Characterization of polyolefins by size exclusion chromatography with low-angle light scattering and continuous viscometer detectors

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(Received 10 February 1991; revised 19 June 1991; accepted 15 July 1991)

Molecular-weight distributions (*MWD*s) of polyolefins are currently measured by high-temperature size exclusion chromatography. The raw data are converted to *MWD*s using universal calibration with a differential refractive index (d.r.i.) concentration detector or by direct molecular-weight measurements with a continuous viscometer (c.v.) or a low-angle laser light scattering (l.a.l.l.s.) detector. None of these techniques provides a picture of the true distribution. Simple d.r.i.–universal calibration may fail to sense the high-molecular-weight tail of the distribution, which is important in some applications. The l.a.l.l.s. technique is most sensitive to high-molecular-weight polymers but is also least precise. The c.v. method is presently the most convenient single technique. The most information is obtained, however, when all these detectors are employed. Both the l.a.l.l.s. and c.v., for example, should be used to verify that the polymer sample is actually dissolved, since dissolution of semicrystalline polyolefins is not a trivial exercise.

(Keywords: polyolefins; size exclusion chromatography; low-angle light scattering; continuous viscometer; characterization; calibration)

INTRODUCTION

Size exclusion chromatography (s.e.c.) analyses of polyolefins are of value in understanding the relations between polymer properties and molecular-weight distributions and hence possibly with polymerization conditions. Characterization of the entire molecular-weight distribution is a desirable objective, of course, but this is not always possible with current analytical techniques. Nevertheless, certain compromises may be acceptable, depending on the polymer properties that are of primary interest in a given situation.

Thus, high-speed extrudability and parison behaviour in blow moulding are more sensitive to the presence of high-molecular-weight species than to any other part of the molecular-weight distribution. Conversely, brittleness of semicrystalline polyolefins may reflect the presence of low-molecular-weight crystallizable polymers. Melt index, which is a prime quality-control parameter, correlates with the weight-average molecular weight M_w of the polymer provided all samples in the comparison are made by the same process and have similar molecular-weight distributions[1]. More generally, melt index is a function of the whole molecular-weight distribution and not just a single average value.

The actual molecular-weight distribution (*MWD*) that is estimated from a given s.e.c. analysis is never completely accurate, with current analytical hardware. The most important techniques involve: (a) calculation of the *MWD* from universal calibration, generally using a differential refractive index (d.r.i.) detector or infrared (i.r.) detector to monitor polymer concentration in the eluant as a function of retention time and hence of hydrodynamic size of the dissolved species; (b) continuous measurement of the molecular weight of the eluting species (actually $\bar{M}_w$) using a low-angle laser light scattering (l.a.l.l.s.) photometer; (c) continuous measurement of the molecular weight (here $\bar{M}_n$)[2] of the eluting species using a continuous viscometer (c.v.).

Method (a) is invalid for mixtures, polymers with significant amounts of long-chain branching and copolymers in which the composition varies with molecular weight. Method (b) is invalid for mixtures and for copolymers with variable compositions. Method (c) is also invalid for mixtures of homopolymers or copolymers but can be used to measure the number-average molecular weight $\bar{M}_n$ of such materials[3]. Method (b) can be used to measure $\bar{M}_w$ of the polymer without analysing the *MWD*.

Here, we restrict ourselves to polyolefins that are analysed in a valid fashion by all three methods. The accuracy and limitations of each method are illustrated, and it is shown, not surprisingly, that valuable information can be obtained when the outputs of all three detectors are considered. It can also be seen that treatment of s.e.c. analyses of current polyolefins as a 'black box' technique can produce incomplete or even misleading results.

EXPERIMENTAL

Instruments

The s.e.c. system used in this study consisted of a Waters Associates 150C ALC/GPC, a Waters differential

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0032-3861/92/091949-04

refractometer (d.r.i.), LDC/Milton Roy's KMX-6 low-angle laser light scattering (l.a.l.l.s.) detector, Viscotek model 100 continuous differential viscometer (c.v.) detector, a Erma Optical Works Ltd ERC-3510 on-line degasser, a Molytek Thermapulse flow meter, and a set of Jordi columns, which consisted of a Jordi-Gel mixed bed column and a 1000 Å linear column. The experiments were run with a flow rate of 1.5 ml min^{-1} at 145°C. A schematic diagram of the apparatus is shown in *Figure 1*.

