

# Chain architecture of LDPE as a function of molar mass using size exclusion chromatography and multi-angle laser light scattering (SEC-MALLS)

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Long chain branching causes a decrease in molecular size and hence in the radius of gyration and the hydrodynamic radius, as compared to polymers having a linear structure and having the same molar mass. In principle there is a simple relation between the ratio of the radii of gyration and the hydrodynamic radii:  $g' = g^b$ . At constant temperature and one solvent/polymer combination, the  $b$ -value is mainly dependent on the chain architecture. In the classical approach, determination of  $b$  as a function of molar mass requires time consuming fractionation with subsequent characterization of the fractions to determine the hydrodynamic radius and the radius of gyration. Fortunately, by application of size exclusion chromatography (SEC) in combination with only multi-angle laser light scattering (MALLS) and using the universal calibration principle, it appeared possible to determine the  $g$  and  $g'$  as a function of the molar mass. Utilization of this method revealed that low density polyethylene (LDPE) exhibits a continuous decrease with increasing molar mass of the  $b$ -value from 1.8 to 1.2 for a tubular product, and from 1.5 to 1 for an autoclave product. This was also expected from the polymerization conditions. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Low density polyethylene (LDPE) has a very complex molecular structure despite the fact that it consists of only one monomeric unit, i.e. ethene. LDPE exhibits a broad molar mass distribution (MMD). As a result of intra- and intermolecular chain transfer reactions, short (SCB) and long (LCB) chain branching exists<sup>1–4</sup>. Revelation of the chain structure is increasingly recognized as a prerequisite, since the reaction kinetics determine the structure which in turn determines the properties. Thus, knowledge about the structure supplies not only information about the reaction kinetics, but also about the relation between chain structure and properties. In the case of LDPE the most pronounced chain feature is the long chain branching (LCB) which can occur in various chain architectures, i.e. comb or random<sup>1,2,5,6</sup>. Revelation of the type as well as the number of LCB is still difficult.

Despite the importance, a general technique to reveal the molecular structure of LDPE is not available. This must be attributed to the complexity of the structure of LDPE. Separation of LDPE exclusively according to one molecular parameter (e.g. molar mass, LCB or SCB), without interference of the other parameters, with subsequent characterization of the fractions according to exclusively another parameter, is nearly impossible<sup>7,8</sup>. Separation according to SCB using TREF is influenced by molar mass and type of SCB<sup>9</sup>. Application of liquid–liquid phase separation results in a separation mainly according to LCB<sup>7</sup>. However, also in this case an influence of molar mass cannot be excluded.

Fortunately, separation of macromolecules using size exclusion chromatography (SEC) is the most unambiguous separation. With the introduction of differential viscometers a significant improvement could be achieved in the characterization of LCB<sup>10–12</sup>. The ratio of intrinsic viscosities ( $g'$ ) can be calculated as a function of molar mass. However, to calculate the number of branches,  $g$  must be calculated using the Zimm–Stockmayer approach<sup>13</sup>. So, *a priori* knowledge about the value for  $b$  in equation (1) must be known:

$$g' = g^b \quad (1)$$

Here  $g'$  is the ratio of the intrinsic viscosities of the polymer having LCB and a linear structure at the same molar mass. The branching index  $g$  is the ratio of the mean square of the radii of gyration of the polymer having LCB and the polymer having a linear structure at the same molar mass. In the case of non-free drained star branched molecules it was derived by Stockmayer that  $b = 0.5$ . Berry assumed that  $b = 1.5$  for comb shaped molecules having branches which are relatively small compared to the backbone<sup>14</sup>. Kuhn and Kromer<sup>1,2</sup> determined  $b$ -values of 1.2 and 2.0 for one zone autoclave and tubular LDPE. Scholte<sup>15</sup> found  $b$ -values ranging from 1 to 0.5 with increasing molar mass for both autoclave and tubular products. Application of the SEC-MALLS technique gives  $g$  directly<sup>16–18</sup>; however, no information is obtained about the  $b$ -value.

