

# High-Temperature SEC Coupled with MALLS Detector for Evaluating the End-Use Performance of LDPE

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## SYNOPSIS

Low-density polyethylene (LDPE) is the most widely used plastic material in the film-packaging industry. To improve its tensile strength and elongation, it is blended with linear LDPE. Three commercial samples of LDPE, which were found to give different performances in the sealing strength of films prepared from their blends, have been evaluated for their molecular weight (MW), molecular weight distribution (MWD), and long-chain branching by high-temperature size exclusion chromatography (SEC) and SEC coupled with a multiangle laser light-scattering (MALLS) detector. It has been shown that the differences in MW and MWD that remain unnoticed by conventional SEC are detected by SEC/MALLS. Wide MWD and a low weight-average MW of the resin has been found to favor film-sealing strength. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Size-exclusion chromatography (SEC) separates molecules according to their hydrodynamic size in solution.<sup>1,2</sup> Hence, the branched molecular species of the same molar mass, due to their smaller hydrodynamic size as compared to the linear ones, elute later from a given column under identical conditions of solvent flow. Molecular weight (MW) and molecular weight distribution (MWD) data obtained from conventional SEC, employing universal calibration,<sup>2</sup> would, therefore, require appropriate correction for branched molecules. SEC coupled with a mass-sensitive light-scattering<sup>3-6</sup> or viscometric detector<sup>7-9</sup> has recently been reported for addressing such problems.

Low-density polyethylene (LDPE), used extensively in film-packaging applications, is generally produced in high-pressure reactors. The long- and short-chain branching, introduced in the polymer chain during polymerization, affects the physical properties of the polymer.<sup>10,11</sup> Additionally, LDPE resins are blended with linear LDPE for improvement in their tensile properties. Such blends, due to incompatibility of either of the resins, sometimes give rise to inferior end-use or processing perfor-

mance. Though such problems can generally be correlated to the variations in MW and MWD of the resins, but identification of the real cause becomes often difficult due to a large number of variables involved between the manufacturing process and their processing and performance behavior.

In the present study, three commercial LDPE resins, which were reported to give different performances in respect to the sealing strength of the films produced from their blend with linear LDPE in a ratio of 5 : 1, were evaluated for their MW, MWD, and long-chain branching parameters by SEC and SEC coupled with a multiangle laser light-scattering (MALLS) detector. MW data obtained using three different sets of SEC columns and those obtained from SEC/MALLS were compared. The performance of LDPE resins was evaluated in terms of their branching distribution and MW data.

## METHODS

The branching parameters  $g$  and  $g'$  are defined by eqs. (1) and (2)<sup>12</sup>:

$$g = \langle s^2 \rangle_b / \langle s^2 \rangle_l \quad (1)$$

$$g' = [n]_b / [n]_l \quad (2)$$

where quantities for branched ( $b$ ) and linear ( $l$ ) species are taken at the same MW,  $\langle s^2 \rangle$  is the root mean-square radius of gyration, and  $[n]$  is the intrinsic viscosity. The parameters  $g$  and  $g'$  were empirically correlated by the equation of the form  $g' = g^k$ , where  $k$  is a constant depending on the polymer and having values ranging between 0.5 and 1.5,<sup>13-15</sup> the value for present work being 0.75.<sup>14</sup> It was shown from the principles of universal calibration<sup>2</sup> that the following relationship exists between the MW of the branched and linear polymers ( $M_l$  and  $M_b$ ) at a given retention volume<sup>10,16</sup>:

$$g' = \left( \frac{M_l}{M_b} \right)^{\alpha+1} = g^k \quad (3)$$

A MALLS detector,<sup>17</sup> coupled with SEC, measures the scattering intensity of the eluting polymer species as an excess Rayleigh ratio<sup>18</sup> at different retention volumes using photodiodes placed around the sample cell in a circular geometry, the scattering angle depending on the refractive index of the solvent. The intercept of a Debye plot,<sup>18,19</sup> constructed from a reduced Rayleigh ratio as a function of the scattering angle, allows computation of  $M_b$  for a given slice, provided that the differential refractive index increment ( $dn/dc$ ) and second virial coefficient ( $A_2$ ) for the polymer sample and solvent system are known. The values of these constants for the present work were<sup>20,21</sup>  $(dn/dc) = (-) 0.091$  mL/g and  $A_2 = 4.20 \times 10^{-4}$  mL mol/g<sup>2</sup>. The corresponding  $M_l$  values, at the same retention volume as that of  $M_b$ , are obtained from a universal calibration curve. The values of Mark-Houwink constants  $K$  and  $\alpha$  for linear polyethylene<sup>22</sup> were  $5.96 \times 10^{-4}$  dL/g and 0.69, respectively, and for polystyrene, the same as those used for the SEC work reported below. The weight-average number of branch points per molecule ( $B_w$ ) for a wide polydispersity polymer having trifunctional branch points with a random distribution are calculated from various values of  $g$ , using eq. (3) and subsequently employing the Zimm-Stockmayer equation.<sup>12</sup> The weight-average number of long-chain branches per 1000 carbon atoms for the  $i$ th slice are given by<sup>23</sup>