The l.a.l.l.s. photometer with a high-temperature flow-through cell was serially connected with the column. The d.r.i. and c.v. detectors were connected in parallel to the l.a.l.l.s. detector. The ratio of the volume of flow between the d.r.i. and c.v. lines was approximately 50:50. A flow meter was connected in series with the d.r.i. to monitor the instantaneous flow rate between the branch during the experimental runs. Polymer concentration in the eluant was monitored with the d.r.i. detector. Scattering intensity data were collected at the 6–7° annulus with a 6328 Å wavelength He–Ne laser. The mobile phase was filtered through an on-line 0.5 μm Fluoropore filter (Millipore Corp.) just before the l.a.l.l.s. cell. The value of dn/dc for the polyethylenes was determined independently with a LDC/Milton Roy's KMX-16 differential refractometer. Using the software package, developed in our laboratory, the analogue data from all three detectors were collected and digitized through a Cyborg A/D interface during a sample run on the s.e.c. system. Collected data were processed with an Apple Macintosh computer using the software package.

Sample preparation

All solutions for analysis were prepared in filtered 1,2,4-trichlorobenzene (TCB), the same solvent used as the s.e.c. eluant. Polymer solutions were prepared by dissolving known quantities of the polyethylenes (PE) and diluted to volume with the filtered TCB solvent. Dissolution of PE samples was achieved by rotating the samples at 160°C for 16–24 h. To prevent oxidative degradation of low-density PE (LDPE), 0.1 wt% of antioxidant (Irganox 1010) was added. The Jordi-Gel mixed bed column was calibrated using 30 polystyrene standard samples with molecular weights ranging from 580 to 15 000 000.

Complete dissolution of the polymers was assumed to have been achieved when the l.a.l.l.s. detector traces were free of spikes[4]. Higher-molecular-weight linear polyethylenes may require longer dissolution times than those used in this study.

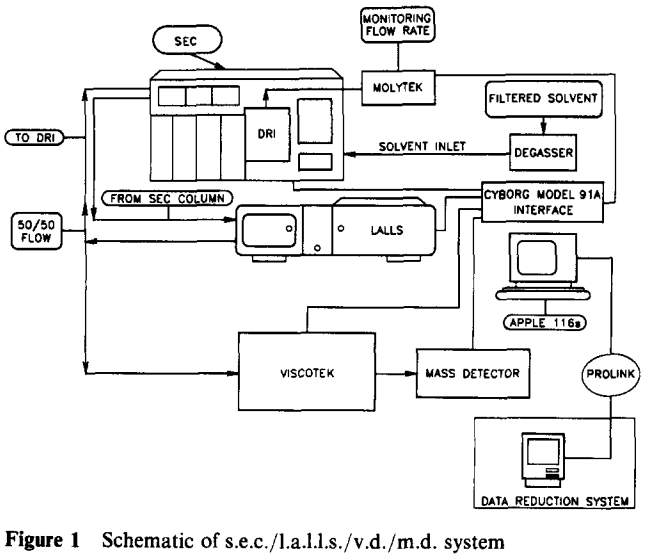

Figure 1 Schematic of s.e.c./l.a.l.l.s./v.d./m.d. system

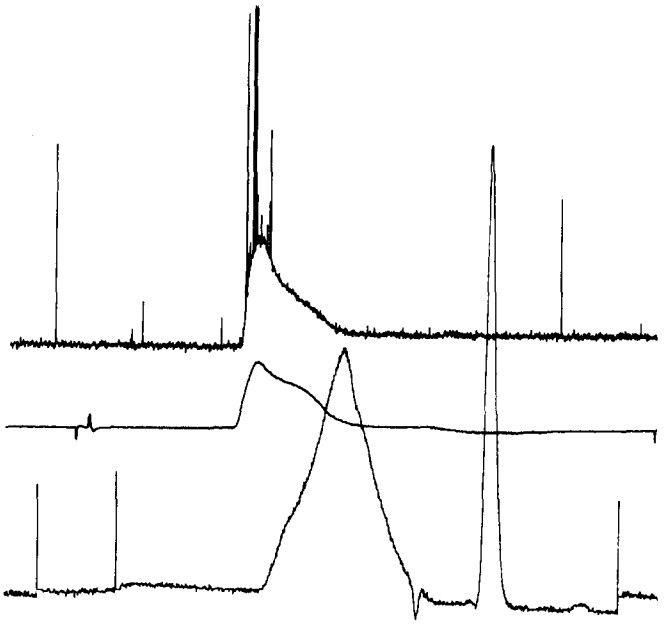

Figure 2 Raw data traces: in descending order l.a.l.l.s., c.v., d.r.i.

