(23) Preston, J. *Encycl. Polym. Sci. Eng.* **1988**, *11*, 381-409.
(24) Du Pont registered trademark.

Registry No. (PPTA)·K (copolymer), 122545-45-3; (PPTA)·K (SRU), 122507-01-1; (PPTA)·Na (copolymer), 105176-75-8; (PPTA)·Na (SRU), 105096-56-8; dibenzoyl-*p*-phenylenediamine, 13755-08-3; dibenzoyl-*p*-phenylenediamine dianion, 124244-56-0; (isophthalic acid)(*m*-phenylenediamine)·K (copolymer), 124244-62-8; (isophthalic acid)(*m*-phenylenediamine)·K (SRU), 124244-59-3; (2,5-benzimidazole) (SRU), 124244-60-6.

The Molecular Structure of Low-Density Polyethylene. 1. Long-Chain Branching and Solution Properties

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ABSTRACT: Light scattering, viscosity, gel permeation chromatography (GPC), and ^{13}C NMR measurements were carried out on fractions of linear high-density polyethylene (HDPE) and branched low-density polyethylene (LDPE). GPC spectra show that the molar mass distribution of branched LDPE can be well fitted by the three-parameter distribution of Hosemann and Schramek. Its nonuniformity coefficient is 10 times larger than one corresponding to the linear polymer of the same molar mass. ^{13}C NMR measurements indicate that the branched LDPE's contain both short (favorably *n*-butyl) and long branches. A comparison of the number-average of long branches per 1000 CH_2, estimated by ^{13}C NMR spectroscopy, with the one calculated by light scattering indicates that the branch points are predominantly tetrafunctional if one assumes random branching. However, an adequate interpretation of the experimental data can also be given by the heterogeneous comb model, developed by Solensky and Casassa. Thus, there exists some doubt concerning the true structure of the branched polymers. Additionally, it seems that LDPE's, prepared by different companies, possess slightly different structures of branching. The following paper, dealing with the particle scattering factor, will hopefully give a deeper understanding of this problem.

Introduction

The behavior of branched chain polymers in solution is of major interest with respect to both technological problems and basic theoretical questions. Branching, which may be characterized as long chain or short chain, can arise through chain-transfer reactions during free-radical polymerization at high pressure or by copolymerization with α-olefins. Short-chain branches influence the morphology and solid-state properties of semicrystalline polymers, whereas long-chain branching has a remarkable effect on solution viscosity and melt rheology. Therefore it is important to get as much information as possible concerning the nature and number of these branches.

This paper, presented here, is part of a series of two papers. Here, we report experimental data of three linear high-density and three branched low-density polyethylene samples by means of light scattering, ^{13}C NMR, GPC, and viscosity measurements to provide data on number- and mass-average molar masses, intrinsic viscosities, mean square radii of gyration, and osmotic second virial coefficients. These data are presented along with treatments allowing the estimation of unperturbed dimensions and long-chain branching indices according to several theories, whereby the "long branch content", estimated by GPC and light scattering, is compared with the equivalent content, obtained by ^{13}C NMR spectroscopy. Two types of branched structures are considered in some detail: (1) randomly branched macromolecules with tri- and tetrafunctional branch points; (2) heterogeneous comb molecules. These classes of structures are of special interest because Kuhn and Krömer[1] showed that randomly branched LDPE is only obtained if the polymerization is carried out in an ideally stirred reactor with the same temperature, pressure, and conversion prevailing all over the reactor. These are conditions that are not fulfilled in almost all large-scale LDPE polymerization processes so that practically all available commercial LDPE types are not randomly branched. A gain in realism can be made by introducing the heterogeneous comb model, derived by Solensky and Casassa.[2]

On the other hand, one cannot expect that a LDPE molecule represents a simple comb molecule because it is an enormous, if not insoluble, task to synthesize molecules with such an architecture, monodisperse with respect to structure. Thus, the real structure of a branched molecule should lie somewhere between that of a comb and that of a random branched tree, where the content of the predominant kind of branching depends on the condition of preparation. Consequently, different companies should produce LDPE's of slightly different structures of branching. To prove these statements, we researched the physicochemical properties of three different LDPE's purchased from two different companies.

It is well-known, however, that much more information on the structure of a polymer can be extracted from the curve of the particle scattering factor than a mere determination of the relationships between the parameters, mentioned above, can yield. The following paper will provide the relevant information.