$$\text{LCB}/1000\text{C} = (B_{wi}/M_{bi}) \times 14,000 \quad (4)$$

## EXPERIMENTAL

### Materials

Narrow dispersity polystyrene standards for SEC column calibration were obtained from Polymer

Laboratories, U.K., and the Waters Division of Millipore, USA. The three samples, designated as #1, #2, and #3, were commercially available LDPE resins produced by a high-pressure tubular reactor process having an MFI of 0.5–0.6. The density of these samples was obtained at  $23 \pm 0.1^\circ\text{C}$  using a six-column density measuring apparatus (Davenport London Ltd., England), whereas crystalline melting point data were determined by a differential scanning calorimeter (Mettler Instruments, Switzerland).

### SEC Equipment and Conditions

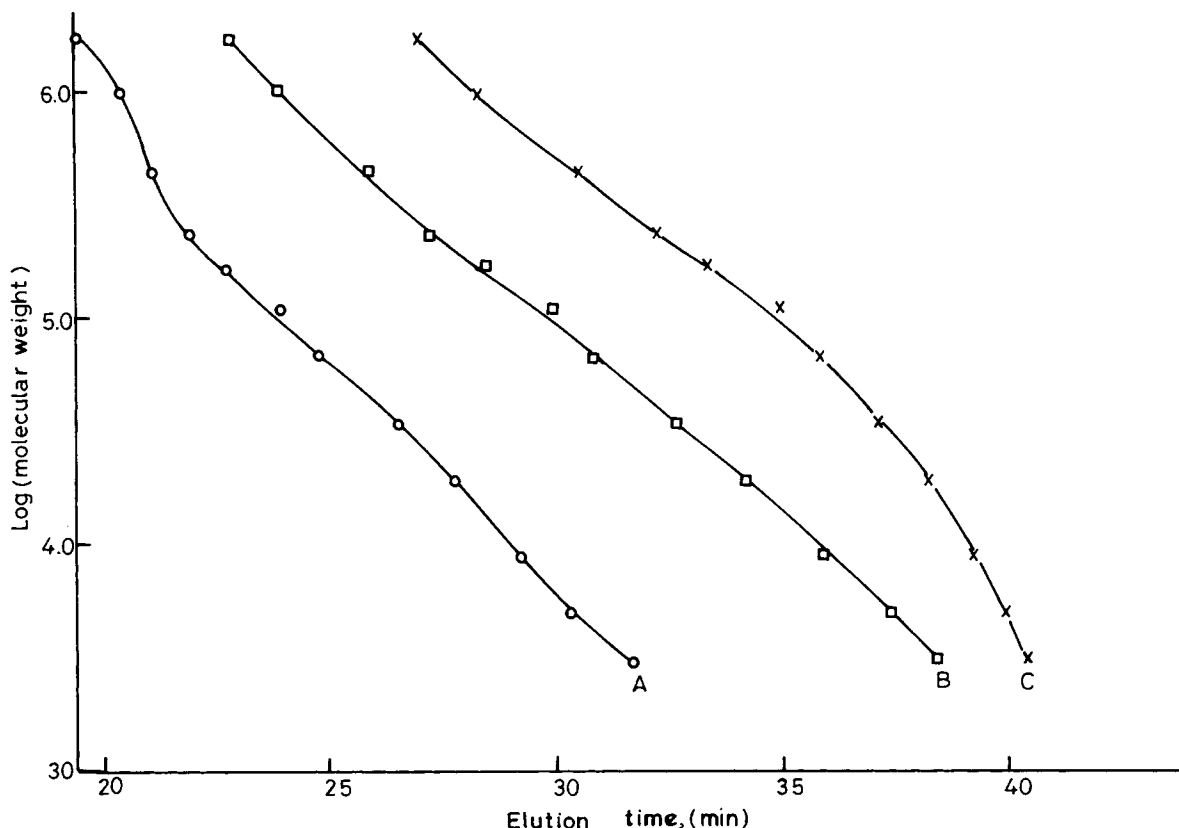
A Waters Model 150 C ALC/GPC liquid chromatograph connected to an additional 25 mm high-pressure SS filter holder with  $0.1 \mu\text{m}$  Millipore filter and a pulse dampener (Alltech Associates, U.S.A.) was used. To select a suitable column set for the samples to be analyzed by SEC and a corresponding range of PS standards, three different sets of Ultrastayragel columns (Waters Division of Millipore), viz., 500,  $10^3$ , and  $10^4$  (Set A);  $10^3$ ,  $10^4$ , and  $10^5$  (Set B); and  $10^4$ ,  $10^5$ , and  $10^6$  (Set C), were evaluated. These column sets are referred to as "A," "B," and "C," respectively, hereafter. A flow rate of 0.8 mL/min and a temperature of  $140^\circ\text{C}$  was used throughout this work. The values of Mark-Houwink constants  $K$  and  $\alpha$ , used for the SEC work, taken from the literature were for polystyrene<sup>24</sup>  $1.21 \times 10^{-4}$  dL/g and 0.707 and for polyethylene<sup>25</sup>  $4.01 \times 10^{-4}$  dL/g and 0.726, respectively.