RESULTS

Sample dissolution

The l.a.l.l.s. detector provides a check on the complete solution of the polymer sample. The d.r.i. and c.v. detectors are not sensitive to the presence of large, presumably undissolved, species or to particulate matter that may be shed by the s.e.c. columns. A 'spiky' l.a.l.l.s. shows incomplete dissolution, which is not seen in the clean c.v. and d.r.i. traces. Polymer solution can be improved by longer 'soaking times' at 145°C or higher temperatures.

The l.a.l.l.s. detector is the most sensitive to high-molecular-weight species and provides an indication whether these polymers have actually been resolved in the s.e.c. columns. *Figure 2* shows raw traces for a polyethylene in trichlorobenzene solution at 145°C. The traces in descending order are from the l.a.l.l.s., c.v. and d.r.i. detectors. Molecular weight decreases from left to right. Note that the l.a.l.l.s. trace rises abruptly when the eluting species appear. It is also somewhat noisy. This shows the presence of some very large species and shows that large molecules were not separated by these columns. The other two detectors are not as sensitive to the high-molecular-weight tail of the distribution.

Data handling

When the MWD is estimated using the c.v. or l.a.l.l.s. detectors, these devices provide measures of the molecular weight of the eluting species. The d.r.i. is needed to estimate the corresponding concentration. It should be remembered that the three detectors differ in sensitivity. The l.a.l.l.s. signal scales with cM (c = concentration, M = molecular weight), while the c.v. responds according to $cM^{0.5}$ to about $cM^{0.8}$, depending on the given solvent[5]. The d.r.i., on the other hand, scales with c. Thus, the

l.a.l.l.s. is most sensitive to high-molecular-weight species and insensitive to small molecules. The d.r.i. has the opposite preference, while the c.v. is intermediate. When the largest molecules appear in the eluant, the l.a.l.l.s. and possibly the c.v. will show positive signals, whereas the d.r.i. indicates zero concentration. At the low-molecular-weight end of the *MWD* the d.r.i. indicates a finite concentration while the l.a.l.l.s. shows zero molecular weight.

This mismatch of sensitivities may result in truncation of the estimated *MWD* for polymers with broad distributions. The resulting errors may or may not be important in particular applications.

In the case illustrated in *Figure 2*, for example, the l.a.l.l.s. calculations were able to use 91.3% of the area under the d.r.i. concentration trace. The corresponding value for the c.v. was 93.7%.

Molecular-weight averages for this polymer illustrate the same phenomenon. These are tabulated in *Table 1*. Evidently, the l.a.l.l.s. value for $\bar{M}_n$ is inaccurate. $\bar{M}_z$ is probably measured best in this case only by the l.a.l.l.s.

Figures 3–5 show the differential and cumulative *MWD*s estimated from universal calibration, continuous viscometer and l.a.l.l.s. analyses. There is no data smoothing here; the noise is recorded. We recommend this procedure. Comparison of different polymers is often best done by overlaying such plots, rather than by comparing averages.

Figure 6 shows the three *MWD*s overlaid. It is clear that the l.a.l.l.s. 'sees' the high-molecular-weight tail best but is too noisy to be useful at all for molecular weights less than about 60 000 in this case. The d.r.i. does not record the high-molecular-weight tail and the c.v. is useful here for molecular weights between about 4000 and 4000 000, although it is quite noisy near these extremes. These comparisons are brought out strongly in *Figure 7*, which is a histogram depiction of the three measured *MWD*s.

