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Determination of molecular dimensions of linear polyethylene by light scattering

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Dedicated to Dr Erhard Brauer on the occasion of his 60th birthday

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Abstract

The molecular dimensions of linear polyethylene published in the literature were reevaluated in order to discuss the radii of gyration R_G and their dependence on molar mass, M. The relationships $R_G = bM^a$ and the exponents a of this equation in comparison with the unperturbed dimensions of linear polyethylene obtained from viscometric measurements allowed the discussion of the reliability of the data and the reasons for deviations. The exponent a determined by light scattering for linear polyethylene in good solvent, tetraline, showed molecular dissolution, whereas in 1-chloronaphthalene and trichlorobenzene, the exponent a is lower than expected for good solvents. Microgels and aggregates of molecules affect the exponents. Radii of gyration measured directly by light scattering at fractions of linear polyethylene in the theta solvent, diphenylmethane, indicate incomplete molecular dissolution and the presence of branched structures.

Keywords: Polyethylene; Molecular dimensions; Light scattering

1. Introduction

Light scattering measurements on polyethylene solutions require temperatures of 80–135°C and more, because the polymer is molecularly dissolved only at temperatures higher than the melting temperature of the crystalline part. The dissolution, the filtration or the centrifugation of the solutions and the measurement of the scattered light has to be performed at these temperatures and in the presence of antioxidants to prevent oxidation and destruction of the macromolecules.

The difficulties connected with the high-temperature measurements are illustrated by the results of the IUPAC Working Party on Molecular characterisation of Commercial Polymers with the lower reproducibility in comparison to the results on other polymers measured by the various participants [1,2]. There, only the values of the molar masses were presented. The unpublished radii of gyration and virial coefficients, measured in the same experiments, cannot be more accurate. However, only the relations between the molar masses and the size parameters (e.g. mean-square end-to-end distance $\langle h^2 \rangle$ and radius of gyration R_G), branching, virial coefficients, and other molecular properties are of interest for the description of the correlation with the molecular structure of polyethylenes.

Theoretically, the simplest correlations are expected with systems at theta condition where the second virial coefficient A_2 vanishes and the chain dimensions, "unperturbed" by the excluded volume effect ($\langle h^2 \rangle_0^{1/2}, R_{G,0}$) for flexible polymer chains, should be proportional to the square root of the molar mass. Solutions of polyethylene in theta solvents were investigated by many authors [18,39,41–43], but no systematic study has been devoted to the estimation of chain dimensions by light scattering. Measurements from three unfractionated polyethylene samples in di-2-ethylhexyl adipate at 145°C [18] are the only exception. All the values of $R_{G,0}/M$ or $\langle h^2 \rangle_0/M$ for linear polyethylenes have been estimated from the intrinsic viscosity.

In the first part of this paper a critical survey of the published molecular dimensions of linear polyethylenes is given to demonstrate the mistakes and to find a way for safe calculations, which are necessary for the exploitation of all the data that one can obtain using modern multi-angle

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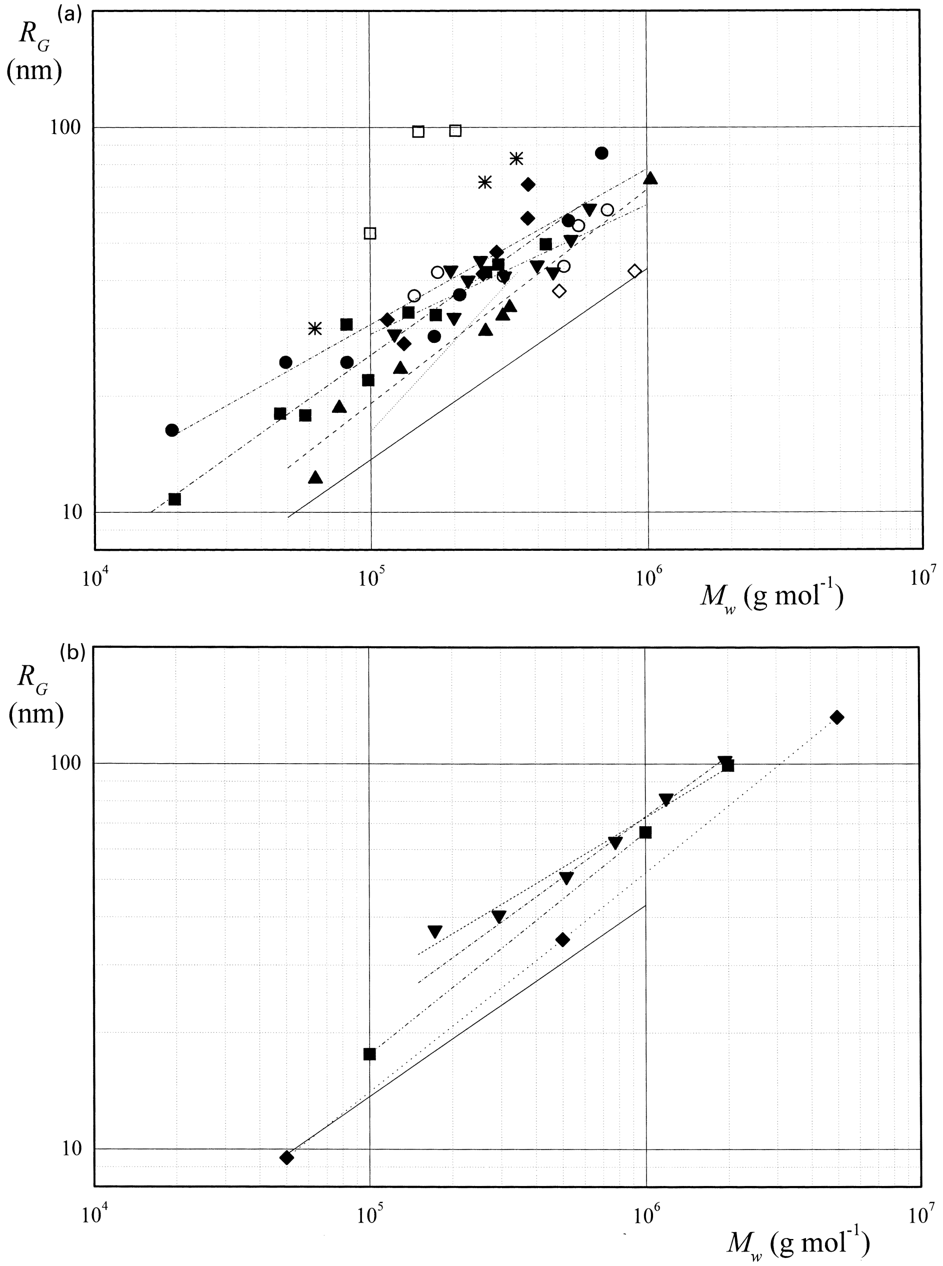