To obtain detailed information about the molecular structure in terms of  $b$  as a function of molar mass, labourious and time consuming fractionation experiments are required with subsequent characterization of the

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fractions. Fortunately, we found that there is a relatively easy route to determine  $b$  as a function of molar mass, namely by application of SEC-MALLS and the universal calibration principle.

## EXPERIMENTAL

### Sample preparation

The polymer samples were dissolved (0.1 w%) in 1,2,4-trichlorobenzene (TCB), which was distilled prior to use, over a period of 4 h at 150°C and stabilized with di-tert-butylparacresol (DBPC) at a concentration of 1 g/L. The solutions were filtered at high temperature (150°C) using a millipore filtration setup (1.2 μm) positioned in a Hereous LUT oven operating at 150°C.

### SEC-MALLS

The separation of the polymer according to molar mass is performed with a Waters M150C GPC. This SEC system is operated at high temperature (column compartment at 140°C, injector compartment at 150°C, and solvent reservoir at 60°C) and a flow of 0.5 mL/min. One Polymer Laboratories GPC column with large particle size (PLgel 20 μm MIXED-A) is used to minimize shear degradation of high molar mass polymers<sup>19</sup>. The light scattering detector (a DAWN DSP multi-angle laser light scattering detector of Wyatt Technology) is placed in line between the GPC and the refractive index detector.

## BACKGROUND

For linear polyethylene polymers the Flory–Fox equation for the non-free draining case (normal case with flexible polymers in solution) is given by<sup>20</sup>:

$$[\eta] = 6^{3/2} \phi < r_g^2 >^{3/2} M^{-1} \quad (2)$$

with  $[\eta]$  the intrinsic viscosity,  $\phi$  the universal constant ( $2.1 \pm 0.4 \cdot 10^{21} \text{ dL mol}^{-1} \text{ cm}^{-3}$ ),  $< r_g^2 >$  the mean square radius of gyration and  $M$  the molar mass. The Mark–Houwink equation for PE in TCB at 135°C is<sup>21</sup>:

$$[\eta] = 4.06 \cdot 10^{-4} M^{0.725} \quad (3)$$

The combination of these last two equations relates the root mean square (R.M.S.) radius of gyration (in nm) with the molar mass by:

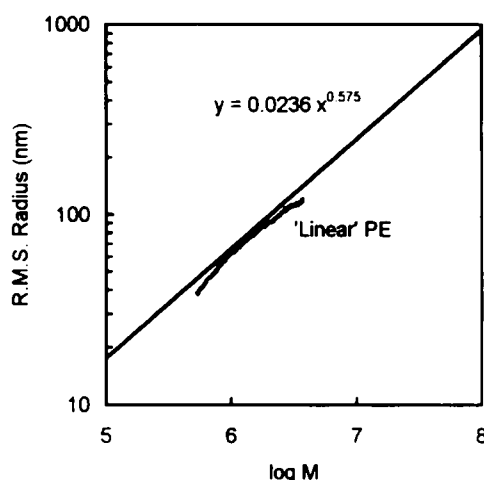
$$< r_g^2 >^{1/2} = (1.32 \cdot 10^{-5} M^{1.725})^{1/3} \quad (4)$$

for linear polyethylene in TCB at 135°C. Equation (4) predicts the radius of gyration for a linear flexible polyethylene in TCB at 135°C from the molar mass of the polymer. For branched polymers, the theoretical approach is much more difficult.

Using size exclusion chromatography, the macromolecules are separated according to hydrodynamic volume<sup>22</sup>. Hence at each retention volume the following equation is valid:

$$[\eta]_1 \cdot M_1 = [\eta]_2 \cdot M_2 \quad (5)$$

Using light scattering, the absolute molar mass can be determined at each retention volume. Applying the Mark–Houwink relation, the left side of equation (5) is known. In case of an unknown polymer having LCB (e.g. LDPE), the molar mass  $M_2$  is determined experimentally. The left side is known from the calibration using polyethylene having a linear structure and, hence, the intrinsic viscosity of the unknown polymer  $[\eta]_2$  can be calculated. Since both



