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Data Evaluation in Light Scattering from Solutions of Branched Polyethylene

Martin Helmstedt*
University of Leipzig, Faculty of Physics and Geosciences,
D-04103 Leipzig, Germany

Jaroslav Stejskal
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

Walther Burchard
University of Freiburg, Institute of Macromolecular Chemistry,
D-79104 Freiburg, Germany

Dedicated to Professor Dr. Gottfried Glöckner on the occasion of his 75th birthday

SUMMARY: The molecular dimensions of branched polyethylene published in the literature were re-evaluated to obtain the radii of gyration R_G and other relevant topological parameters. By means of the exponent a_s in the relationships $R_G = b \cdot M^{a_s}$ the reliability of the data and reasons for deviations were discussed. Linear and branched polyethylenes are molecularly dissolved only in the good solvent, tetralin, whereas in 1-chloronaphthalene and 1,2,4-trichlorobenzene the exponent a_S is lower than expected for good solvents. Microgels and aggregates affect the exponents. After correction of the data by a two component separation method in combination with model calculations and the analysis of scattering curves, a consistent picture is obtained. This procedure is demontrated with fractions of branched polyethylene in the theta solvent diphenylmethane, which are indicating incomplete molecular dissolution.

Introduction

In the first part[1)] of this series of papers the molecular dimensions of polyethylene from published literature data of linear polyethylene were critical evaluated and confronted with own data measured in theta solvents. Obviously, the great experimental difficulties with polyethylene were reason to avoid the use of static light scattering for determining the molecular parameters

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*To whom correspondence should be adressed (e-mail: helmstedt@physik.uni-leipzig.de).

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of linear and branched polyethylenes. In comparison to the high number of viscometric investigations, the stock of results from light scattering is old and limited, and only a critical discussion of the known data and the combination with other methods could help to avoid errors and to attain safe conclusions.

The results obtained by multiangle detectors require knowledge of how to treat the data for proper evaluation. Long-chain branching of low-density polyethylenes reduces the molecular dimensions. The contraction factor $g_s = \langle s^2\rangle_b / \langle s^2\rangle_l$ of the mean square of the unperturbed radii of gyration $R_G \equiv \langle s^2\rangle_z^{1/2}$ of the branched (b) and linear (l) macromolecules was determined by Zimm and Stockmayer[2)] as a measure of the degree of branching. A corresponding equation for the contraction factor of intrinsic viscosities $g_\eta = [\eta]_b \,/\, [\eta]_l$ was derived only for star-branched macromolecules by Zimm and Kilb[3)], but a general relationship is not yet available. On the basis of the result of Zimm and Kilb and from a sift of in those days existing experimental data Kurata et al.[4)] made the empirical suggestion of a power law correlation $g_\eta = g_S{}^b$ with an exponent b ≈ 0.6.[2-6)]

For branched polymers, like the technically very important low-density polyethylene, the absolute method of static light scattering could be a powerful tool for estimating the molar mass and molecular dimensions. In principle the contraction factor can be determined experimentally from the radii of gyration at theta conditions (Dautzenberg[7)]), if the corresponding reference curves for monodisperse linear chains were available. Difficulties in realizing this idea became already evident in 1971 when the results of the Working Party of the IUPAC Macromolecular Division[8,9)] were published. The more sensitive results of radii of gyration and virial coefficients were not published, but even the data for the molar mass, M_w, showed an intolerably large scatter. This could be retraced to the presence of highly stable crystal nuclei, which can only be dissolved by increasing the temperature of measurements to 80°–145°C, depending on the solvent used.

Critical analysis of the literature data from light scattering

In this contribution a collection of data is revisited which were measured in solvents of different thermodynamic quality and are characterized by exponents a_s in the R_G–M_w relationships.

1-Chloronaphthalene (CN) dissolves polyethylenes at temperatures higher than 125°C, and is favorable for light scattering because of a high refractive index increment ($dn/dc = -0.190$ cm^3 g^{-1})[10)]. Therefore, the accuracy of these results (Figure 1) should be best in comparison to data from other solvents. From the results with unfractionated samples of Casper et al.[11] we found the relationships $R_G = 0.0833\ M_w^{0.477}$ (nm) (based on three values, 20 CH_3/1000 C) and $R_G = 0.327\ M_w^{0.357}$ (nm) (based on four values, 25 CH_3/1000C).

