

Note

Size Exclusion Chromatography and Low-Angle Laser Light Scattering. Application to the Study of Long Chain-Branched Polyethylene

INTRODUCTION

While the number, type, and distribution of both short-chain and long-chain branching in polyethylene is of considerable importance in determining the rheological and morphological properties of the polymer, the accurate measurement of these parameters has proven to be difficult. Quantitative investigations have relied on such methods as infrared spectroscopy,¹ carbon-13 Fourier transform nuclear magnetic resonance spectroscopy,² gel permeation chromatography (or more correctly, size exclusion chromatography),³ and viscosity measurements.⁴

With respect to the determination of long-chain branching, the most promising techniques appear to be C-13 NMR and size exclusion chromatography (SEC), particularly when the latter method is coupled with automatic viscometry⁵ or low-angle laser light scattering (LALLS) measurements.⁶ It has only recently become practical to combine these last two techniques to provide a real time analysis of the SEC effluent, but it was considered to be an open question as to the accuracy of an SEC/LALLS combination in determining long-chain branching as a function of molecular weight.⁷

Therefore, the purpose of the present note is to illustrate the applicability and accuracy of the LALLS photometer, not only as a continuous monitor of molecular weight but also as a continuous monitor of long-chain branching.

The sample investigated, NBS 1476, has been previously characterized^{8,9} and as such represents one of the best materials available for such a test.

As the experimental parameters are of great importance in this instance, and as a detailed comparison of the present results with literature data will be made, a brief summary of the equations and approximations made will be given.

The relationship probed by the experimental procedure to be described is summarized quantitatively by the relationship¹⁰ given in eq. (1):

$$M_{b_i}^{a+1} g^k(\lambda, M_{b_i}) = M_{l_i}^{a+1} \quad (1)$$

where M_{b_i} is the molecular weight of the branched polyethylene obtained in the SEC separation at elution volume i , M_{l_i} is the molecular weight of the linear polyethylene having the same elution volume as the branched polyethylene with weight M_{b_i} , a is the Mark-Houwink constant (taken as 0.725), k is taken as 0.5, and g is a function of the branched molecular weight, the degree, and the distribution of the long-chain branching. In the present case the LALLS data provide an absolute measure of M_{b_i} , while M_{l_i} is calculated from calibration constants determined from analysis of a sample of known molecular weight (NBS 1475).

The equation chosen for g is that used in ref. 8, since the data in that reference are to be compared with ours. Obviously, other choices can be made, but it is not the purpose of the present work to argue the relative merits of available models but rather to illustrate that the SEC/LALLS approach can lead to results consistent with other more time-consuming methods. The determination of the most reliable model(s) will probably rest with comparison of SEC/LALLS data with an independent, absolute method such as C-13 NMR (this latter experiment requiring fractions for study).

The equation for g used, and first derived by Zimm and Stockmayer,¹¹ is

$$g = \frac{6}{n_w} \frac{1}{2} \left(\frac{2 + n_w}{n_w} \right)^{1/2} \ln \left[\frac{(2 + n_w)^{1/2} + n_w^{1/2}}{(2 + n_w)^{1/2} - n_w^{1/2}} - 1 \right] \quad (2)$$

and characterizes a randomly branched polydisperse polymer having trifunctional branch points. The total number of branches per molecule, n_w , is given by the product of the number of branches

per unit molecular weight λ and the molecular weight M . Thus, the only experimental variable is λ , and this parameter can be adjusted to satisfy eq. (1). The advantage of this experiment and analysis is that it does not involve the assumption of constant branching density over the whole molecular weight distribution.

EXPERIMENTAL

A du Pont 830 liquid chromatograph with an infrared detector and with an attached Chromatix KMX-6 low-angle laser light scattering photometer were employed for this work. Raw data from these detectors were stored in a microprocessor and subsequently printed out on paper tape for analysis. A polymer concentration of 8.953 mg/ml and a flow rate of 0.9761 ml/min in 1-chloronaphthalene at 150°C were used. The 2 mW He-Ne laser source had a wavelength of 6328 Å. The field stop was 0.15 mm, a 6–7° annulus was used, and the integration period was 3 sec. Column packings consisted of bimodal pores of porous silica microspheres the details of which may be found elsewhere.¹²

The sample investigated was a National Bureau of Standards standard reference material designated 1476. It was the low conversion product of tubular reactor and had a density of 0.931 and a melt index of 1.19.¹³

Following the notation of Ouano,⁶ the actual data analysis was performed as follows. The excess Rayleigh scattering intensities were obtained from the equation

$$R_{\theta_i} = K_1 Y_i$$

and the concentration from

$$C_i = K_2 x_i / \sum x_i$$

where the Y_i and x_i values are the digitized LALLS and IR data, respectively, and

$$K_1 = FG/P_0$$

The transmittance of the attenuators F used in the calculation of the attenuated, unscattered laser intensity P_0 was determined to be 1.305×10^{-8} , while P_0 itself had a value of 340. The instrumental constant G , related to the solid angle of detected scattered light and the length of the scattering volume parallel to the laser beam, had a value of 1000.8. Finally,

$$K_2 = WT/\Delta V$$

where WT is the total sample weight injected and ΔV is the volume increment of the effluent.