**Figure 1** The root mean square radius of gyration of a linear polyethylene as a function of molar mass as measured with SEC-MALLS compared with the theoretical root mean square radius of gyration

$[\eta]_1$  and  $[\eta]_2$  are known, the branching index  $g'$  can be calculated according to equation (6):

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \quad (6)$$

So, it is possible to determine the ratio of intrinsic viscosities without application of a viscometer. Application of MALLS also reveals the mean square radius of gyration  $< r_g^2 >$  as a function of the molar mass and hence the branching index  $g$ , which is defined according to equation (7):

$$g = \frac{< r_g^2 >_{\text{branched}}}{< r_g^2 >_{\text{linear}}} \quad (7)$$

From a measurement of SEC-MALLS the  $g$  and  $g'$  are determined and thus  $b$  is calculated as a function of the molar mass.

## RESULTS AND DISCUSSION

### Linear polyethylene

The radius of gyration of a linear polyethylene as measured with SEC-MALLS as a function of molar mass is compared with the predicted values for linear polyethylene (equation (4)) in Figure 1. From this plot it is clear that the experimental curve is slightly deviating from the predicted curve. In the low molar mass region, the light scattering signal is too low to accurately measure the radius of gyration. In the high molar mass region, this so-called linear polymer might have some branching, and thus a lower radius of gyration. It is important to state that for this measurement only 9.5% of the total polymer mass is taken into account (high molar mass part). It is also important to understand that although the radius of gyration can only be determined over this small molar mass range, the absolute molar mass could be determined over the entire molar mass region. It is easier to determine a large intercept (related to molar mass) than a small slope (related to the radius of gyration). Furthermore, a linear polyethylene has a lower light scattering signal than a branched polyethylene with the same radius of gyration, because a branched polymer has more additional mass than a linear one. This means that it is easier to measure molar masses and radii of gyration of branched polymers.

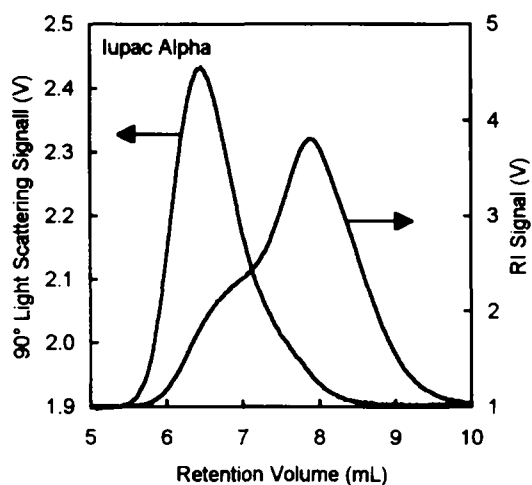


Figure 2 The 90° light scattering signal and the refractive index signal for the IUPAC Alpha

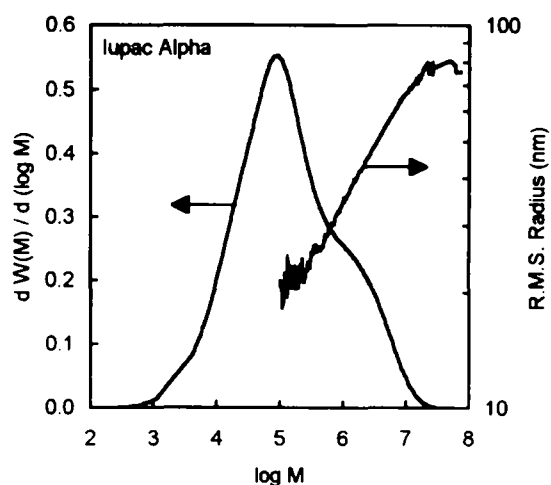


Figure 4 The mean square radius of gyration plotted across the molar mass distribution for the IUPAC Alpha