### Sample Preparation

Polystyrene standards (0.2% w/v) were dissolved in 1,2,4-trichlorobenzene (TCB) (Merck, Germany) and filtered at ambient temperature through a  $0.45 \mu\text{m}$  Millipore filter (Millipore Corp., Bedford, MA, USA). The solutions were heated to  $140^\circ\text{C}$  for 20 min in the injector compartment of 150C before injection. Polyethylene samples (0.2% w/v) in TCB were kept in an oven at  $140^\circ\text{C}$  for 18–20 h for dissolution and allowed to stand for 1 h in the injector compartment of 150C before injection. Irganox 1076, 0.2% (w/v) (Ciba-Geigy, Switzerland), was added to the mobile phase and TCB, used for dissolving the polymers, for preventing thermal degradation during dissolution and analysis.

### MALLS Detector

A MALLS detector, Model DAWN-F (Wyatt Technology Corp., Santa Barbara, CA) was connected to the GPC 150C, as described by Jackson et al.<sup>26</sup>



**Figure 1** Elution behavior of polystyrene standards from different columns "A," 500,  $10^3$ , and  $10^4$ ; "B,"  $10^3$ ,  $10^4$ ; and  $10^5$ ; and "C,"  $10^4$ ,  $10^5$ , and  $10^6$ .

## RESULTS AND DISCUSSION

The elution behavior of narrow MWD polystyrene standards, from "A," "B," and "C," is shown in Figure 1. It is observed that "B" has a better linearity as compared to the other two-column sets. However, for polyethylene analysis by SEC, both "B" and "C" were used, whereas for SEC/MALLS data collection, only "B" was employed. The polyethylene calibration equation for a column set used for the SEC work was obtained by transformation of the polystyrene peak MW-retention volume data using the principles of universal calibration and subsequent regression analysis on a computer.

The weight- and number-average MW data for the three resins determined from SEC are given in Table I. The data obtained from "B" and "C" show minor variation, which is considered to be due to the difference in the elution characteristics of the two-column sets. The three samples, as evaluated by SEC, however, do not show any significant difference that can reflect on film-sealing strength. The MW averages determined by SEC/MALLS are substantially higher as compared to SEC (Table I),

samples #2 and #3 showing more variation as compared to #1. Grinshpun et al.<sup>27</sup> pointed out that such discrepancies in the results obtained from SEC and SEC coupled with a low-angle laser light-scattering detector may be due to high MW species remaining undetected by the refractive index detector used in the SEC analysis.

To investigate the dependence of the refractive index and the MALLS detector response on the MW of the eluting species, cumulative MWD, calculated from the data obtained from both, was plotted for sample #1 (Fig. 2). It can be seen that the data obtained by SEC/MALLS is higher than those obtained by SEC for the entire weight fraction range, the difference, however, narrowing down in the middle region. Another significant observation is that the detectability of SEC/MALLS in the low MW region is poor and the fraction detected by SEC in the high MW region is less as compared to SEC/MALLS. Such curves in respect of samples #2 and #3 are expected to be farther apart from each other due to a larger variation in their MW average values. It is observed that the reason for the difference in the data obtained by the two techniques is due to

