular characterization of polyolefins, demonstrate that the classic field of molecular characterization of plastics in dilute solution is still an important link between synthesis and structure, including

TABLE 5. Characteristic Data of Two PE-HD Grades (ethylene-1-butene copolymers) with Different Environmental Stress-Cracking Resistance (ESCR). ESCR Measured by Application of Internal Pressure to Bottles Filled with Surfactant (internal test procedure of PCD Polymere GmbH, Linz)

Quantity	Dimension	Grade I	Grade II
Density	g/cm^{-3}	0.954	0.954
M_w	kg/mol	146.7	146.3
M_n	kg/mol	24.4	15.9
$\text{CH}_3/1000\text{C}$	—	2.50	2.11
MFI 190/2.16	dg/min	0.20	0.20
ESCR	h	124.0	35.0

structure formation, in the bulk phase. For further improvement of the high quality of today's polymeric materials, an even more detailed knowledge of structure/property relations is a prerequisite; this requires stronger efforts in this classic field of polymer research.

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