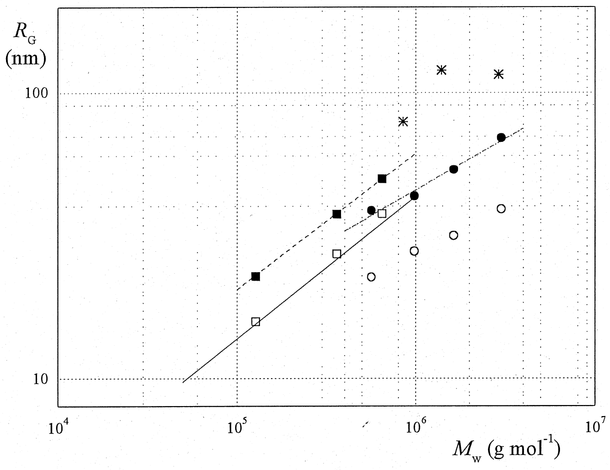

Fig. 1: Radii of gyration R_G vs. M_w of branched polyethylenes in CN at 125 °C, and 127 °C, resp., Casper et al.[11], 127 °C: ---■--- 20 CH_3 /1000 C, □ corrected according to Orofino and Flory[12]; -.-●-.- 25 CH_3 /1000 C, ○ corrected according to Orofino and Flory[12]; unfractionated samples: ✱ Moore and Peck[13], 125 °C; — unperturbed dimensions of linear polyethylene (Wagner and Hoeve[14]).

The authors corrected these data for theta conditions according to Orofino and Flory[12], as described for linear polyethylene in the first paper of this series[1] . The corrected values are shown in Figure 1 and can be compared with the unperturbed dimensions for linear polyethylene[14]. Unfortunately, one of the corrected sets of the *branched* samples yields dimensions higher than the unperturbed dimensions of *linear* polyethylene. Shirayama[15] published results for the mean-square end-to-end distance derived from the dissymetry of the scattering intensity. The data are not reliable because the end-to-end distance is not measurable. Moreover, the particle scattering factors are different from those of linear molecules of normal particle density. The results of Moore and Peck[13], obtained with unfractionated samples, do not agree with the data of fractions.

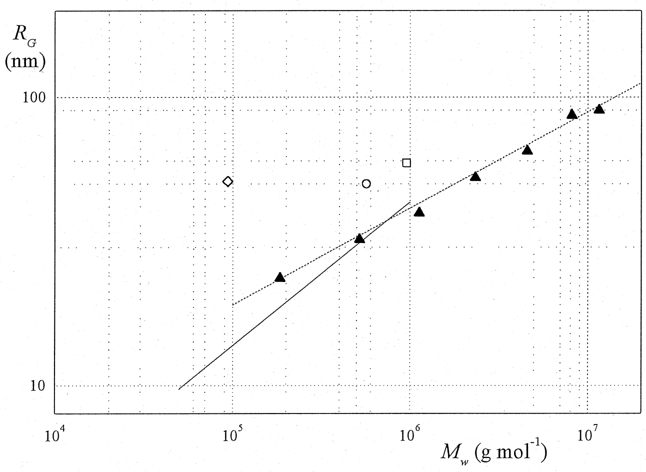

Fig. 2: Radii of gyration R_G vs. M_w of branched polyethylenes in TCB at 135°C
---▲--- Hert and Strazielle[16);
unfractionated samples: ○ Pope and Chu[17), □ Chu et al.[18), ◇ Stejskal et al.[19);
——— unperturbed dimensions of linear polyethylene[14).

Linear regression of the data of Hert und Strazielle[16) measured in 1,2,4-trichlorobenzene (TCB, Fig. 2) for fractions of branched polyethylene of unspecified density gave the relationship R_G=0.384 $M_w^{0.336}$ (nm) with a very low exponent a_s = 0.34. However, this is an unrealistic value for fully dissolved flexible macromolecules of low molar mass and may be due to a small part of highly branched and incompletely dissolved molecules in the fractions. Already a percentage of < 1 % in mass of aggregates causes a scattering of light larger than the main part of molecularly dispersed macromolecules with $M = 10^5$ g mol^{-1}. Results for unfractionated samples were also given by Pope and Chu[17), Chu et al.[18) and Stejskal et al.[19)

In Fig. 3, the data of Kuhn et al.[20) of two sets of fractions from the samples A and B of branched polyethylene in tetralin with different long-chain branching are given with $R_G = 0.245\, M^{0.407}$ and $R_G = 0.220\, M^{0.395}$ (nm). Nicolas[21) published data obtained only with unfractionated samples. Nonetheless, the congruence of results measured in a broad temperature region is here of interest. For linear and branched polyethylenes in tetralin a consistent picture is obtained. Further data were published by Schröder, Arndt et al.[22,23) in graphical form, for five fractions of branched polyethylene in *o*-dichlorobenzene and *n*-decane.