**Table 1** Molecular Weight Data from SEC and SEC/MALLS

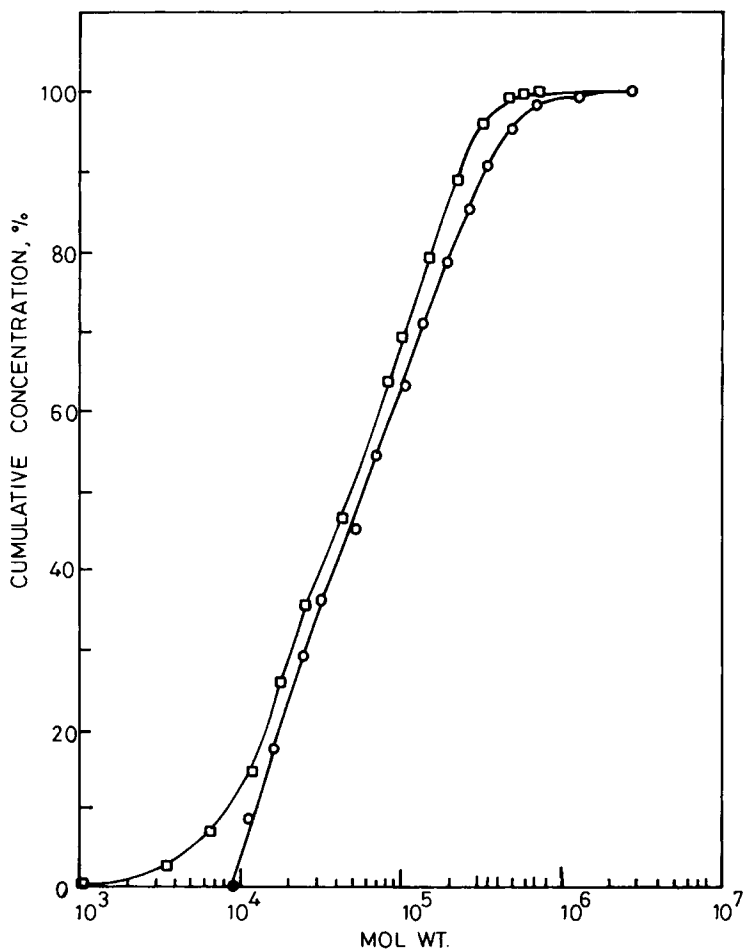
Method	Column	MW Data	Sample #1	Sample #2	Sample #3
SEC/MALLS	"B"	$\bar{M}_w \times 10^{-4}$	13.20	20.17	19.47
		$\bar{M}_n \times 10^{-4}$	02.45	04.98	05.01
		$\bar{M}_w/\bar{M}_n$	05.39	04.05	03.89
SEC	"B"	$\bar{M}_w \times 10^{-4}$	10.02	10.16	09.79
		$\bar{M}_n \times 10^{-4}$	02.38	02.75	02.88
		$\bar{M}_w/\bar{M}_n$	04.21	03.70	03.40
SEC	"C"	$\bar{M}_w \times 10^{-4}$	10.14	09.79	09.96
		$\bar{M}_n \times 10^{-4}$	02.13	02.27	02.29
		$\bar{M}_w/\bar{M}_n$	04.76	04.31	04.35

"B" = Ultrastyrigel column set  $10^3$ ,  $10^4$ , and  $10^5$ . "C" = Ultrastyrigel column set  $10^4$ ,  $10^5$ , and  $10^6$ .  $\bar{M}$  = Weight-average molecular weight.  $\bar{M}$  = Number-average molecular weight.

the presence of long-chain branching, which is discussed below.

The Mark-Houwink constants used for the SEC work were considered to be applicable to branched

polyethylene resins as they have been used to evaluate similar samples. But they do not appear to be applicable here and, hence, contribute to the present variation. The fractionation of these resins or other