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Table I
Refractive Indices and Refractive Index Increments of LDPE in n-Decane at 130 °C

λ, nm	366	436	546
dn/dc, cm^3/g	0.117	0.114	0.112
n	1.3925	1.3844	1.3779

Experimental Section

Sample Preparation. Three commercial branched low-density polyethylene (Lupolen 1840 D (BASF), LDPE 1 and LDPE 3 (RAPRA, Great Britain)) were dissolved in n-decane (Riedel de Haen) that had been double distilled and filtered through an activated aluminium (Al_2O_3) layer. The solutions were prepared by directly weighing the polymer and the solvent and then maintained at 130 °C with gentle stirring for 5 h. For clarification all samples were transferred into a heated centrifuge cup (Heraeus Christ, Model Junior 15000) and then centrifuged for 1 h at 10 000 rpm. At last the purified solutions were filled into a scattering cell, which was released of dust by repeated rinsing with condensed vapor of refluxing acetone.

Light Scattering. Light scattering measurements were carried out with a photometer FICA 50 from Sofica, which supplies vertically polarized light at three different wavelengths (366, 436, and 546 nm). Decalin was used as the cell thermostating medium. The photometer was calibrated with benzene, checking the resulting calibration with standard fractions of polystyrene. The scattering intensity was found for all cells to be constant within 0.3% over the angle range of 37.5–142.5°. Four concentrations, ranging from 0.8 to 3.6 g/dm^3 at 130 °C, were employed for the present study.

Values concerning the refractive index n of the solvent and the refractive index increment dn/dc were reported previously by Kratochvil et al.[3] They are summarized in Table I.

GPC Measurements. The Waters ALC/GPC 200 instrument was equipped with four PL Gel 10 columns of the nominal pore sizes 10^3, 10^4, 10^5, and 10^6 Å. Decalin (Merck) was used as the mobile phase, stabilized with Irganox B 225 (Ciba-Geigy GmbH). The temperature of the oven (Knauer), into which the columns were placed, was kept constant between 125 and 135 °C. An increase in temperature was always performed at a rate of 5 °C/h to avoid a loss of resolution of the column. The flow rate stability (0.3 mL/min) was excellent, the pressure drops for pure solvent was 2.0 bars, and the base-line noise less than 2 mbars. In all cases the injected volumes (2 mL) as well as the solute concentrations (0.7 g/dm^3) were kept constant.

The calibration curve, $\log M = f(V_e)$, was determined with polystyrene standards purchased from Pressure Chemical Co., Waters, Knauer, and Polysciences Inc. For control analysis we used polyethylene standards with an exactly known molar mass and MWD, obtained from National Bureau of Standards, Polysciences, and Hoechst AG.

Viscosity Measurements. Intrinsic viscosities, $[\eta]$, were determined in n-decane at 130 °C by Ubbelohde viscometers. Temperature stability was within 0.1 °C. The solutions contained Irganox B 225 as stabilizer. Kinetic energy and shear rate corrections were applied. Efflux times for the solution were larger than 400 s in all cases. Intrinsic viscosities were estimated from plots of reduced and specific viscosities against concentration.

^{13}C NMR. The polymers were observed as 20% (m/v) solutions in 1,2,4-trichlorobenzene at 118 °C. Experimental details have been reported elsewhere.[4]

Results and Discussion

The structural characterization of the polymer samples, studied here, has been made basically by intrinsic viscosity, GPC, and light scattering measurements. The results are summarized in Table II. M_n denotes the number-average, M_w denotes the mass-average, and M_z denotes the z-average molar mass. The nonuniformity coefficient, $U = (M_w/M_n) - 1$, is a measure of the width of the molar mass distribution. A_2 describes the second osmotic virial coefficient. $\langle S^2\rangle_z^{0.5}$ is called the z-average radius of gyration.