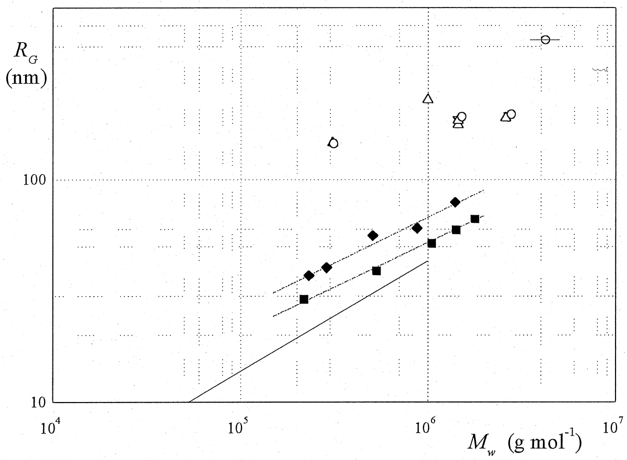

Fig. 3: Radii of gyration R_G vs. M_w of branched polyethylenes in tetralin at various temperatures; Kuhn et al.$^{20)}$, 120 °C: -··-◆-··- sample A, -·- ■ -·- sample B; unfractionated samples: Nicolas$^{21)}$ △ 80°C, ▽ 100°C, ○ 120°C or 125 °C, resp.

The very broad range in scatter of data, measured in the same solvent, can be explained by the differences in the preparation of solutions in various laboratories. Different dissolution temperatures and different clarification procedures (mostly by filtration) were used. Furthermore, poor instrumental alignment for measurements at high temperatures could be another reason for lack in precision and reproducibility. All the exponents are unexpectedly low for flexible macromolecules in good solvents, even for branched ones. TCB is thermodynamically a good solvent for polyethylenes, because the second virial coefficients A_2 are relatively high (Fig. 4): The virial coefficient decreases with increasing molar mass but also with increasing branching. Theory predicts the general behaviour $A_2 = 4\pi^{3/2}\, N_A\, (R_G^3 / M^2)\ \Psi^*$ from which the scaling relationship between the corresponding exponents in the molar mass dependencies follows $a_{A2} = 3a-2 = 3/d_f - 2$, where $d_f = 1/a$ is the fractal dimension of the particle or macromolecule. In the equation for A_2, the function Ψ^* represents the coil-coil interpenetration function that, in a good solvent is molar-mass independent but increases with branching$^{24)}$. Linear flexible chain molecules in good solvents have dimensions of $d_f = 1.7$ and of $d_f = 3.0$ for hard spheres$^{6,25)}$. The mentioned scaling law often holds also for branched self-similar materials. Almost all data from the quoted authors are in the region of good solvent behaviour. Thus, differences in the solvent quality cannot be the reason for observed deviations. The same holds for tetralin and CN as solvents for polyethylene.

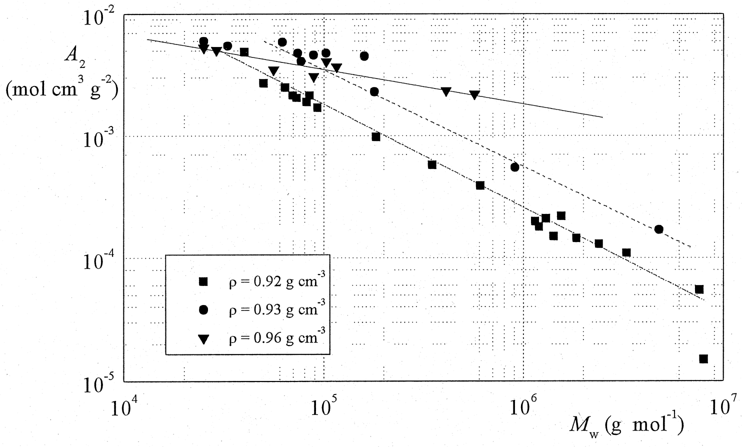

Fig. 4: Second virial coefficient, A_2, of polyethylene fractions of different density, ρ, in TCB at 135°C as a function of molar mass, M_w.