Fig. 1. Radii of gyration R_G vs. molar masses M_w of linear polyethylene. (a) In CN: fractions — (---■---) Casper et al. [3], 127°C; (∗) Chiang [4], 135°C; (- - ▲ - -) Chiang [5], 135°C; (-··· ▼ ···-) Tung [6], 125°C; (◆) Tung [7], 125°C; (--- ○ ---) Frolen et al. [8], 135°C; (······) Henry [9], 135°C; unfractionated samples — (◇) Shirayama [10], 125°C (two values only); (□) Chiang [4], 135°C; (○) Kokle et al. [11]; (—) Unperturbed dimensions [12]. (b) In TCB at 135°C: (▼) Hert and Strazielle [13]; (- - -) linear regression of the logarithms of all (six) values; (-·-·-) linear regression of the four higher values; (··◆··) Frye and Capaccio [14]; (-···■···-) Tackx and Tacx [15]; (—) unperturbed dimensions [12]. (c) In tetralin: (··▲··) Trementozzi [16], 105°C; (— —) relation for $R_{G,0,w}$; (··▼··) Kuhn et al. [17], 120°C; (■) Tung [7], 125°C.

equipment. For comparison, the radii of gyration R_G instead of their squared data are used, in order to help the reader to better visualise molecular dimensions.

In the second part we present the results ($R_{G,0}$ and M_w) from our measurements by light scattering carried out with dilute solutions of several sets of linear polyethylene fractions in diphenyl methane (DPM) at 142°C. A two-component separation treatment is applied to the data of the angular dependence to explain the anomalous correlations of $R_{G,0}$ vs. M_w.

2. Critical analysis of published data on M_w and R_G for linear polyethylene in good solvents

In this section, published data for R_G determined by light scattering for linear polyethylene in good solvents (1-chloronaphthalene (CN), 1,2,4-trichlorobenzene (TCB), tetralin (Fig. 1a–c) are discussed. R_G is based on the *z*-average. In some cases the type of the average has not been explicitly specified. The data were usually reported as $\langle h^2 \rangle$ values