We note also that the c.v. may be used to check the analysis. Universal calibration is by means of the parameter $[\eta]M$ (refs. 6, 7) using the intrinsic viscosities $[\eta]$ of standard polymers with known values of M. Since

Table 1 Molecular-weight averages for polymer of *Figure 2*

(a) $\bar{M}_n$			
Universal calibration 11 000	C.v. 18 000	L.a.l.l.s. 78 000	C.v. alone 18 000
(b) $\bar{M}_w$			
Universal calibration 231 000	C.v. 286 000	L.a.l.l.s. 309 000	L.a.l.l.s. alone 289 000
(c) $\bar{M}_z$			
Universal calibration 1120 000	C.v. 1418 000	L.a.l.l.s. 4039 000	

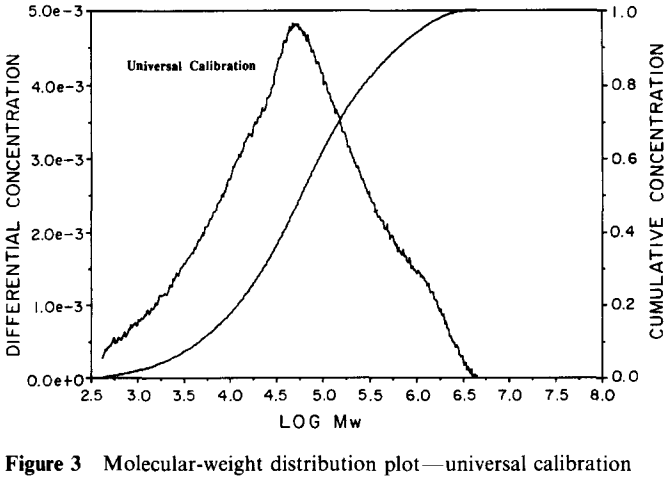

Figure 3 Molecular-weight distribution plot—universal calibration

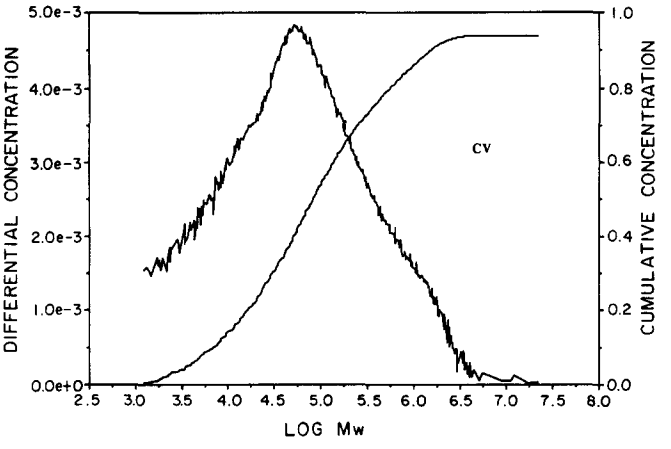

Figure 4 Molecular-weight distribution—continuous viscometer

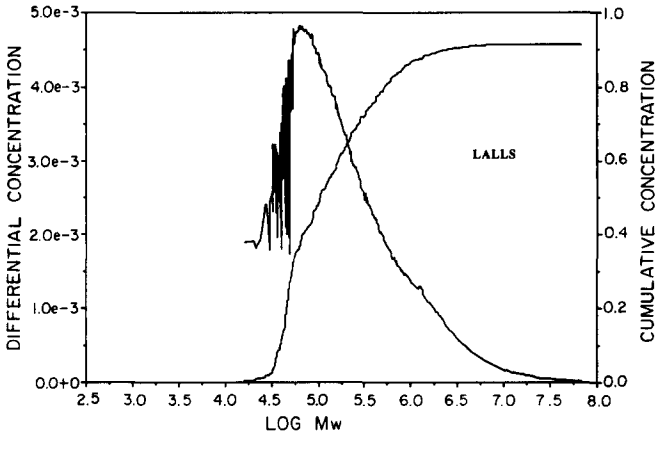

Figure 5 Molecular-weight distribution—l.a.l.l.s.