Problems of solution preparation

It can be assumed that the preparation of the polymer solutions was different in various laboratories. Most of the authors have not defined their working conditions. According to our own experience the temperature of dissolution of the polymer is a crucial parameter. It should be high enough to guarantee diffusion of the solvent into the semicrystalline part of the partially ordered polymer. This is the case at T>120°C for tetralin and T> ~150°C for CN and TCB. For clarification a heated filter set would be the simplest equipment. Filtration and especially the pore size of chosen filters influence the results. The results of a quantitative weight analysis of dried filters after filtration are given in Table 1. A ‚fractionating‘ filtration clearly becomes noticable when the pore size was decreased. The same effect is recognized in Fig.5 from Zimm plots obtained with the same solution of branched polyethylene after filtration through filters of different pore diameters.

Table 1: Selective (‚fractionating') filtration of low density polyethylene in tetralin

ρ (g cm^{-3})	$10^{-6} M_w$ (g mol^{-1})	Pore diameter (μm)	Residue (wt. %)
0.918	1.03	0.5	0.61
		5	0.34
0.925	0.70	0.5	1.3
		5	0.15
0.927	0.96	0.5	1.28
		1.5	0.21
		5	0.18

Additionally, in the course of filtration the original pore diameter can be narrowed by particles which cannot pass the filter. Reproducible results can be obtained, howewer, by first filtering a stock solution at a temperature slightly above the temperature for measurement followed by its dilution to the desired concentrations. Only in this way *differences* in selecting big particles from solutions of different concentration are avoided. A not defined fraction of the substance is retained by the filter. With increasing molar mass a larger pore diameter has to be applied, still the molecular parameters not necessarily will agree with those obtained by size-exclusion chromatography and viscometry. Other authors used a heated centrifuge for the clarification of the solutions, but also in this case the effect depends on the conditions of the applied special procedure.

Chemical problems, for instance caused by peroxides in tetralin, or the stability of the dissolved macromolecules and solvents against oxygen at the elevated temperatures, can be overcome by addition of antioxidants. Reproducible results can be expected if all these conditions are standardized.

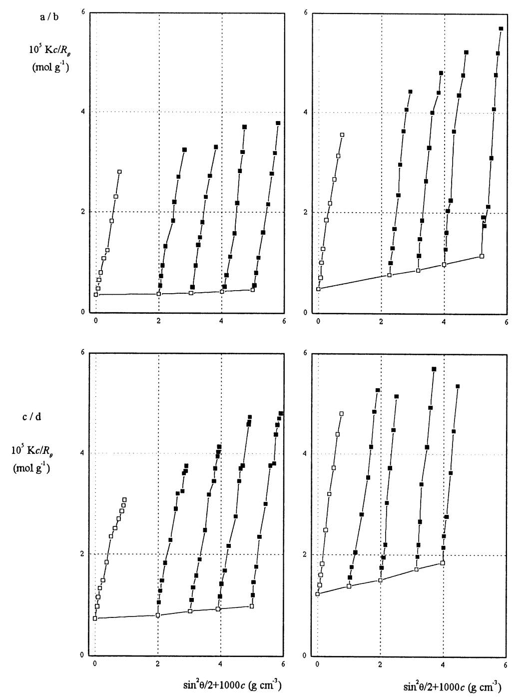

Fig. 5: Zimm plots of a low-density polyethylene solution in tetralin at 100°C, filtered through
(a) cellulose filter for chemical analysis, degree "hard"; ↪ $M_w = 1.3\cdot10^6$ g mol^{-1};
(b) SYNPOR® filter, pore diameter 1.5 μm; ↪ $M_w = 9.3\cdot10^5$ g mol^{-1};
(c) Millipore SOLVINERT® filter, pore diameter 0.45 μm; ↪ $M_w = 6.0\cdot10^5$ g mol^{-1};
(d) Millipore FLUOROPORE® filter, pore diameter 0.3 μm; ↪ $M_w = 4.0\cdot10^5$ g mol^{-1}.

Scattering standards at elevated temperatures

For comparison of results a standardization of scattering standards becomes necessary. Pure aromatic hydrocarbons, as for instance, benzene and toluene, distilled into dust-free ampoules and sealed, are the best scattering standards at room temperature. Their absolute scattering intensities at different wavelengths were published by Millaud and Strazielle[26)] and were accepted and applied by most laboratories. Also standardized glass cylinders have been well introduced. In contrast to liquids, their scattering intensity is stable over a broad temperature range at least up to 200°C and, according to our own experience, for decades of years. For the calibration it is only necessary to measure the relation between the scattering intensities at defined room temperature (e.g. 25°C), and that of the glass standard at the elevated measuring temperature (e.g. 200°C). Production and distribution of scattering standards, especially for measurements at elevated temperatures, are an urgent request to producers of equipment and national standardization bureaus, which contemporarily is missing.