To interpret the measured data of LDPE with regard to branching, one needs the equivalent data of HDPE, which possess equal molar mass. None of the HDPE's used here fulfill exactly this requirement. Thus, in order to get the correct values of $[\eta]_l$, $A_{2,l}$, and $\langle S^2\rangle_z^{0.5}$ which can be compared with one of LDPE, we performed measurements on 10 HDPE standards of known molar mass with respect to viscosity and light scattering. The data we get obey the simple molar mass relationships, listed in eq 1–4.

$$[\eta]_l = 1.65 \times 10^{-2} M_w^{0.83} \tag{1}$$

$$[\eta]_b = 5.06 \times 10^{-2} M_w^{0.70} \tag{2}$$

$$\langle S^2\rangle_{z,l} = 9.08 \times 10^{-18} M_w^{1.16} \tag{3}$$

$$A_{2,l} = 4.70 \times 10^{-3} M_w^{-0.17} \tag{4}$$

The subscripts l and b refer to linear and branched, respectively. Inserting the molar masses, estimated for LDPE, gives the reference data for HDPE, summarized in Table II. Relationship 2, derived from Rapra, was used to obtain the viscosity molar mass of LDPE.

Excluded Volume. In order to compare the experimental results with theory, i.e. to estimate chain expansion and long-chain branching, it is necessary to eliminate the effects of excluded volume and polydispersity. This was done in the following manner.

The second virial coefficient, A_2, is often[5] written in the form

$$A_2 = 4\pi^{3/2} N_A (\langle S^2\rangle_z^{3/2}/M_z^2)\Psi \tag{5}$$

Here, N_A denotes Avogadro's number. Ψ is called the interpenetration function, which indicates the degree of interpenetration of two polymer molecules, when their effective volumes are taken to be proportional to $\langle S^2\rangle_z^{3/2}$.

Different theories of A_2 predict different functional forms for Ψ. Three types may be classified: (I) logarithmic divergence, (II) slow divergence, and (III) early convergence. Although various approximate theories of the expansion factor, $\alpha = (\langle S^2\rangle_z/\langle S^2\rangle_{z,\Theta})^{0.5}$, have been developed, there exist only very few expressions for Ψ, which can be chosen for a given theory of α if we insist on the self-consistency of intramolecular and intermolecular theories of interaction

type 1
$$\Psi(\bar{z}) = \ln(1 + 2.30\bar{z})/2.30 \tag{6}$$
$$z = (\alpha^5 - \alpha^3)/2.60$$

type 2
$$\Psi(\bar{z}) = \ln(1 + 5.73\bar{z})/5.73 \tag{7}$$
$$z = (\alpha^5 - \alpha^3)/1.28$$

type 3
$$\Psi(\bar{z}) = 0.55(1 - (1 + 3.90\bar{z})^{-0.47}) \tag{8}$$
$$z = 0.17\left(\left(\frac{\alpha^2 - 0.54}{0.46}\right)^{2.17} - 1\right)$$

where $\bar{z} = z/\alpha^3$, z being the excluded volume variable,[5] and $\langle S^2\rangle_{z,\Theta}^{0.5}$ is the z-average unperturbed radius of gyration. Equations 6–8 apply to linear polymers, whereas actual analysis must be made for branched polymers. However, there exists no alternatively convincing theory, which could be used here.

In order to analyze the experimental data, we first substituted the observed values of A_2, $\langle S^2\rangle_z^{0.5}$, and M_z into eq 5 to obtain the value of Ψ. Then we evaluate from eq 6–8 the value of the expansion factor, α, which yields

Table II
Physicochemical Properties of Linear and Branched Polyethylene in *n*-Decane at 130 °C

	samples						
method	HDPE 1	HDPE 2	HDPE 3	Lupolen 1840 D	LDPE 1	LDPE 3	error, %
GPC							
$10^{-5}M_n$, g/mol	2.8	1.3	0.8	0.20	0.14	0.08	10
$10^{-5}M_w$, g/mol	4.2	1.7	1.0	4.2	1.7	1.0	10
				3.2[a]	1.9[a]	1.1[a]	
$10^{-5}M_z$, g/mol	9.7	3.6	1.8	15.0	5.3	3.2	10
				18.0[a]	5.4[a]	3.1[a]	
U	0.5	0.3	0.3	20	12.5	11.4	15
light scattering							
$10^{-5}M_w$, g/mol	6.0	5.2	3.1	6.0	5.2	3.1	10
10^4A_2, (cm^3·mol/g^2)	4.8	5.0	5.4	1.9	2.0	2.4	5
$\langle S^2\rangle_z^{0.5}$, nm	68	61	46	64	57	48	15
viscosity							
$[\eta]$, cm^3/g	414	308	194	260	202	136	5
$10^{-5}M_\eta$, g/mol	2.0	1.4	0.8	2.0	1.4	0.8	10

[a] Estimated by the best-fit for the three-parameter distribution of Hosemann and Schramek.