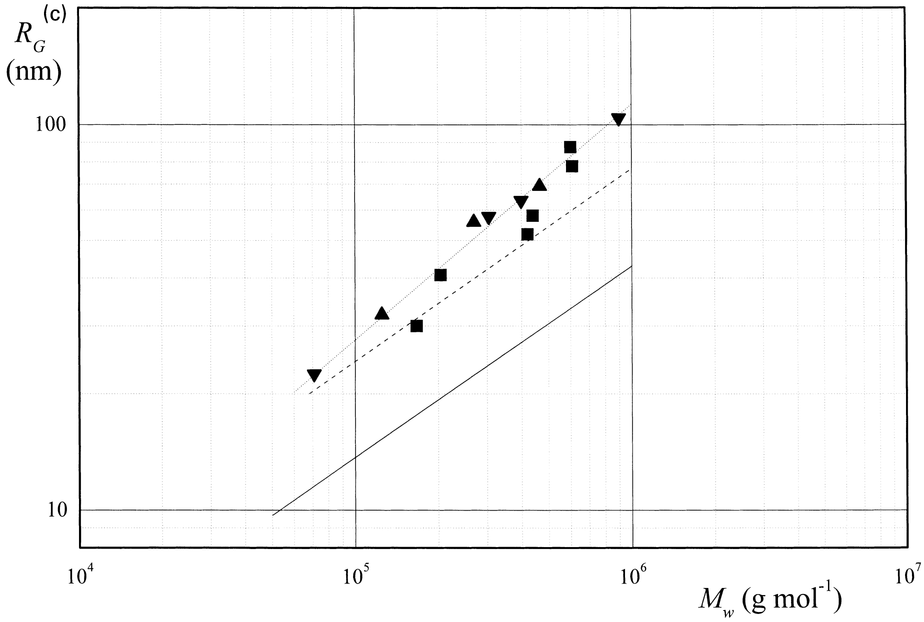

Fig. 1. (*continued*)

estimated from Zimm plots. As no details of the estimation were given, we converted them into R_G by the equation $R_G^2 = (1/6)\langle h^2 \rangle$, realising that, strictly taken, this formula is valid only for unperturbed dimensions. The z-averages of R_G should be correlated to the corresponding M_z values or should be converted to $R_{G,w}$. Unfortunately, neither of these corrections can be made because no polymolecularity characteristics were given in most papers. Full lines in the figures of this paper represent the molar mass dependence of unperturbed dimensions for linear polyethylene as determined by Wagner and Hoeve [12] from viscosity. In contrast with the results of light scattering the viscometric results are less influenced by microgels and aggregation and, therefore, may serve as “reference data“. The high absolute value of the refractive index increment of linear polyethylenes in CN should guarantee good reproducibility and precision of the results. Despite this, the scatter of data points is very large. The same applies to tetralin and TCB, the data are less accurate because of the lower refractive index increment.

The molar mass dependence of the radii of gyration is currently described by the equation

$$R_G = KM^a \tag{1}$$

We have evaluated the parameters of this equation by linear regression of the log–log plots of R_G vs. M_w. These are listed in Table 1. The values of the exponent cover a broad range, from 0.25 to 0.77. The highest of these are strongly above the upper bound ($=0.6$) to the interval for good solvent systems. The value 1/2 based on the data of Casper et al. would indicate CN to be a theta solvent. The data of some other authors lead to exponents even below the value 1/2. These findings would suggest poor solution behaviour in contradiction to other solution properties, e.g. positive values of the second virial coefficient, the exponents of the Mark–Houvink–Kuhn–Sakurada equation, absence of a liquid–liquid phase separation on cooling.

This situation may be a combination of several factors. (a) Measurements by different authors in the same solvent were carried out at different temperatures (125–135°C in CN, 80–120°C in tetralin). However, these are good solvents, and this fact is of negligible importance. (b) Differences in the distribution of molar masses might be more important depending, among others, on the method and efficiency of fractionation. For reasons mentioned above, this effect cannot be assessed from the existing data. Some measurements were made with non-fractionated samples of unknown polymolecularity, possibly comprising highly branched molecules of very high molar masses. (c) The methods of calibration of the light scattering instruments were not unified at the time when the first papers on polyethylene were published. (d) Based on our experience with theta systems we believe that the main reason for the scatter of the R_G values and the parameters of Eq. (1) is a contamination by a relatively small amount of aggregated or highly branched molecules.

In view of this, the dissolution procedure (temperature, stabilisation of solutions against degradation, duration of heating) becomes a very important issue and may be responsible for differences in the results, even of the same author. As an example, the values $a = 0.35$ and 0.67 derived from the data reported by Tung [6,7] may be mentioned. The high value may indicate good dissolution of fractions, but it significantly exceeds the limiting value for random coils in good solvents ($=0.6$). The solutions of six non-fractionated high-density polyethylene samples were cleaned by ultracentrifugation and, therefore, may be incomparable with solutions of fractions prepared by filtration [11].

Table 1
Results of correlations of R_G vs. M_w for linear polyethylene in good solvents (reported values are R_G, in some papers specified as $R_{G,z}$, in Refs. [6,8] $\langle h^2 \rangle$)

Solvent	Ref.	Temp. (°C)	Samples[a]	Range of M_w (10^3 M)	K[b]	a[b]	X^2
CN	3	127	F		0.083	0.50	0.947
	4		3, F		0.036	0.61	0.998
	5	135	F		0.033	0.55	0.944
	6	125	10, F	120–600	0.541	0.35	0.735
	7		7, F	120–2600	0.0123		0.67
	8				0.23	0.42	0.909
	9				0.0023	0.77	
	11		6, NF		1.71	0.26	0.747
TCB	13	135	6, F	170–1950	0.172	0.44	0.975
	14			$< 5 \times 10^{-4}$	0.0197	0.57	
Tetralin	16	105	3, F		0.031	0.59	0.975
	17	120	4, F		0.027	0.60	0.977

[a] Number and type of samples (F — fractions, NF — non-fractionated samples).