The literature data discussed in this review were not obtained under such standardized conditions. This is one reason for avoidable deviations. Other deviations result from the polymerization procedure, which may contain a different microgel content or different chemical compositions. Also the fractionation procedure may result in a different molar mass distribution for the fractions.

Measurements in diphenylmethane at theta conditions

Experimental part

Diphenylmethane (DPM) was distilled under vacuum before use. The samples were dissolved by shaking at 160°C for four hours. Stock solutions were filtered by means of an electrically heated filtration set with polytetrafluorethylene membrane filters of 25 mm diameter and of 1 μm pore diameter (FLUOROPORE® FH, Millipore, USA) together with measured quantities of the pure solvent into glass ampoules, which then were sealed. The skeleton of polypropylene at the filter surface was dissolved before the first filtration at elevated temperature, and then the filter was rinsed with pure hot solvent. The light scattering measurements were carried out with Photogoniomètre FICA 50 at 142°C. A FICA glass standard was used for calibration. The Rayleigh ratio was calculated from the data of Millaud and Strazielle26) for the absolute scattering intensity of benzene and toluene, and $K = 4\pi^2 n^2 (dn/dc)^2 / \lambda_0^4 N_A$ from data of Stejskal et al.19) for $(dn/dc)_{546}^{142} = -0.120$ cm^3 g^{-1} and $n_{546}^{142} = 1.525$.

Data evaluation

Parallel to our measurements on fractions of linear polyethylene at theta conditions we examined a set of branched fractions in diphenylmethane at 142° C and tried to get the unperturbed dimensions of the branched material. The experimental conditions and equations used are given in the first part1) of this series. The fractions were prepared by elution fractionation and characterized through GPC by Brauer et al.27) The characteristic data of the fractions and results of the standard evaluation by a Zimm plot are given in Table 2.

Table 2. GPC and LS results on fractions of branched polyethylene ($\rho = 0.91$ g cm^{-3}) in DPM at 142°C, and results of two-component separation (TCS; see text).

	U*	$10^{-3} M_\mathrm{w}$ (GPC) (g mol^{-1})	$10^{-3} M_\mathrm{w}$ (LS) (g mol^{-1})	R_G (nm)	$R_\mathrm{G,1}$ (TCS) (nm)	$10^{-3} M_\mathrm{w,1}$ (TCS) (g mol^{-1})	$10^{-6} M_\mathrm{w,2}$ (TCS) (g mol^{-1})
1	0.16	126	256	150	15	113	1058
2	0.78	170	287	143	16	170	400
3	0.24	273	512	234	20	273	509
4	0.66	635	1786	208	27	635	28
5	(1.49)**	647	*(820)**	*(124)**	*(20)**	279*	223*

* $U = (M_\mathrm{w} / M_\mathrm{n}) - 1$;

** Not relevant because of the broad distribution of molar mass.

The angular distribution of the scattered light (extrapolated to $c = 0$) is shown in Fig. 6.

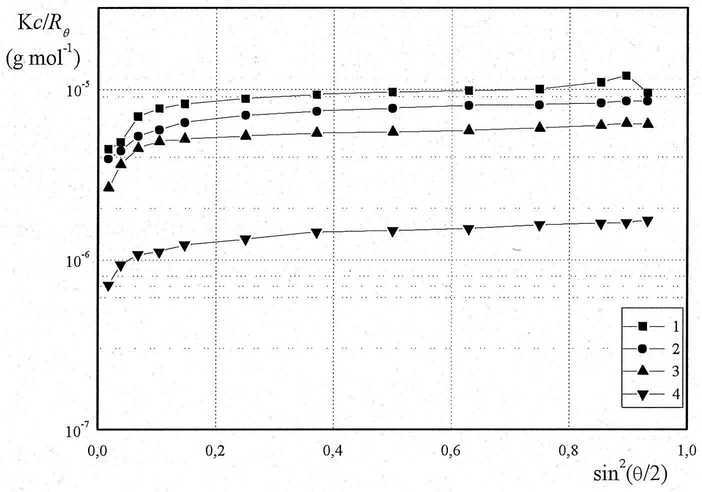

Fig. 6: Angular dependences of scattered light, Kc/R_θ, of selected polyethylene fractions (see Table 1) in DPM at 142°C.