The second virial coefficient A_2 was incorporated in the data analysis as a function of the molecular weight using the relationship⁶

$$A_{2_i} = K_3 M_i^{-a}$$

where K_3 (1.003×10^{-2}) and a (1.675×10^{-1}) were determined from the available literature.¹⁴ The molecular weight was computed iteratively using the equation

$$\frac{K_4 C_i}{R_{\theta_i}} = \frac{1.0}{M_i} + 2A_{2_i} C_i$$

where K_4 (of the order of 0.3×10^{-6}) depends on the viewing angle, the solvent refractive index, and the refractive index increment (with a change in concentration dn/dc). Corrections were made to K_4 as a function of the molecular weight dependence of this latter parameter.¹⁵ The corrections related to A_2 and dn/dc were relatively minor, however.

Due to the low LALLS sensitivity at very high ($>10^6$) and very low ($<10^3$) molecular weights (since the minimum detectable concentration is of the order of $1/M_w$), data in these regions were obtained by extrapolation from the data preceding these ranges. The procedure is sufficient in that the data obtained on a known linear sample compare well with the data obtained by linear calibration methods. Smoothing of the raw LALLS data was performed to remove any effects of spikes caused by the presence of particulate matter (e.g., dust) in the sample. Careful filtering minimizes this problem.

The linear calibration constants used to calculate M_{i_i} were obtained from a study of NBS 1475.¹⁶ No corrections for dispersion were made.

TABLE I
 NBS 1476 Molecular Weight and Branching Data

Elution volume, ml	Molecular weight		Long-chain branches per 1000 Carbons ^d
	LALLS ^a	Linear ^{b,c}	
17.08	981 596	462 028	0.5
17.24	834 612	401 470	0.5
17.41	709 636	348 850	0.6
17.57	603 373	303 127	0.6
17.73	513 016	263 394	0.7
17.89	436 199	228 872	0.7
18.06	370 882	198 873	0.8
18.22	315 343	172 806	0.8
18.38	268 123	150 157	1.0
18.54	227 975	130 477	1.0
18.71	193 836	113 374	1.1
18.87	164 810	98 514	1.2
19.03	140 133	85 603	1.2
19.19	119 148	74 382	1.3
19.36	101 306	64 633	1.4
19.52	86 136	56 161	1.4
19.68	73 238	48 800	1.5
19.85	62 271	42 404	1.5
20.02	52 946	36 846	1.5
20.17	45 018	32 017	1.5
20.33	38 277	27 820	1.5
20.50	32 545	24 174	1.5
20.66	27 672	21 005	1.4
20.82	23 528	18 252	1.3
20.98	20 005	15 860	1.2
21.15	17 009	13 781	1.0
21.31	14 462	11 975	0.7
21.47	12 297	10 405	0.4
21.63	10 455	9041	0.1
21.80	8896	7856	0.0
21.96	7559	6827	0.0
22.12	6427	5932	0.0

^a Low-angle laser light scattering-SEC results.

^b Calculated from linear calibration constants derived from NBS 1475 standard.

^c Data given correspond to those reported in refs. 8 and 9 only; very high and very low molecular weight data not included.

^d Calculated from eqs. (2) and (1).

RESULTS AND DISCUSSION

The chromatograms obtained from the two detectors were analyzed to yield the absolute and "linear" molecular weights and branching as a function of elution volume (Table I). The long-chain branching values of Table I were recast in terms of the total number of branch points per molecule and plotted as a function of molecular weight in Figure 1. All relevant molecular weight data are summarized in Table II.

For M_b , (i.e., LALLS) values greater than about 8000, the level of long-chain branching becomes significant, gradually increasing in magnitude up to a molecular weight of about 60,000, at which point it begins to gradually decrease. The exact nature of this trend is obscured at very high molecular weights [greater than $(8-10) \times 10^5$] by the fact that the linear calibration curve derived from the NBS 1475 standard may not yield reliable molecular weights.¹⁶ Wagner and McCrackin⁸ found in their study of viscosities that there was little or no long-chain branching below molecular weights of about 10,000, and this is true also of the SEC/LALLS calculations.

The data presented in Table II are important in that they verify that the molecular weight pa-

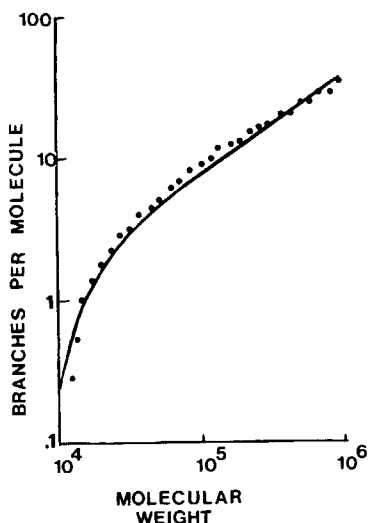


Fig. 1. Branch points per molecule as function of molecular weight for NBS 1476. Solid curve represents data from refs. 9 and 8, and solid circles are data from the SEC/LALLS experiment of the present work.

rameters available in the literature for NBS 1476 can be reproduced by the LALLS data. As corroborating data, the NBS 1475 standard was analyzed by the same technique yielding molecular weight values that are in good agreement also with literature values.