[b] Parameters of Eq. (1), X correlation coefficient according to

$$X^2 = \frac{\left[\sum(xy) - \dfrac{\sum x \sum y}{n}\right]^2}{\left[\sum(x^2) - \dfrac{(\sum x)^2}{n}\right]\left[\sum(y^2) - \dfrac{(\sum y)^2}{n}\right]}.$$

(The usual sign for this coefficient is r. X was used here in order to prevent confusion with the radii R and the Rayleigh ratio.)

Some other authors [22–24] presented data for unfractionated polyethylenes. These data are less valuable because of their broad (and sometimes very broad) distribution of molar masses and partially because of their content of branched macromolecules [21].

Already, in 1963 Kurata and Stockmayer [51] tried to include data of light scattering measurements on polyethylenes in their review on unperturbed dimensions of long chain molecules. They concluded "it seems much more likely that the well known difficulties of clarifying polyethylene solutions for light scattering measurements have persisted to some degree in spite of the strong efforts of even the most skilled workers". This remark remains valid even now.

On the other hand, viscometric measurements on polyethylene solutions are not seriously affected by the difficulties of scattering experiments from the same subject. In Table 2, the (viscosimetrically determined) unperturbed dimensions of linear polyethylenes in various solvents are collected. The results for different theta solvents agree well.

Table 2
Unperturbed dimensions $\langle h_0^2 \rangle / M$ of linear polyethylene in various theta solvents, determined from viscometry, according to $\langle h_0^2 \rangle / M = (K_\Theta / \Phi_0)^{2/3}$, with Φ_0 being the Flory constant ($C_n = \langle h_0^2 \rangle / n l^2$ is the chain stiffness, with n number and $l = 0.1533$ nm [37] the distance of carbon atoms; σ steric factor as a measure for the hindrance of free inner motion of the chain)

Theta solvent	Θ (°C)	$10^4 K_\Theta$	$10^{16}\langle h_0^2 \rangle / M$ (cm^2 mol g^{-1})	C_n	σ	Ref.
Diphenyl	128	38	1.288	7.67	1.95	[39]
	127.5	33	1.20[a]	7.10	1.88	[41]
Diphenylmethane	142.2	32.2	1.18[a]	6.99	1.87	[41]
1-Octanol	(140)	–	1.13[b]	6.69	1.82	[39]
1-Decanol	(140)	–	1.13[b]	6.69	1.82	[39]
1-Dodecanol	144.5	32.8	1.168	6.95	1.85	[39]
			1.14[c]	6.77	1.83	[42]
Diphenyl ether	163.9	30.9	1.15[a]	6.80	1.84	[41]
3,5,5-Trimethyl-hexylacetate	126	34.6	1.210	7.21	1.89	[39]
Bis-2-ethyl-hexyl adipate	145	(22.5)	(0.884)	(5.24)	(1.61)	[18]
			(1.513)	(8.96)	(2.11)	[18]
			1.145	6.78	1.84	[43]

[a] Measurement of temperature of precipitation.

[b] Calculated according to data of Chiang [38] for 140°C.

[c] Calculated by Wagner and Hoeve [39].

Table 3
Unperturbed dimensions of linear polyethylene, determined by light scattering and viscometric measurements in good solvents at the temperatures δ using various correction procedures

Solvent	δ (°C)	$10^4 K_\Theta$	$10^{16}\langle h_0^2\rangle/M$ (cm^2 mol g^{-1})	C_n	σ	Ref.
Decalin	140	–	1.14[a]	6.77	1.83	[5,38]
TCB	140	29.6	1.13[b]	6.50	1.82	[39]
	135	28.7	1.10[c]	6.52	1.80	[13]
	135	34.4	1.24[d]	7.38	1.91	[36]
CN	140	30.6	1.13[b]	6.50	1.82	[40]
	135			6.5–7.1		[19]

[a] $[\eta]$ in decalin, M_w in CN.

[b] Calculated by the method of Burchard [25], Stockmayer and Fixman [26] without correction for polydispersity.

[c] Calculated by the authors of this paper from the data of Hert and Strazielle [13].

[d] Calculated by the authors of this paper from the data of Peyrouset et al. [36].

As before, we used the unperturbed dimensions as an indicator for the quality of the data of other co-workers.

By reduction of data measured by viscometry in good solvents to theta conditions by the methods of Burchard [25], Stockmayer and Fixman [26] (Table 3), unperturbed dimensions were obtained, which fit the picture of data determined by viscometry directly in the theta solvent.

2.1. Reduction to the unperturbed state

There are some procedures [27–30] for reduction of the dimensions determined by light scattering in good solvents to the unperturbed state. These are well established for polymers such as polystyrene or polymethylmethacrylate. Here we present a collection of results for polyethylenes with recalculations of the data which were not subjected to such procedures by the authors.

