International Union of Pure and Applied Chemistry

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PHASE 1: IUPAC SEC/GPC Round Robin Project Report

Title: Repeatability and Reproducibility of Sample Preparation and Analysis in High-Temperature SEC

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1. Background

High temperature size exclusion chromatography (HT-SEC), also commonly known as gel permeation chromatography (HT-GPC), is widely used to measure molecular weight properties of polyolefins. Experimental results from HT-GPC, like most other analytical techniques, are subject to variability resulting from several sources such as sample preparation, experimental conditions, inherent instrument variability, data handling, etc. The following molecular weight properties can be obtained from a single GPC analysis.

- Number average molecular weight (M_n)
- Weight average molecular weight (M_w)
- Z average molecular weight (M_z)
- Z+1 average molecular weight (M_{z+1})
- Polydispersity (PDI)
- Peak molecular weight (M_P)
- Molecular weight distribution curve (MWD)

As a result of the above-mentioned sources of variability, different laboratories analysing same sample would give different molecular weight values.

The aim of the project is to standardize the experimental conditions for the HT-SEC analysis of polyolefins. Particular emphasis is on the sample preparation with regard to dissolution temperature and time, the sample measurement with regard to column temperature and the column set, and with regard to the detection technique (RI, IR, ELSD, Viscometer, LS). Although there is an ASTM and ISO method for the analysis of polyolefins by HT-SEC (ASTM D 6474, ISO 16014-1/16014-2/16014-4), procedures for sample preparation are not addressed adequately.

One major source of error in HT-SEC is the thermo-oxidative instability of the sample. To dissolve the sample high temperatures, extended dissolution times and sample agitation are required. It is known that polyolefins may degrade under these severe conditions. The dissolution temperature and time depends on the molecular characteristics of the sample (molecular weight, crystallinity, chemical composition, branching). Therefore, quite diverging results can be expected if the sample preparation is not done properly, i.e. when too long dissolution times and too high dissolution temperatures are used.

The existence of several detection methods as well as data handling are also some of major sources of errors in HT GPC. Several calibration methods can be used to obtain data from HT GPC experiments. Below are some of the common ones:

(1) Relative calibration:

PS, PE or PP calibration (retention time or volume vs. logM). This results in PS, PE or PP equivalent molecular weights depending on the calibrants.

(2) Universal calibration but single detector system:

Calibration with PS using Mark Howink constants (retention time or volume vs. logM*intrinsic viscosity (IV)). This results in corrected PE or PP molecular weights if proper Mark Howink constants are used. This is also known as conventional calibration.

(3) Universal calibration multiple detector system

Uses dual detector system (concentration and online viscometer.):
Calibration with PS using concentration and IV (measured), retention time or volume vs. logM*IV

(4) Absolute MW determination by Light Scattering (LS):

Data fitting and calculation procedures need to be specified (e.g. LALS, RALS, DALS or MALS)

In the first phase of the project, six polyolefin samples were selected for analysis. These were distributed to the participants. Participants analysed them using experimental conditions employed in various laboratories. The same samples will be used in the second and third phase.

Statistical evaluations of these results were carried out. The results were standardised using the statistical parameter known as the Z-Score. The Z-score is basically a measure of how far away a measurement is from the mean, measured in standard deviations. It provides a simple

measure by which different measurements from different laboratories can be compared in terms of their deviation from the mean. The following formula is used to measure the Z-score:

- Z-score = (lab average –total average) / total standard deviation

General rules about Z-Scores are as follows:

- A Z-Score outside +/-2.0 should cause a laboratory to review their test data for any possible systematic error.
- Z-scores outside this range should occur only about one time in twenty, if a laboratory has average capability running the method.
- Laboratories should strive to obtain Z-score values close to zero.

The first phase results from almost all the participants have been received. The details of the preliminary analysis of the first round results are outlined in Appendices and a separate Excel spread sheet file. The summary of these results is discussed below.