Contrary to expectation no linear q^2 dependence ($q = (4\pi n_0/\lambda)\sin(\theta/2)$) is observed, but a steep increase at small angles is found that flattens at larger scattering angles. Such behaviour is characteristic for the presence of large particles besides the dissolved polymer. According to the strong upturn at small angles the radii of gyration are much higher than the unperturbed dimensions of linear polyethylene and show no regularity.

The influence of these large particles can be separated and characterized by a two-component analysis[28-30] which we applied to linear polyethylene[1]. A similar but independent procedure can be performed by dynamic light scattering results applying a Laplace inversion of the time correlation functions. In principle the angular scattering envelope, consisting of the Kc/R_θ data, measured at various angles and extrapolated to $c = 0$, is divided into two parts and interpreted as two not necessarily monodisperse species.

A sensible separation of the measured scattering curve into two components is possible if certain assumptions on the structure of the particles and macromolecules are made. In the original paper the variety of linear macromolecules as the first component, calculated by Debye's famous equation for monodisperse random coils[31], were separated from the second species, whose scattering behavior is simulated by $P(q)$ of hard spheres (Rayleigh)[32]. On the example of linear polyethylene the assumption to be made was obvious.

The evaluation for branched polyethylene is more involved. The major weight fraction consisted of molecularly dispersed chains with a molecular polydispersity ratio of $M_w/M_n = 1.5 - 2.0$ and could thus be well approximated by the simple Zimm equation $P_1(q) = [1 + (1/3)\langle s^2\rangle_z q^2]^{-1}$ that was derived from Debye's formula[31] for linear coils after averaging over the Schulz-Zimm molar mass distribution[34]. The second part very likely resulted from not dissolved stable crystallites which are globular and certainly polydisperse. Such structures are well represented, e.g., by the Guinier approximation $P_2(q) = \exp[-(1/3)\langle s^2\rangle_z q^2]$. The particle scattering factor for the aggregated chains will not have changed much and could again be described by the Guinier approximation, but the major dissolved component 1 may deviate from Zimm's equation. However, the difference will be small and scarcely detectable if $qR_g < 0.8$. The procedure was successfully applied, e.g., to the separation of microgels in copolymers by Glöckner and Francuskiewicz[33]. In any case the weight fraction of the second component is often no more than a correction to the weight fraction of the first (main) component.

For larger macromolecules application of Debye's formula for the scattering of coils from linear and flexible macromolecules to the evaluation of branched polymers leads to remarkable errors. This was demonstrated already 1978 by Toporowsky and Roovers with branched polystyrene[35].

Thus our model calculations for a fit of the experimental data were made on the basis of models for branched macromolecules.

$P(q)$ and the light scattering of branched polymers

The scattering of visible light from various types of branched polymers in dilute solutions is well described[36-50]. Already 1953 Benoit[43] derived in an elegant short communication the scattering function for star-branched macromolecules. He also indicated the direction how to proceed further by introducing the number and density of segments between branching points and discussed various models of branching. Orofino[44] derived a first equation for the scattering of comb-like macromolecules. This derivation was confirmed by Kolbovskii[45,46]. A collection of final equations were given by Dautzenberg and Ruscher[47-50] for stars, combs and cascades. Casassa and Berry[51] specified the calculation to various types of comb-like molecules taking into account non-uniformity of composition and polydispersity of the backbone length. Fundamental studies of both the static *and* dynamic scattering behavior of randomly, and hyperbranched macromolecules including a broad molar mass distribution were derived by Burchard et al.[37-41] on the basis of Gordon's cascade theory[38,40]. The latter authors also introduced the soft-sphere model [41], which describes the scattering of regular multiply branched molecules, now better known as dendrimers. The influence of branching on the scattering envelope is masked by the molar mass distribution (Kratochvíl[36]), and for randomly branched unfractionated samples the scattering envelope becomes indistinguishable from that of a polydisperse chains which obey the Schulz-Flory most probable length distribution[40]. Simulations of unfractionated polyethylenes with the model for comb-like polymers of Solensky and Casassa[52] were published by Nordmeier et al.[53]