**Figure 2** Cumulative MWD of resin #1: (□) SEC; (○) SEC/MALLS.

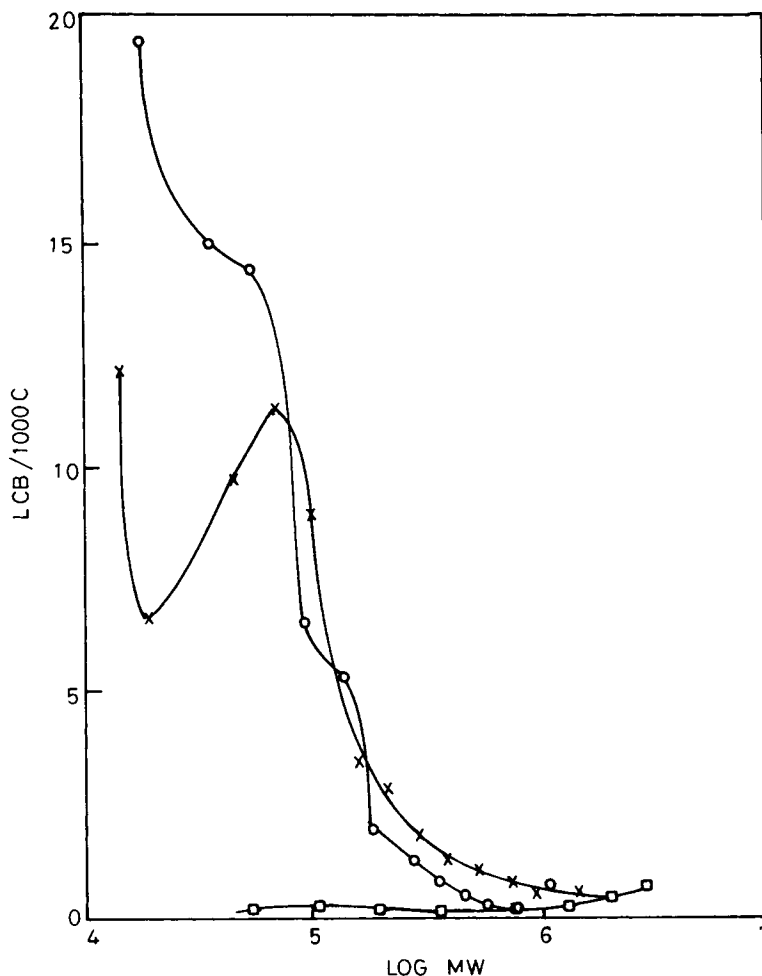


Figure 3 Branching distribution of polyethylene: (□) resin #1; (X) resin #2; (○) resin #3.

means for determining these constants was considered to be out of the scope of the present work and, hence, no attempt was made for their determination. The films produced from blends by adding 20% linear LDPE (MFI 1.0 g/10 min) to the samples investigated in the present study were reported to behave differently in their sealability. The films are sealed at temperatures ranging from 115 to 120°C. Resin #1 (MFI 0.5 g/10 min) had no sealing problem, whereas #2 and #3 (MFI 0.6 g/10 min) were reported to have poor sealing and a narrow heat-sealing range. Since an equal amount of linear LDPE was blended with the three resins, its effect on sealing strength was considered to be a common factor and evaluation of its MW was considered to provide any additional information. The density of these samples was found to be 0.920, 0.923, and 0.923 g/cc, respectively, whereas the crystalline melting points were 109, 111, and 111°C in the same order. The difference in physical properties of these resins

is considered to be minor, having a negligible effect on the film-sealing strength. It is noted that the MW data obtained in the present work are in accordance with the physical characteristics.

The branching distribution of LDPE resins is known to influence the viscoelastic properties of the melt. With a view to have its impact known, the branching distribution for the three resins was determined assuming a random trifunctional branching distribution (Fig. 3). It is observed that the branching frequency increases progressively for #2 and #3 with decreasing weight-average MW, which is in line with the results reported in the literature.<sup>28</sup> Sample #1 has been found to have < 1 branch per 1000 carbon atoms and this appears to be the reason for less variation in its MW data obtained by the two techniques. A higher branching frequency is expected to give better sealing strength due to more entanglement. The criticality of branch length for its effect on sealing is not known as the present setup

does not have facilities for such calculations. It is also not known as to how the branching geometry, viz., comb, treelike, or star, would affect the sealing characteristics. Since all the resins evaluated for the present work were produced by the tubular reactor process, they are expected to have a comblike branching structure.<sup>29</sup>

It is concluded that, under the present conditions, a low value of weight-average MW and wider MWD help in the proper sealing of the film produced from resin #1, which has similar physical characteristics as those of #2 and #3. High MW and narrow MWD of #2 and #3, as obtained by SEC/MALLS, are expected to have a narrow heat-sealing range and a higher sealing temperature, which is in accordance with their reported behavior.

The encouragement, guidance, and permission for publication of this work by Dr. I. S. Bhardwaj, Director, IPCL Research Center, are gratefully acknowledged. The author is also thankful to Drs. A. B. Mathur and S. K. Mehta for helpful discussions and to Mr. G. M. Mehta for carrying out a part of the experimental work.

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Received September 13, 1993

Accepted March 1, 1994