Table III
Molecular and Conformational Parameters of Linear and Branched Polyethylene in *n*-Decane at 130 °C

	HDPE 1	HDPE 2	HDPE 3	Lupolen 1840 D	LDPE 1	LDPE 3
Ψ	0.05	0.06	0.05	0.14	0.12	0.09
$\bar{\alpha}$	1.10	1.10	1.06	1.18	1.13	1.10
$\langle S^2\rangle_{z,\Theta}^{0.5}$, nm	62	55	43	54	50	44
$\langle S^2\rangle_{w,\Theta}^{0.5}$, nm	41	38	32	28	28	25
$[\eta]_\Theta$, cm^3/g	371	270	169	243	186	125

$\langle S^2\rangle_{z,\Theta}^{0.5}$. To obtain the weight-average value $\langle S^2\rangle_{w,\Theta}^{0.5}$, we may use the expression $\langle S^2\rangle_{z,\Theta}/\langle S^2\rangle_{w,\Theta} = M_z/M_w$, which holds for all molar mass distributions.[7] The values of $\langle S^2\rangle_{w,\Theta}^{0.5}$ are given in Table III. Here, the values of Ψ are relatively small; thus α is independent of the particular theory, and we can use its average, $\bar{\alpha}$. The data, we get, are summarized in Table III. Values of $\bar{\alpha}$ are affected by an error of 10%, which shows that there is no difference in $\bar{\alpha}$ according to HDPE or LDPE. However, the values of $\bar{\alpha}$ for LDPE seem to be a little larger than for HDPE.

The experimental error of Ψ lies between 15 and 20%. Values of Ψ for LDPE are larger, by about a factor of 2 or 3 than is the case for HDPE. Thus, this difference lies outside the experimental error bar. It indicates that the degree of interpenetration for a branched molecule is smaller than one for a linear molecule. Additionally the degree of interpenetration of Lupolen 1840 D seems to be smaller than that of LDPE 1 or LDPE 3. This is a clear evidence that Lupolen (BASF) possesses a somewhat different kind of molecular structure to LDPE 1 or LDPE 3 (both Rapra).

Polydispersity. Next, we must eliminate the effect of polydispersity. High-temperature GPC experiments yield the molar mass distribution, $f(M)$. A typical $f(M)$ curve is given in Figure 1. To provide an adequate fit for the fractionation data, we used the three-parameter distribution of Hosemann and Schramek[6]

$$f(M) = ad^{(k+1)/a}\Gamma^{(-1)}((k+1)/a)M^k \exp(-dM^a)$$

with $\Gamma(t) = e(-x)x^{t-1}\,dx$; a, k, and d are parameters, which may be estimated by the principle of least squares. They are summarized in Table IV. Now, we can evaluate M_n, M_w, and M_z. It is also the case that

$$M_i = \Gamma((k+i)/a)\Gamma^{(-1)}((k+i-1)/a)$$

where $i = 1$ corresponds to M_n, $i = 2$ to M_w, and $i = 3$ to M_z. See Table II.

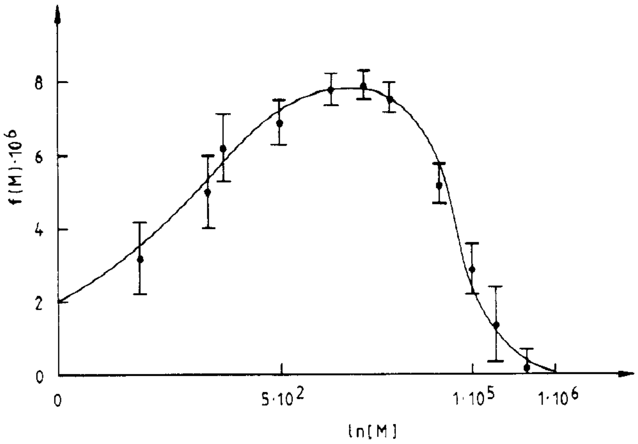

Figure 1. LDPE 1: molecular mass distribution.