Casper et al. [3] calculated the expansion factor α

$$\alpha^2 = \frac{\langle s^2\rangle}{\langle s_0^2\rangle} \tag{2}$$

according to the relationship of Orofino and Flory [31]

$$\alpha^2 = 1 + \left(\frac{4}{\pi}\right)^{1/2}\left(\exp\left[\frac{3^{3/2}}{16\pi N_A}\frac{A^2 M_z^2}{\langle s^2\rangle_z^{3/2}}\right] - 1\right). \tag{3}$$

Here, A_2 is the second virial coefficient of osmotic pressure and N_A the Avogadro number.

Analysing the data given by the authors, we got an exponent of 0.5, indicating theta conditions in the good solvent CN in contradiction to the expansion values $\alpha^2 > 1$. Therefore, the correction for theta conditions could not be successful and would give an exponent $a = 0.44$. We suspect that the higher intensity of scattered light for aggregated macromolecules influences M_w as well as A_2 and R_G, and the reduction of dimensions to theta conditions using A_2 and M_w from the same experiment becomes wrong. Even the correction of data for polydispersity was not successful, because the degree of molecular dissolution cannot be improved by this way.

We applied the procedures of Kurata et al. [29] and Stockmayer and Fixman [26] for the correction of the dimensions obtained by measurements in good solvents also to the data of Hert and Strazielle [13] (Fig. 2). In addition, the correction of the molar mass and the size by Bareiss et al. [32–35] for the influence of a broad molecular mass distribution was used (Fig. 3). The correction factors are based on a logarithmic normal distribution for the fractions, which may be more or less fulfilled in this case. The data corrected by this procedure correlate better now in this context.

2.2. Data in theta solvents

For many linear polymers reliable results were obtained in theta solvents by light scattering measurements. Probably because of the problems with dissolution and possible mistakes in the determination of molar masses for linear polyethylenes, this route is not practicable. Kotera et al. [18] published $\langle s_0^2\rangle_z$ for three fractions of polyethylene from measurements in the theta solvent di-2-ethyl-hexyladipate at 145°C (see Fig. 2). Stejskal et al. [20] used the same solvent and the mixed theta solvent CN/acetophenone and Agarwal et al. [21] characterised DPM solutions, without publishing the molecular dimensions.

2.3. Measurements by dynamic light scattering

Pope and Chu [22] and Chu et al. [23] published results of dynamic light scattering measurements from dilute polyethylene solutions. All these data were obtained from unfractionated samples, because the aim of that work was the determination of molecular mass distribution. The published hydrodynamic radii show the same trend as the radii of gyration obtained by static light scattering.

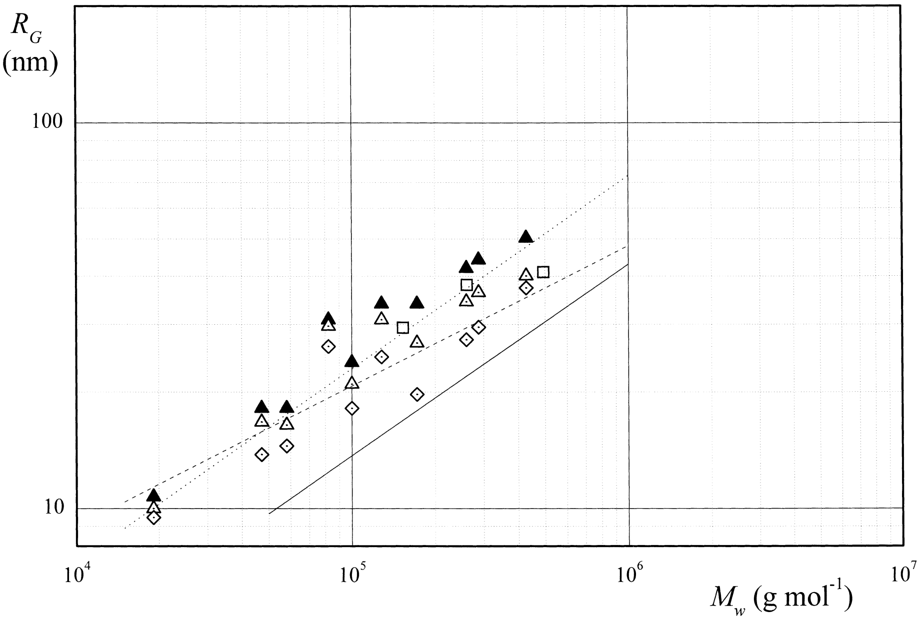

Fig. 2. Unperturbed radii of gyration $R_{G,0,z}$ vs. molar masses of linear polyethylene, calculated from the data of various authors: (▲) Casper et al. [3], $R_{G,z}$ measured in CN at 127°C; (··△··) corrected by these authors according to Orofino and Flory [30] for theta conditions, $R_{G,0,z}$; (- - ◇ - -) corrected by these authors according to Orofino and Flory [30] for theta conditions, $R_{G,0,w}$; (□) Kotera, Matsuda and Wada [18], unfractionated samples, dissolved in the theta solvent, di-2-ethylhexyl adipate, at 145°C; (—) unperturbed dimensions of linear polyethylene [12].