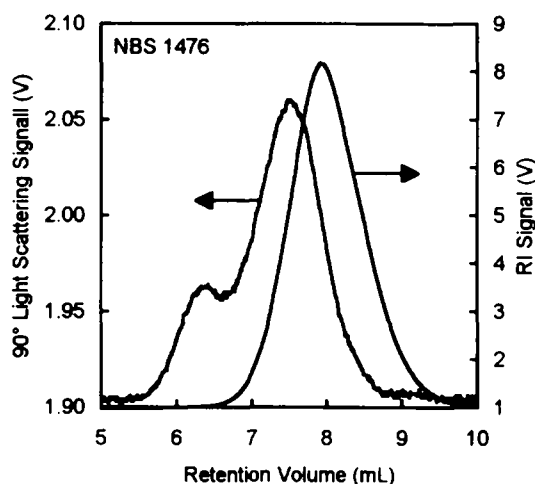


Figure 3 The 90° light scattering signal and the refractive index signal for the NBS 1476. The high molar mass tail of the NBS 1476 is clearly visible in the light scattering signal (at low retention volume) but is not present in the RI signal, because its concentration is too low

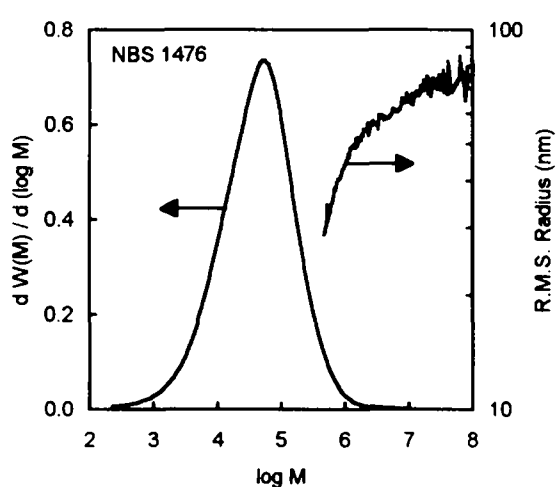


Figure 5 The mean square radius of gyration plotted across the molar mass distribution for the NBS 1476

### Branched polyethylene

Two branched low density polyethylene polymers were characterized with the SEC-MALLS technique. The first one is a one zone autoclave LDPE (IUPAC Alpha), and the second one is a tubular LDPE (NBS 1476). The tubular product has a typical high molar mass tail, hardly visible in a normal concentration chromatogram. This is clearly visible in Figures 2 and 3, where the concentration signal and the 90° light scattering signal for the two LDPEs are plotted in the same graph. In Figures 4 and 5, the mean square radius of gyration of these LDPEs are plotted over the molar mass distribution, as measured with SEC-MALLS. As stated earlier, it is much easier to measure an absolute molar mass than it is to measure an absolute radius of gyration. This strongly depends on the signal to noise ratio. For the IUPAC Alpha, reliable radius information could be obtained over 54% of the total polymer mass. For the NBS 1476, only 3% of the total polymer mass gave relevant radius data.

With equation (6) the branching index  $g'$  can be calculated for both LDPEs as a function of molar mass. Since light scattering measures also the absolute radius of gyration, the branching index  $g$  can also be determined as a function of molar mass by equation (7). Because the determination of the radius of gyration of linear polyethylene is very difficult due to the low signal to noise ratio,

the predicted radius of gyration is calculated using equation (4). From the measured radius of gyration of the branched polyethylene and the predicted radius of the linear polyethylene, the branching index  $g$  can be calculated.

The relation between the radius of gyration based branching index  $g$  and the intrinsic viscosity based branching index  $g'$  is given by equation (1). In Figures 6 and 7, the branching indices  $g'$  and  $g$  and the exponent  $b$  for the IUPAC Alpha and the NBS 1476 are plotted as a function of molar mass. We find for both samples that the exponent  $b$  decreases with increasing molar mass. Furthermore, from these figures it is clear that the one zone autoclave product has a lower  $b$ -value than the tubular sample at high molar masses. Scholte<sup>15</sup> found for the tubular and two zone autoclave products that  $b = 1$  and for the one zone autoclave that  $b = 0.8$ . For the IUPAC Beta sample a value of  $b = 0.9$  was found by Kulin<sup>7</sup> for the whole polymer. The  $b$ -value for the highest molar mass fraction of this sample appeared to be 0.5, indicating that the chain architecture is not only dependent on the number of branches but also the characteristics of the branch, which may vary as a function of molar mass, which in turn is determined by the polymerization conditions. Kuhn<sup>1</sup> also found average  $b$ -values of 1.2 for the one zone autoclave and 2.0 for the tubular product. These values seem to be rather high, but a similar trend is observed between their