Model calculations

Our model calculations were carried out on the basis of the Casassa and Berry equation[51] for the particle scattering factor of heterogeneous comb-like branched macromolecules

$$P(q)=\frac{2/u^2}{1+(1-L)^2/f}\left[u-(1-e^{-uL})+(1-e^{-u(1-L)/f})\left(f-\frac{2(1-e^{-uL})}{uL/f}\right)+(1-e^{u(1-L)/f})^2\left(\frac{uL-(1-e^{-uL})}{(uL/f)^2}\right)\right]$$

with $u = \mathrm{k}N = (4\pi/\lambda)^2 (Nb^2/6) \sin^2(\theta/2)$ and λ the wavelength of the laser light in the medium. The parameter $L = N_0 / N$ is the fraction of the main chain in the molecule, with $N = N_0 + \mathrm{f} N_\mathrm{b}$ the total number of segments in the molecule and N_0 the number of segments in the backbone. f is the number of branches per molecule, each with N_b segments, and b = 0.153 nm[51)] the bond length. Nordmeier et al.[53)] found the segment length for branched polyethylenes to ≈ 1 nm. The data in the present paper were calculated using the data of Eckhardt et al.[54)] for this tubular-type low density polyethylene. A decrease of f with increasing M_w is unlikely (Schröder and Maderek[55)]), and solutions on this basis have to be rejected. The fraction of segments in the backbone was varied from L = 1,...,0 to include linear (L = 1), branched ($1>L>0$) and star-like chains (L = 0). Examples of the model calculations are shown in Figures 7 and 8.

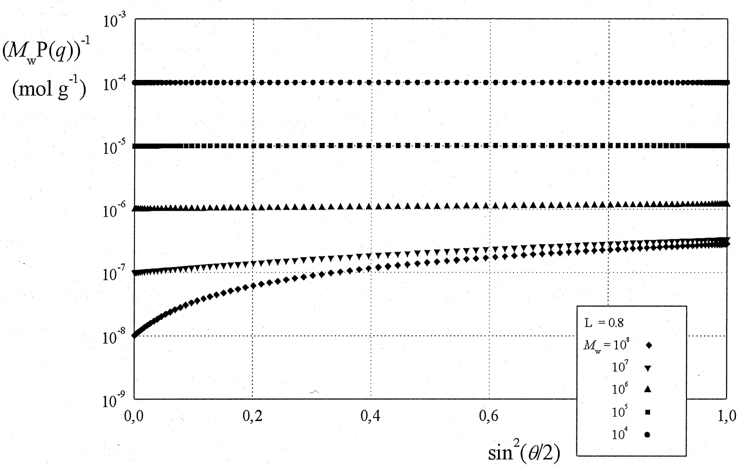

Fig. 7: Model calculations of $1 / M_\mathrm{w} P(q)$ vs. $\sin^2(\theta/2)$ for polyethylene in DPM at 142°C, with L = 0.8, according to 1.5 long chain branches / 1000 C atoms. (For other parameters see text.)

It might be questionable, whether the scattering behavior of Fig. 8b could be represented by a curve analysis on the basis of the Casassa and Berry model as shown in Fig. 8a. However, good fits were obtained with L = 0.6,...,0.8 leading to N_b ≈ 40,...,100 segments in the side chain. These values appear realistic, if considered as a weight average. On the other hand, the high number of short chain branches with 2-5 C atoms may arise the question whether they exert a measurable influence on the scattering behavior and, in a positive case; whether they can be realized by the used model.

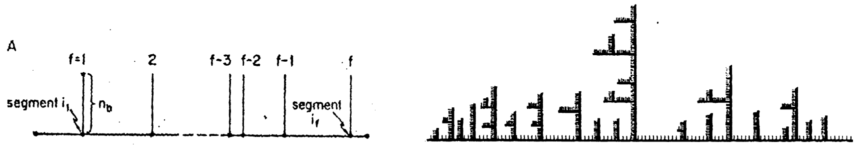

Fig. 8: Chain model of irregular comb[51)] (left) and tubular process low-density polyethylene[27)] (right).

For comparison the particle scattering factors for a few other branched architectures are shown in Figure 9.