3. Measurements at theta conditions

To study and assess the differences between the results and the reasons for them we carried out static light scattering measurements on sets of fractions of linear polyethylene in the theta solvent diphenylmethane (DPM) [38]. The procedure for the precipitation fractionation of the samples A–C is described in Ref. [21] and that for the elution fractionation of sample D in Ref. [44].

3.1. Experimental part

The fractions were dissolved in vacuum distilled diphenylmethane at 145° C. The solutions of the fractions from samples A–C were cleaned by filtration through sintered glass filter Jena G5, the fractions from sample D through Millipore filters MITEX® with a pore diameter of 5 μm, both preheated to the same temperature. All the measurements were carried out with a FICA 50 Photogoniodiffusometer and unpolarised light of wavelength 546 nm. The z-averaged mean-square radius of gyration R_G is calculated from the light scattering experiments according to

$$\frac{Kc}{R_\vartheta} = \frac{1}{M_w}\left(1 + \frac{16\pi^2}{3\lambda^2}R_G^2 \sin^2\frac{\vartheta}{2}\right) + 2A_2c + \cdots \qquad (4)$$

where c is the polymer concentration, R_ϑ Rayleigh ratio at the angle ϑ, λ wavelength of the light in the medium, A_2 second virial coefficient and K the optical 'contrast' factor, given here for unpolarised light:

$$K = \frac{4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2}{\lambda_0^4 N_A}\,\frac{1+\cos^2\vartheta}{2} \qquad (5)$$

(n being the refractive index of the solvent [45], here 1.525 at 142°C and 546 nm, dn/dc the refractive index increment [45,46], here $-0.125\ \mathrm{cm^3\,g^{-1}}$) and N_A the Avogadro constant).

3.2. Results and discussion

Properties of the fractions and the results of light scattering measurements are shown in Table 4. In Fig. 4 the radii of gyration R_G, obtained by 'wide-angle' evaluation of the data, are plotted against M_w of the fractions. The open points represent data of the small-angle evaluation (Zimm plot) for the fractions of sample D, which differ very strongly from the expected unperturbed dimensions [12]. Also, the results of 'wide-angle' evaluation (90–150°), which better represent the main part of the samples, are higher than those data.

By linear regression of log R_G vs. log M_w over all fractions we find

$$R_G = 0.5857 M_w^{0.325}\ (\mathrm{nm};\ X^2 = 0.864).$$

The exponent is far from 0.5 expected for flexible linear macromolecules at theta conditions. Very likely a small amount of undissolved, aggregated or highly branched [21] (even though we work with 'linear' polyethylene) molecules increased both the molar mass and the size. The scattering envelope differs at small angles strongly from the expected behaviour for small linear macromolecules.