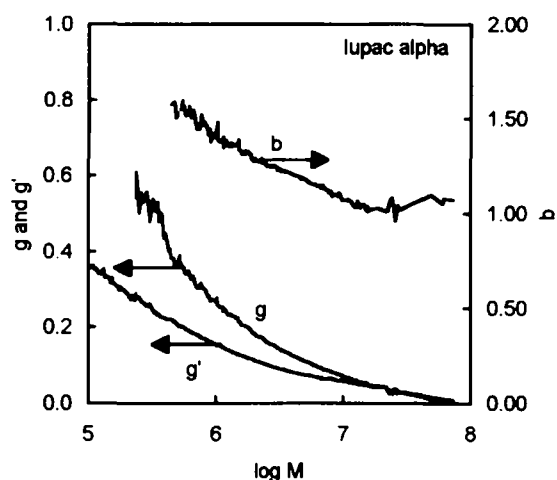


Figure 6 The branching index  $g'$  and  $g$  and the exponent  $b$  for the IUPAC Alpha as a function of molar mass

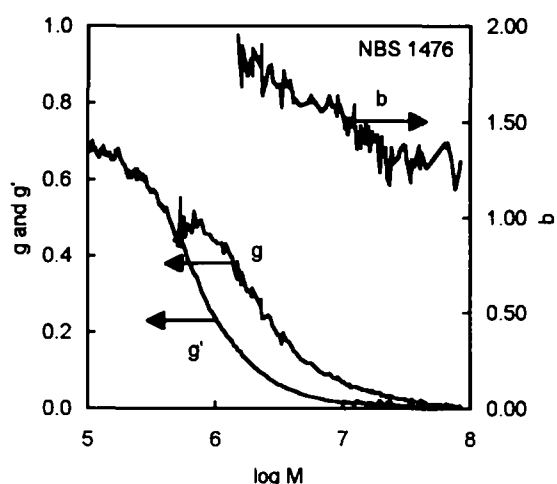


Figure 7 The branching index  $g'$  and  $g$  and the exponent  $b$  for the NBS 1476 as a function of molar mass

results and ours: the  $b$ -value for the tubular product is higher than the  $b$ -value for the one zone autoclave product. Although only 3% of the total polymer mass is characterized in the tubular LDPE, we believe that the differences in  $b$ -value between the one zone autoclave and the tubular product are truly present. Moreover, these preliminary results inevitably indicate that  $b$  is a function of molar mass.

The changes in the  $b$ -value might be explained tentatively in terms of a change in the ratio of the length between two branch points and the length of the branch. This can be understood by taking into account this ratio for the star branched polymer and the linear having only short chain branching. This ratio is zero and infinite, respectively, while the  $b$ -value increases simultaneously from 0.5 to 1.5. From this simple concept it can be understood that the value for a tubular product is higher than the value for the one zone autoclave product. The branches of the tubular product are made in zones having a higher temperature and therefore will be shorter.

The combination of size exclusion chromatography with a light scattering detector and a concentration detector allows the determination of branching indices  $g'$  and  $g$ . Normally, a viscosity detector is used to determine this  $g'$ , but as long as the universal principle holds, it can be determined from SEC-MALLS measurements. The

structural parameter  $b$  determines the type of branching and can be used to correlate the structure of the polymer with the properties and rheological behaviour of the material. The SEC-MALLS technique is a very powerful tool in the revelation of the polymer chain microstructure. In our investigation we used a 5 mW HeNe laser. By application of a more powerful laser (with lower wavelength), the radius of gyration can be measured over a broader molar mass range. This forms subjects for future investigations.