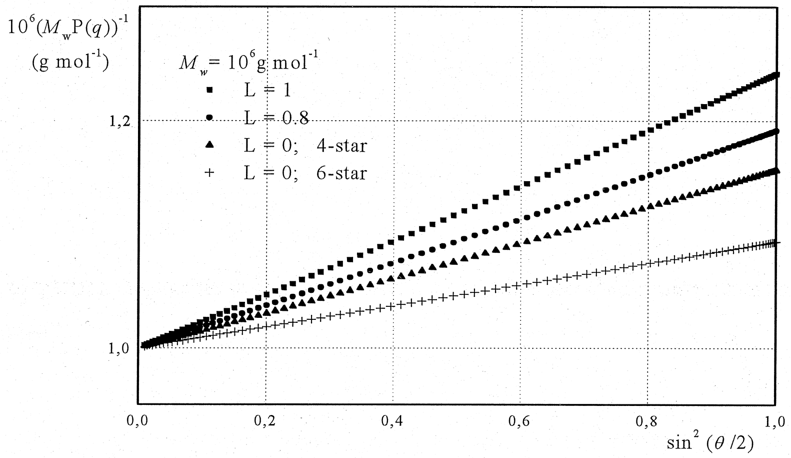

Fig. 9: Model calculations of scattering envelopes $1/M_wP(q)$ vs. $\sin^2(\theta/2)$ for linear ($L = 1$) and branched ($L = 0.8$) polyethylenes and for different star-like polymers ($L = 0$).

Two-component separation including simulation of branched macromolecules

The two-component separation was done in combination with simulations of the same type of branching for both components. An example is given in Fig.10.

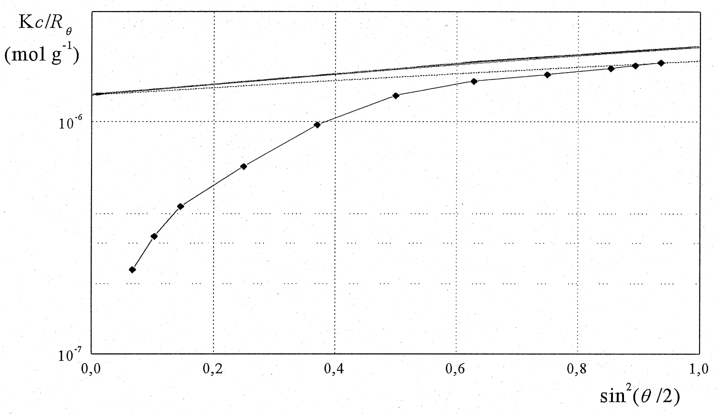

Fig.10: Particle scattering functions Kc/R_θ vs. $\sin^2(\theta/2)$ for fraction 4 in DPM at 142° C; —■—■— measured data of Kc/R_θ; ——— simulation of linear polyethylene molecules with $M_w(GPC) = 7.66\cdot10^5$ g mol^{-1} and $R_G = 36.4$ nm; -------- branched polyethylene with the same parameters, $L = 0.62$ and $f = 38$ long chain branches/molecule.

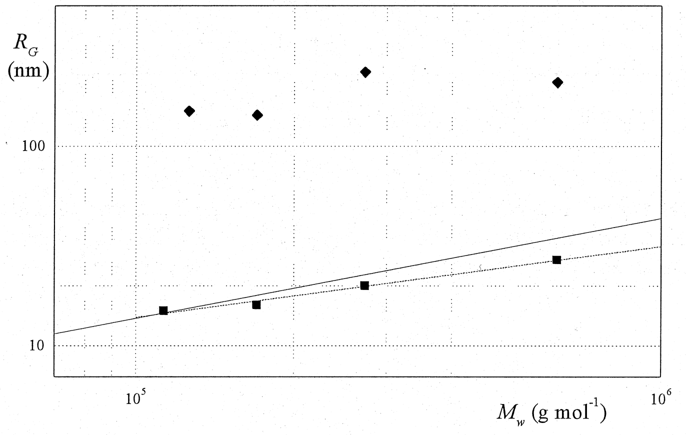

Fig.11: R_G vs. M_w for fractions of branched polyethylene in DPM at 142°C.
◆ uncorrected data of Kc/R_θ; —— unperturbed dimensions of linear polyethylene[14)];
--■-- corrected data $R_{G,1} / M_{w,1}$; $R_{G,1} = a\,M^{0.355}$

We started the simulation with the parameters as given above and with M_w obtained from GPC. Fraction 5 gave incomparable results because of a broad molar mass distribution. The results for $M_{w,1}$, $M_{w,2}$ and $R_{G,1}$ are given in Tab. 2 and show the success of the procedure.

The same combination of separation and simulation will be applied in a forthcoming paper to fractions of low density polyethylene in the good solvents TCB and tetralin. The results can be compared with those obtained the modern and important technique of multi-angle light scattering detectors in combination with size exclusion chromatography[57,58)].

In conclusion we may note that a satisfacting evaluation of parameters of the molecular architecture can be obtained by model simulation, if a suitable model is chosen. Mostly such models can be deduced from the mechanism of the polymerization kinetics which significantly reduces the width of arbitrariness.

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