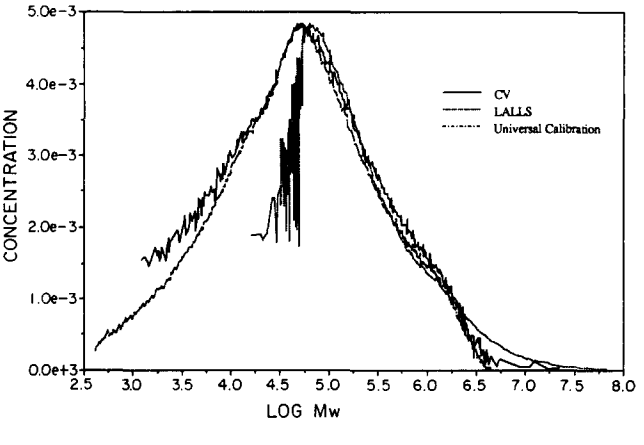

Figure 6 Molecular-weight distribution plots overlaid

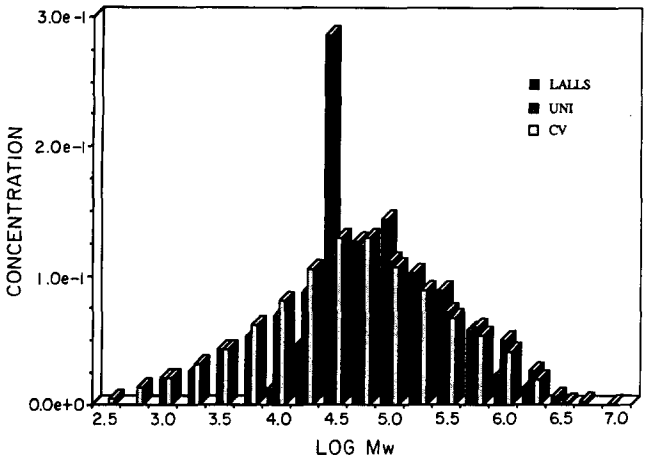

Figure 7 Molecular-weight distribution comparison

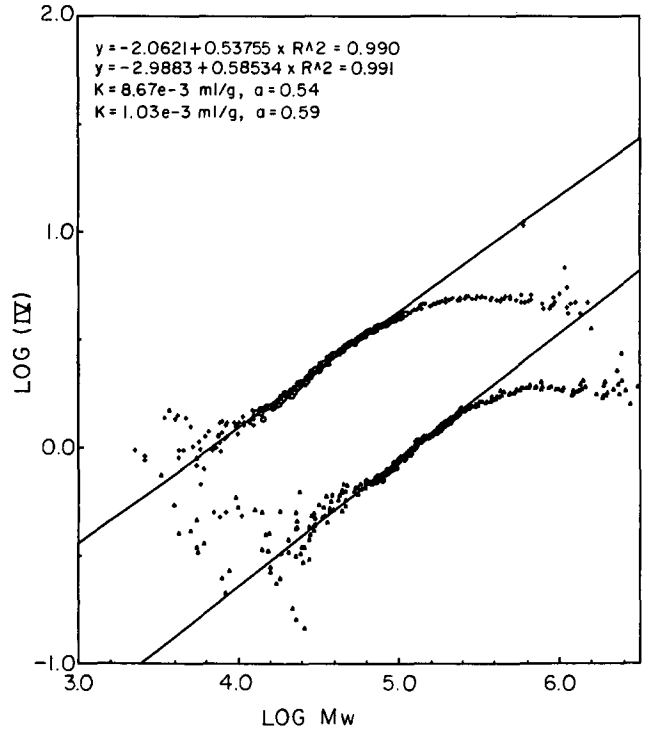

Figure 8 Mark–Houwink plots, synthetic elastomer in toluene at 28°C

the c.v. measures $[\eta]$ continuously, it can be used with universal calibration to produce corresponding values of $[\eta]$ and M. These provide Mark–Houwink plots according to the familiar equation:

$$[\eta] = KM^a \quad (1)$$

Figure 8 shows such a plot for two samples of a synthetic elastomer in toluene at 28°C. These conditions are used for quality-control measurements of solution viscosity of this polymer. We note here that the Mark–Houwink exponent is 0.5–0.6 for this material for molecular weights up to about 100 000. At higher molecular weights the slope of the curve decreases to zero. This indicates limited solubility for higher-molecular-weight species of this polymer in this solvent at the given temperature. It shows that these conditions are not suitable for s.e.c. analysis.

CONCLUSIONS

No current s.e.c. technique provides a picture of the true molecular-weight distribution of a polyolefin polymer with wide *MWD*. Conventional d.r.i.–universal calibration procedures may fail to detect the high-molecular-weight region, which may be involved in processability problems. Use of a continuous l.a.l.l.s. detector is very sensitive to high-molecular-weight species but tends to be noisy and imprecise. The continuous viscometer is intermediate in sensitivity. The most pressing current need in high-temperature s.e.c. is for a more sensitive concentration detector, to reduce the mismatch in useful ranges of the d.r.i. and the c.v. or l.a.l.l.s.

ACKNOWLEDGEMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada. This report is based on a paper given at Retec VII, Houston, Texas, February 1991.

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