Long Branching of Random Branched Polymers. Now, we are able to evaluate the expansion of long-chain branching, independent of excluded volume and polydispersity. Zimm and Stockmayer have related the number of branch points per molecule, m, to the branching index $g_{s,\Theta}$, defined by

$$g_{s,\Theta} = \langle S^2\rangle_{w,\Theta,b}/\langle S^2\rangle_{w,\Theta,l} \tag{9}$$

where the linear reference polymer has the same molar mass as the branched counterpart. m may be determined by one of the following frequently encountered relationships, derived for randomly branched macromolecules with tri- and tetrafunctional branch points:[8]

$$g_{s,\Theta,3} = ((1 + (m_3/7))^{0.5} + (4m_3/9\pi))^{-0.5} \tag{10}$$

$$g_{s,\Theta,4} = ((1 + (m_4/6))^{0.5} + (4m_4/3\pi))^{-0.5} \tag{11}$$

In eq 10 and 11, m_f is the number average of branches per molecule and f = 3 or 4, respectively. Values of $g_{s,\Theta}$ can be calculated from the data of $\langle S^2\rangle_{w,\Theta,b}$ and $\langle S^2\rangle_{w,\Theta,l}$, given in Table III. Then, resolving eq 10 or 11 with respect to m_3 or m_4, one gets the number-average value of branches per molecule. For comparison, Table V contains also the branching indices g_s for the non-Θ state and the branching indices $g_{\eta,\Theta}$ for the Θ state related to viscosity. Values of $g_{s,\Theta}$ and $g_{\eta,\Theta}$ may be related to the exponent σ, introduced by Thurmond and Zimm,[9] by

$$g_{\eta,\Theta} = \frac{[\eta]_{\Theta,b}}{[\eta]_{\Theta,l}} = g_{s,\Theta}{}^{\sigma}$$

where $[\eta]_{\Theta,b}$ and $[\eta]_{\Theta,l}$ are the intrinsic viscosities of

Table IV
Fit Parameters for the Hosemann–Schramek Distribution

	Lupolen	LDPE 1	LDPE 3
a	0.2	0.5	0.5
k	1.0	0.22	0.22
d	1.29	0.0067	0.0089

Table V
Branching Indices

	$10^5 M_w$, g/mol	g_s	$g_{s,\Theta}$	$g_{\eta,\Theta}$	m_3	m_4	σ
Lupolen 1840 D	6.0	0.53	0.47	0.66	18.5	7.2	0.55
LDPE 1	5.2	0.58	0.54	0.69	12.5	4.8	0.60
LDPE 3	3.1	0.64	0.63	0.74	7.5	3.0	0.65

Table VI
Branch Frequencies of LDPE's

	samples		
branch points	Lupolen 1840 D	LDPE 1	LDPE 3
"short"			
methyl	2.3	1.1	1.9
ethyl	8.4	7.6	4.1
n-butyl	10.6	11.2	9.8
n-amyl	2.9	2.9	2.9
total "short"	24.2	22.8	18.7
"long"			
^{13}C NMR	3.3	2.9	2.9
light scattering			
trifunctional	9.1	4.5	4.2
tetrafunctional	3.5	1.7	1.7
w, %	0	42	48
"total"	27.5	25.7	21.6

Table VII
Comb Molecule Parameters

	parameter					
sample	P	N	N_0	$\bar{f}$	n_b	$\langle S^2\rangle_{z,e}^{0.5}$, nm
Lupolen 1840 D	0.007	21 430	20 140	141	9	65
LDPE 1	0.007	18 870	15 430	108	32	56
LDPE 3	0.009	11 070	7110	64	62	36

branched and linear macromolecules, respectively, of the same molar mass in the Θ state. Values of $[\eta]_{\Theta,b}$ and $[\eta]_{\Theta,l}$ may be obtained from eq 12. See Table III. At the present time σ cannot be related exactly to the conditions of preparation. Different authors[11,12] suggested values in the range of 0.5 and 1.5. Here, we get the relation

$$[\eta]_{\Theta,l(b)} = [\eta]_{l(b)}\left[\left(\frac{2}{\sqrt{\pi}}\left[\exp\left(\frac{9.37\times10^{-2}\,A_2M_w}{[\eta]_{l(b)}}\right)-1\right]\right)+1\right]^{-1.5} \tag{12}$$

$$g_{\eta,\Theta} = g_{s,\Theta}^{\;0.6\pm0.05} \tag{13}$$

where σ is a function of molecular mass. See Table V.