Finally, the most important data are plotted in Figure 1. The solid black line denotes the literature results (from ref. 8 and Fig. 4 of ref. 9) on NBS 1476, and the superimposed black points are the experimental SEC/LALLS results obtained in the present study. The agreement is quite good over the whole range of molecular weights. A C-13 FT NMR study of two of the fractions⁹ supports the validity of these analyses also.

CONCLUSIONS

It has been shown that, for a well-characterized branched polyethylene, a low-angle laser light scattering photometer, in conjunction with a concentration detector and size-exclusion chromatograph, can provide relatively fast and accurate continuous determinations of long-chain branching as a function of molecular weight.

TABLE II
Summary of Molecular Weight Parameters of NBS Standards 1475 and 1476

	NBS 1476 ^a		NBS 1475 ^b	
	Literature	Present work ^c	Literature ^d	Present work ^c
M_n	2.10 ^e	2.01 ^f	2.18	1.80
M_w	8.22	9.09	7.61	5.27
M_w/M_n	3.91	4.52	3.49	2.92

^a Branched polyethylene ($M \times 10^{-4}$).

^b Linear polyethylene ($M \times 10^{-4}$).

^c Obtained by SEC and low-angle laser light scattering.

^d From ref. 17, SEC, standard deviations are 1250 (M_n) and 2140 (M_w).

^e From ref. 16, SEC-intrinsic viscosity measurement.

^f From ref. 8, SEC-intrinsic viscosity measurement.

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References

1. (a) A. H. Willbourn, *J. Polym. Sci.*, **34**, 569 (1959); (b) C. Baker and W. F. Maddams, *Makromol. Chem.*, **177**, 437 (1976); (c) M. A. McRae and W. F. Maddams, *Makromol. Chem.*, **177**, 449 (1976).
2. (a) D. E. Axelson, L. Mandelkern, and G. C. Levy, *Macromolecules*, **10**, 557 (1977); (b) D. E. Axelson, G. C. Levy, and L. Mandelkern, *Macromolecules*, **12**, 41 (1979); (c) J. Spevacek, *Polymer*, **19**, 1149 (1978); (d) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 275 (1973).
3. (a) E. E. Drott and R. A. Mendelson, *J. Polym. Sci. Part A-2*, **8**, 1361, 1373 (1970); (b) E. P. Otocka, R. J. Roe, M. Y. Hellman, and P. M. Muglia, *Macromolecules*, **4**, 507 (1971); (c) T. Hama, K. Yamaguchi, and T. Suzuki, *Makromol. Chem.*, **155**, 283 (1972).
4. (a) L. Wild and R. Guliana, *J. Polym. Sci. Part A-2*, **5**, 1087 (1967); (b) J. Miltz and A. Ram, *Polymer*, **12**, 685 (1971); (c) L. Wild, R. Ranganath, and T. Ryle, *J. Polym. Sci. Part A-2*, **9**, 2137 (1971); (d) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. Part B*, **5**, 754 (1967).
5. (a) D. Constantin, *Eur. Polym. J.*, **13**, 907 (1977); (b) C. Meyerhoff, *Makromol. Chem.*, **118**, 265 (1968); (c) D. Goedhart and A. Opschoor, *J. Polym. Sci. Part A-2*, **8**, 1227 (1970).
6. (a) A. C. Ouano and W. Kaye, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1151 (1974); (b) A. C. Ouano, *J. Chromatogr.*, **118**, 303 (1976).
7. G. Scholte and N. L. J. Meijerink, *Br. Polym. J.*, **9**, 133 (1977).
8. H. L. Wagner and F. L. McCrackin, *J. Appl. Polym. Sci.*, **21**, 2833 (1977).
9. F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, *Macromolecules*, **9**, 76 (1976).
10. L. Westerman and J. C. Clark, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 559 (1973).
11. B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
12. W. W. Yau, C. R. Ginnard, and J. J. Kirkland, *J. Chromatogr.*, **149**, 465 (1978).
13. L. Wild, R. Ranganath, and A. Barlow, *J. Appl. Polym. Sci.*, **21**, 3331 (1977).
14. L. J. Frolen, G. S. Ross, A. M. Wims, and P. H. Verdier, *J. Res. Natl. Bur. Stand. Sect. A*, **76**, 156 (1972).
15. H. L. Wagner, *J. Res. Natl. Bur. Stand. Sect. A*, **76**, 151 (1972).
16. A. Barlow, L. Wild, and R. Ranganath, *J. Appl. Polym. Sci.*, **21**, 3319 (1977).
17. G. Ross and L. Frolen, *J. Res. Natl. Bur. Stand. Sect. A*, **76**, 163 (1972).

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