As a general note it can be stated that the  $b$ -value for linear structures is very difficult to determine. Since both  $g'$  and  $g$  are equal to 1 for linear polymers, the exponent  $b$  in equation (1) is not defined, since any  $b$ -value will fulfil the equation.

## CONCLUSIONS

A multi-angle laser light scattering detector was recently coupled with the Waters M150C GPC to characterize polyolefins at high temperature. With this technique, absolute molar masses (and an absolute molar mass distribution) can be measured without the need for SEC column calibration. At the same time, information about the radius of gyration and molecular structure  $b$  as a function of molar mass is obtained. Furthermore, differences in polymer structure can be observed depending on the polymerization conditions.

The branching index of two LDPE polymers (one autoclave and one tubular product) was measured with SEC-MALLS. To our knowledge it is the first time that the branching indices  $g'$ ,  $g$  and  $b$  were determined simultaneously with a dual detector SEC system. Furthermore, the results obtained compare well with SEC-DV measurements ( $g'$ ) and fit well with the accepted reaction process.

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## REFERENCES

1. Kuhn, R., Kromer, H. and Rosmanith, G., *Angew. Makromol. Chem.*, 1974, **40**, 361.
2. Kuhn, R. and Kromer, H., *Colloid and Polym. Sci.*, 1982, **260**, 1083.
3. Luft, G., Kampf, R. and Seidl, H., *Angew. Makromol. Chem.*, 1982, **108**, 203.
4. Luft, G., Kampf, R. and Seidl, H., *Angew. Makromol. Chem.*, 1983, **111**, 133.
5. Nordmeijer, E., Lanver, U. and Lechner, M., *Macromolecules*, 1990, **23**, 1072.
6. Nordmeijer, E., Lanver, U. and Lechner, M., *Macromolecules*, 1990, **23**, 1077.
7. Kulin, L. I., Meijerink, N. L. J. and Starck, P., *Pure and Appl. Chem.*, 1988, **60**(9), 1403.
8. Bergstrom, C. and Avela, E., *Appl. Polym. Sci.*, 1979, **23**, 163.
9. Soares, J. B. and Hamilic, A., *Polymer*, 1995, **36**(8), 1639.
10. Lew, R., Suwanda, D., Balke, S. T. and Mourey, H., *J. Appl. Polym. Sci.*, 1993, **52**, 125.
11. Shiga, S., *Polym. Plast. Technol. Eng.*, 1989, **28**(1), 17.
12. Yau, W. W., *Chemtracts*, 1990, **1**, 1.
13. Zimm, B. H. and Stockmayer, W. H., *J. Chem. Phys.*, 1949, **17**, 1301.
14. Scholte, Th. G., *Developments in Polymer Characterization*, Vol. 4, ed. J. V. Dawkins, Chapter 1. Applied Science, Essex, 1984.
15. Scholte, Th. G. and Meijerink, N. L. J., *Br. Polym. J.*, 1974, **133**, 9.

16. Wyatt, P. J., *Anal. Chim. Acta*, 1993, **272**, 1.
17. Podzimek, S., *J. Appl. Polym. Sci.*, 1994, **54**, 91.
18. Dayal, U., *J. Appl. Polym. Sci.*, 1994, **53**, 1557.
19. deGroot, A. W. and Hamre, W. J., *1991 International GPC Symposium Proceedings*. Waters Chromatography Division, Millipore Corp., Milford, MA, 1991, p. 353.
20. Flory, P. J. and Fox, T. G., *J. Am. Chem. Soc.*, 1950, **73**, 1904.
21. Scholte, Th. G., Meijerink, N. L. J., Schoffeleers, H. M. and Brands, A., *J. Appl. Polym. Sci.*, 1984, **29**, 3763.
22. Grubistic, Z., Rempp, R. and Benoit, H., *J. Polym. Sci. B*, 1967, **5**, 753.