Comparison of the Results, Derived by Light Scattering, with ^{13}C NMR Measurements. In Table VI the branch content is presented, expressed according to the number-average molar mass as branch points per 1000 CH_2 groups. The predominant type of short branch is a trifunctional n-butyl, with a smaller content of ethyl. We further observe that there is a substantial probability of trifunctional n-amyl branch formation. Since the sites of long branches cannot be distinguished a priori as tri- or tetrafunctional branch points, m, the number of the "long branch points", has been calculated with two different assumptions: (a) all long-chain branch points are trifunctional; (b) all long-chain branch points are tetrafunctional. In fact, it is likely that LDPE's contain both tri- and tetrafunctional branch points. To evaluate the content w of trifunctional branch points per 1000 carbon atoms, we use the relationship $f^{13}{}_{\mathrm{C}} = wf_3 + (1 - w)f_4$. Here, $f^{13}{}_{\mathrm{C}}$ denotes the long branching frequency, estimated by ^{13}C NMR spectroscopy. f_3 and f_4 are the corresponding tri- and tetrafunctional frequencies, obtained by light scattering. Apparently, all branch points of Lupolen 1840 D are tetrafunctional, whereas nearly 45% of the branch points of LDPE 1 or LDPE 3 are tri- and 55% tetrafunctional. We believe that this is unlikely because it states that two long branches would emanate from a single branch site in nearly all cases. Rather, this may indicate, as Kuhn and Krömer[1] postulated, that commercially produced LDPE's do not possess a molecular structure like a random branched tree. But, again it seems that Lupolen 1840 D and LDPE 1 and LDPE 3 possess slightly different branched structures. To prove this, we need another model. A good test subject may be the "heterogeneous comb model", developed by Solensky and Casassa.[2]

Heterogeneous Combs. To generate this ensemble of branched molecules, we can imagine that a long number of backbone chains, each of length N_0, is allowed to react at random with $\bar{f}$ backbone chains of uniform length n_b. We let $\bar{f}$ be smaller than N_0 and let the coupling reaction go to completion. The resulting system is heterogeneous in molar mass since it contains subgroups of molecules, each characterized by a certain number, $0 \leq \bar{f} \leq N_0$, of branches per molecule. The macromolecules are also heterogeneous in spite of the fact that the placement of the branch points along the backbone is also random. For simplicity Solensky and Casassa considered the case of the probability, p_f, that a molecule has f branches, given by the binomial distribution where p

$$p_f = \binom{N_0}{f} p^f (1-p)^{N_0-f} \tag{14}$$

denotes the probability that a backbone segment chosen at random will be found to bear a branch. By confining excluded volume, Casassa and Solensky derived for the branching index, g_s, the following expression:

$$g_s = (1 + \bar{f}p(2 + 3p + p^2) + \bar{f}^{\,2}p^2(1 + 3p))/(1 + \bar{f}p)^3 \tag{15}$$

It holds that $p = \bar{f}/N_0$ and $N = N_0 + \bar{f}n_b$, where N is the total average number of segments. The molar mass of a segment may be 28 g/mol; g_s is known from light scattering measurements; see Table V. ^{13}C NMR measurements yield $\bar{f}$. So, a simple calculation gives the values of p, N_0, and n_b, which are listed in Table VII.

We now see that the content of branch points related to the total number of segments does not depend on the kind of LDPE. It holds that $\bar{f}/N = 0.006 \pm 0.0004$. In contradiction, the number of segments per branch is relatively large for LDPE 1 or LDPE 3 and relatively small for Lupolen 1840 D, although LDPE 1 and Lupolen contain nearly an equal number of total segments. This gives us a third opinion that the kind of branching for Lupolen and LDPE 1 or LDPE 3 may be somewhat different.

Next, it is interesting to evaluate the radius of gyration for a linear macromolecule containing N_0 segments, called the equivalent radius of gyration, $\langle S^2\rangle_{z,e}^{0.5}$. *To do this, we use eq 3. Values of* $\langle S^2\rangle_{z,e}^{0.5}$, summarized in Table VII, agree well with those of $\langle S^2\rangle_{z,b}^{0.5}$, estimated by light scattering. This shows that the extension in volume of a comb-branched molecule is predominantly affected by the number of segments per backbone and not, as could be thought, by the total number of segments of the macromolecule. Indeed, it is not expected that this behavior will prove to be general.

Conclusions

The results on HDPE and LDPE obtained lead to the following conclusions.

(1) Different physical techniques yield different molar mass data, $M_w^{\mathrm{GPC}} < M_w^{\mathrm{LS}}$, which confirms the observations of other groups.[13,14]

(2) As a result of the formation of long branches, the distribution of molar mass in polyethylenes is very broad. Nonuniformity coefficients as high as 10 or 20 are not uncommon.