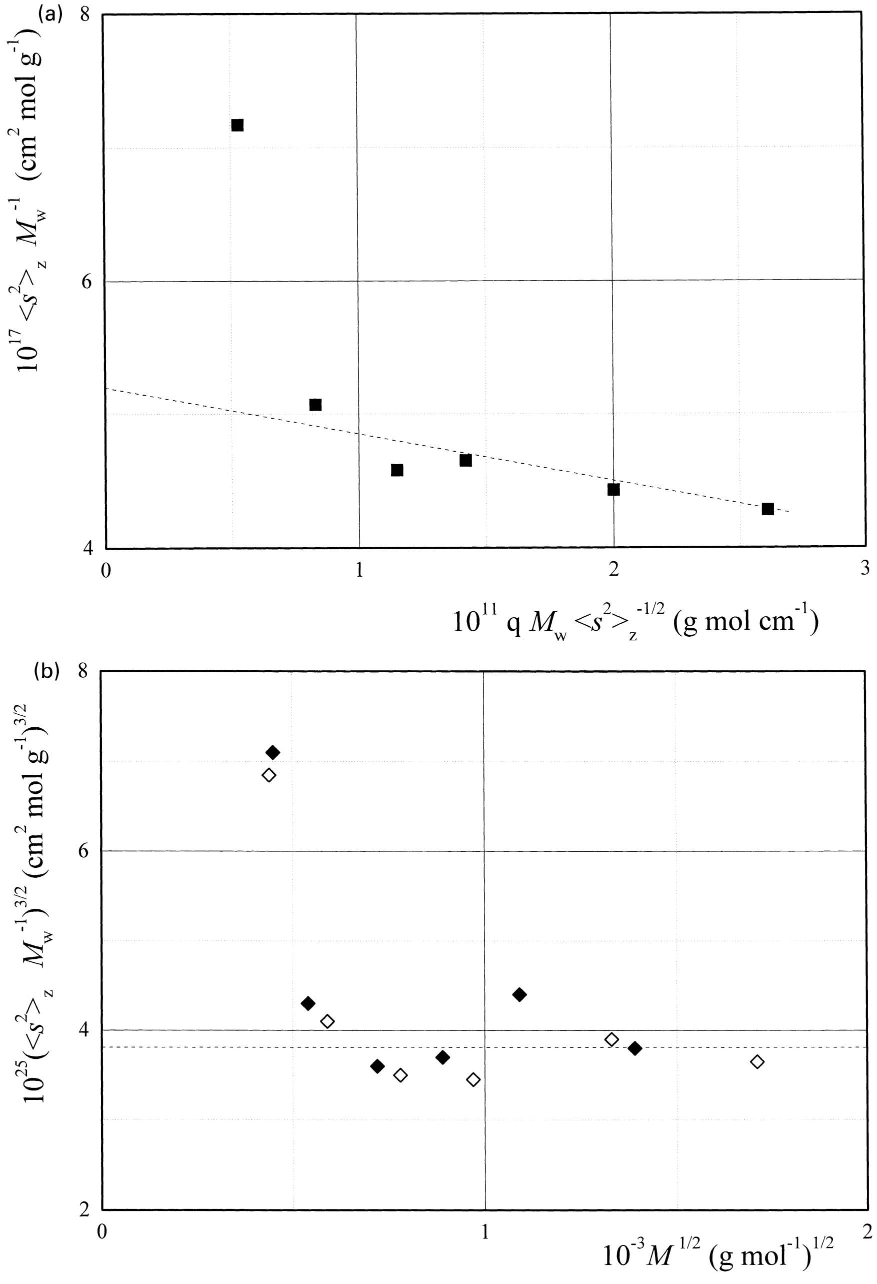

Fig. 3. Determination of the unperturbed dimensions of linear polyethylene from the data of Hert and Strazielle [13] using the correction factors of Bareiss et al. [32–35] for molar mass distribution: (a) by the method of Baumann et al. [28,29]; (b) by the method of Burchard [25], Stockmayer and Fixman [26] — (◆) uncorrected; (- - ◇ - -) corrected.

3.3. Two-component separation

After good experience in other fields [47,48] we applied a two-component separation procedure in the version described by Francuskiewicz and Dautzenberg [49] in order to separate the contribution of linear macromolecules of polyethylene from a second component that falsified the data. The unperturbed dimensions have to be valid in this case and can be used as a basis for the calculation of both the components using the formula of Debye [50] for scattering of linear macromolecules assuming the second component to result also from that polymer. Here is a variation to the procedure [49]: Whereas in the Dautzenberg calculation the substance is divided into a main part of coils and a small part of spherical scatterers, we split the substance into two parts, both obeying the approximation

$$w_1 + w_2 = 1 \qquad (6)$$

and

$$w_1 M_{w,1} + w_2 M_{w,2} = M_w. \qquad (7)$$

The calculation of Kc/R_Θ of the first component using the

Table 4
Characterisation of fractions and data of static light scattering in diphenylmethane

Sample		M_w (GPC) ($\mathrm{g\ mol^{-1}}$)	M_w/M_n (GPC)	$10^{-3}M_w$ (SLS) ($\mathrm{g\ mol^{-1}}$)	R_G (nm)
LITEN® MACRO	A 7	27	1.42	26	20
	A 8	47	1.33	41	16
	A 9	44	1.33	45	21
	A 10	92	1.38	99	21
	A 11	115	1.44	110	23
	A 12	230	1.42	230	27
	A 13	590	1.74	570	50
LITEN® 1302	B 4	12	1.26	15	17
	B 5	19	1.24	22	14
	B 6	29	1.65	37	20
	B 7	42	2.33	43	21
	B 8	42	1.54	45	20
	B 9	110	1.45	120	22
	B 10	140	2.11	175	29
	B 11	170	1.48	190	28
	B 12	430	3.10	410	47
	B 13	610	2.04	570	51
HOSTALEN® GM 9255 F	C 3	–	–	1000	53
	C 4	–	–	435	33
	C 6	–	–	223	26
	C 8	–	–	146	25
	C 10	–	–	33	13
	C 14	–	–	125	28
	C 15	–	–	330	52
	C 16	–	–	790	45
	C 17	–	–	1380	61
HOSTALEN® GM 5050	D 8	89	1.11	98	51
	D 11	150	1.16	149	127
	D 12A	226	1.20	252	63
	D 12B	261	1.22	158	89
	D 13A	339	1.28	382	82
	D 13B	422	1.30	287	112

R_G–M_w-relation of the unperturbed dimensions starts at the wide-angle region (90–150°). In this region, the difference between the measured data and the calculated angular scattering envelope for the first component is small, but mostly not negligible. This difference (‘residue’) is interpreted as second component and dominates the small-angle region (15–75°). The procedure consists of the splitting of Kc/R_Θ measured at various angles into two components and the approximation of both with sets of data for M_w and R_G. At the end of the approximation, Eqs. (6) and (7) and the R_G–M_w-relation have to be fulfilled and a closed picture of both components is reached. Important for the visualisation of the results is to take into consideration that for $w_2 \ll 1$, the apparent molar mass in the calculation is very small compared with the real mass of the macromolecules with an apparently disproportionately high size.