(3) The radius of gyration of a linear HDPE molecule is larger than the radius of the corresponding branched species, expressed by $g < 1$. The degree of branching increases with increasing molar mass. Simultaneously the ratio $A_{2,\mathrm{b}}/A_{2,\mathrm{l}}$ of the second virial coefficients decreases, which points out that branching decreases the degree of solvatation of a LDPE molecule.

(4) It should be noted that the numerical values of the branching index g are of an approximative nature. They are based upon many assumptions: for instance, on the presence of an appreciable excluded volume effect, on correctly calculated properties of linear polyethylene analogues, on the dependence of g on the distribution of molar mass, etc. Thus, it seems likely that the present calculations have a more relative than an absolute meaning.

(5) Several workers have used the relation $g_{\eta,\Theta} = g_{\mathrm{s},\Theta}^{0.5}$ to compute average values of the branching frequency $\bar{f}$ for LDPE, and moreover they assumed that $\bar{f}$ is constant and independent of the molar mass. From the viewpoint mentioned above, these treatments are not valid, since $\sigma \neq 0.5$ and $\partial\sigma/\partial m < 0$.

(6) LDPE's contain short as well as some longer branches. Butyl branches are found in substantially higher concentrations than other branches. Amyl branches, as well as n-alkyl branches, longer than C_5, have been found in relatively low concentrations, where the number of long branches increases with molar mass. Similar results were observed by other authors.[15]

(7) It is very difficult to say with certainty something about the real molecular structure of the LDPE's, researched here. It only seems certain that Lupolen 1840 D possesses a somewhat different structure of branching than LDPE 1 or LDPE 3. This is consistent with the statement of Kuhn and Krömer[1] that LDPE's produced by different companies possess slightly different branched molecular structures.

If one takes the value of the interpenetration function Ψ as a base, which is independent on the special model of branching, it seems that Lupolen possesses a somewhat more compact molecular structure than LDPE 1 or LDPE 3. This is consistent with the finding that Lupolen contains a much higher content of tetra- than trifunctional branch points per molecule compared to that of LDPE 1 or LDPE 3.

On the other hand, taking the heterogeneous comb model as the base, the finding that Lupolen possesses long branches, in an order of magnitude equal to LDPE 1 or LDPE 3, but with respect to the length of the branches, about a factor of 3 or 6 shorter than those of LDPE 1 or LDPE 3, indicates that the opposite may also be true. Obviously, comb molecules of short branches should be interpenetrated by each other somewhat more than comb molecules of longer branches.

However, the absolute values of Ψ are relatively small; thus the comb hypothesis may be still true for LDPE 1 or LDPE 3, as postulated by Kuhn and Krömer.[1] Lupolen 1840 D may then possess a branched structure, which lies somewhere between that of a comb and that of a random tree. These statements must, however, be proved, and a more complete understanding will be acquired by investigations on the particle scattering factors, which will be dealt with in the following paper.

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References and Notes

(1) Kuhn, R.; Krömer, H. *Colloid Polym. Sci.* **1982**, *260*, 1083.
(2) Solensky, P. J.; Casassa, E. F. *Macromolecules* **1980**, *13*, 500.
(3) Horska, J.; Stejskal, J.; Kratochvil, P. *J. Appl. Polym. Sci.* **1979**, *24*, 1845.
(4) Mandelkern, L.; Glatin, M.; Benson, R. A. *Macromolecules* **1981**, *14*, 22.
(5) Yamakawa, A. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(6) Hosemann, R.; Schramek, W. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *A1*, 109.
(7) Greschner, G. S. *Maxwellgleichungen*; Hüthig & Wepf: Basel, 1981; Band 2.
(8) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(9) Thurmond, C. E.; Zimm, B. H. *J. Polym. Sci.* **1952**, *8*, 477.
(10) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1076.
(11) Lecacheoux, D.; Lesec, J.; Quiveron, C. *J. Appl. Polym. Sci.* **1982**, *27*, 4867.
(12) Bugada, D. C.; Rudin, A. *Eur. Polym. J.* **1987**, *23*(11), 847.
(13) Strazielle, C.; Benoit, H. *Pure Appl. Chem.* **1971**, *26*, 451.
(14) Strazielle, C. *Pure Appl. Chem.* **1975**, *42*, 615.
(15) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.