In Table 5 the results of the separation are shown for the fractions from sample D. The results of the Zimm plot

Table 5
Two-component separation of light scattering data of selected fractions of linear polyethylene HOSTALEN® GM 5050 in DPM at 142°C

Fraction	$10^{-3}M_w$ ($\mathrm{g\ mol^{-1}}$)	R_G (nm)	R_{G1} (nm)	$10^{-3}M_{w1}$ ($\mathrm{g\ mol^{-1}}$)	w_2	R_{G2} (nm)	$10^{-6}M_{w2}$ ($\mathrm{g\ mol^{-1}}$)
D 8	97.5	21	9	47	0.004	145	12
D 11	149	24	11.2	70	0.003	210	24
D 12A	252	36	13.6	102	0.011	250	34
D 12B	158	26	13.5	100	0.004	161	14
D 13A	382	38	16.3	147	0.016	233	30
D 13B	287	33	15.4	132	0.008	280	43

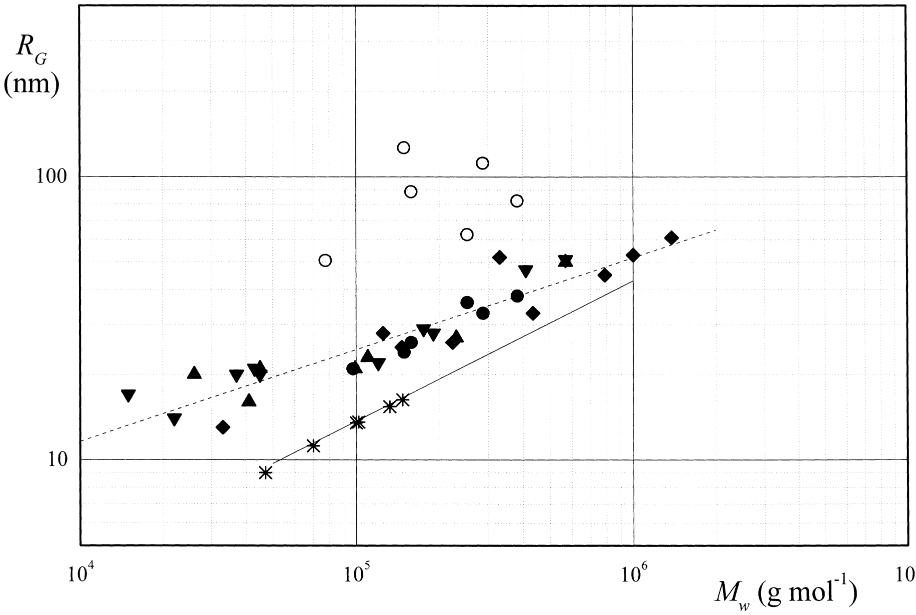

Fig. 4. Radii of gyration R_G vs. M_w, both determined by static light scattering in DPM at 142°C. Fractions of: (▲) sample A, (▼) sample B, (◆) sample C, (●) sample D ('wide-angle' evaluation), and (○) sample D ('small-angle' evaluation). Two-component separation of the fractions of the sample D: (∗) component 1; and (+) component 2. (—) Unperturbed dimensions [12].

including the small-angle region of the data are given in Fig. 4 ('small-angle' evaluation). The main advantage is that, in the case of linear polyethylene, we are able to use the R_G–M_w-relation corresponding to the unperturbed dimensions directly for the calculation of the first (main) component. *Therefore*, by definition, all the points are located on the line for the unperturbed dimensions, and for the main component, reliable data are obtained.

As a second step, we use the same relation for the calculation of the residue representing the second component and demonstrate that only 1% of the polymer substance or less increases strongly as molar mass, M_w, as the size parameter R_G. One could filter off this component before the measurement more or less quantitatively, but we included it in the measurement *and* the evaluation. According to the mass and size as given in Table 5 (w_2, M_{w2}, R_{G2}) and the characteristic angle dependency of scattering intensity, this component seems to consist of aggregates or big molecules, because all the data fulfil Eqs. 6 and 7 *and* the same R_G–M_w-relationship, as we used for the first component, is applicable. Considering the quality of description of the properties of the macromolecules in the fractions, the second component is unfortunately not more than a correction factor. On the other hand, we are now able to quantify the errors and the strong falsification of the data measured by light scattering, because we exactly know the deviation from the dimensions of macromolecules in the theta solvent of our measurements. We consider the calculations on linear polyethylene and their consistency as a proof for the reliability of this procedure. In a future paper we want to check it with a more difficult system.

4. Conclusions

The goals of the first part of our work were to demonstrate the mistakes in the stock of literature data and to select the best available data as a basis for safe calculations. The molar mass and molecular size are increased strongly by a very small amount of substance, whereas the exponent of the R_G–M_w-relationship is decreased in the same manner as we also observed in all cases of the 'historic' data for the unperturbed dimensions of linear polyethylene obtained by light scattering. Finally, the development of a new generation of light scattering detectors will open the way to new experiments in this field. Nevertheless, it seems necessary to learn the relations between the mass and the size of macromolecules as a basis for their molecular characterisation, which can be overcome by calculations like those we presented here. In the second part of the paper we will discuss light scattering measurements on branched polyethylenes.

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