2. Experimental Conditions

The information gathered from the participants indicate that laboratories around the world employ different experimental conditions from sample preparation, column sets to detection and calculation methods hence the need to standardise, were possible, some of these conditions. Dissolution temperature for sample preparation ranges from 1 to 4 hours whilst columns temperature ranges between 130^{o}C to 160^{o}C. While there are few participants using absolute detection methods such as light scattering, majority of the participants use traditional refractive index method of detection. Besides the option of using either classical polystyrene or polyethylene standards for contracting calibration curve, some participants convert the results obtained from these calibration methods further to the universal calibration using Mark Howink constants.

For better comparison, only four molecular weight properties (Mn, Mw, Mz and PDI) were ultimately used for this study since other participants did not submit the results for Mp and Mz+1. Although it was agreed in the beginning that all participants should repeat the

measurements three times, others only submitted a single value for each of the above mentioned properties. Where participants submitted a single value for a particular property, it was assumed that the value was as a mean of three repeat measurements. Furthermore, no RSD values from those particular laboratories are available. This is also indicated (assignment of either 0 or n/a) in the data table of results (Appendices).

Where a Laboratory has two labels e.g. Lab1A and Lab1B, it indicates that that particular laboratory measured the samples using two different set of conditions.

It is also possible that some participants have been grouped under wrong category unintentionally. For example, a participant using universal calibration grouped under polystyrene may be due to the fact that the experimental condition form was not completed properly. However, this will be corrected before the final release of the report and will be avoided in future.

3. Sample Selection

- The following samples were selected for the study
- LDPE1: Low density polyethylene
- LDPE 2: Low density polyethylene with broad molecular weight distribution
- LLDPE C4: Linear low density polyethylene with 1-butene as a comonomer
- LLDPE C6: Linear low density polyethylene with 1-hexene as a comonomer
- PP: Polypropylene homopolymer
- PP/PE: Impact propylene-ethylene copolymer

4. Results and Discussion

4.1 General Trends

There is a very good spread between the number participants using Polystyrene and Universal Calibration methods i.e. the number of participants using Polystyrene calibration is very similar to those using Universal. Very few participants are using Polyethylene or Light Scattering calibration or detection methods.

The average (mean) values of all the molecular weight properties (Mn, Mw and Mz), with the exception of PDI, from participants using polystyrene calibration method, were generally higher than those using Universal and Polyethylene calibration methods.

There is a fair agreement on average molecular weight values of Mn, Mw, Mz and PDI amongst the participants using Universal calibration especially on samples LLDPE C_4 an LLDPE C_6 while those using Polystyrene calibration method are generally far apart from each other.

No meaningful comparison could be made about participants using either Polyethylene and Light Scattering since only two participants per category are using these methods. However, in most cases their molecular weight average values were closer to those using Universal calibration.

The average RSD values (for intra-laboratory comparison) are low in all the calibrations methods used meaning that the reproducibility within laboratories is good. However, within a particular calibration method, the overall RSD (for inter-laboratory comparison) is very high, again confirming that the measured average values are far apart from each other in most cases.

In general, the PDI values were very similar regardless of the calibration or detection method used. This is probably due to the fact that PDI values are ratio between Mw and Mn.

4.2 Laboratory Trends

Some consistent bias was noticed, e.g. within Polystyrene calibration, Labs 3, 11, and 13 tended to be on the higher side while and Lab 5 and 12 tended to be on the lower side of the mean value compared to other participants. As a result, there are few instances were the Z-cores of Labs 11 and 12 were equal or higher than 2. Any Z-score less than 2 is acceptable while a Z-score above 2 should raise some concern. It is suspected that Lab 5 may have been grouped under polystyrene incorrectly and should in fact belong to universal calibration. If this is the case then the statistics for this participant should improve significantly. The participant will be contacted to confirm this before the final release of the report.

There is no obvious bias on average molecular weight values amongst participants using universal calibration although the results from Lab 3 tended to be on the higher side in most instances while Lab 14 tended to be on the lower side. The Z-scores in this category of calibration are fairly acceptable.

5. Conclusions

The inter-lab RSD values indicated a wider spread as seen in data tables (Appendices). This means that for the same sample measured and evaluated using same method of calibration statistically different results from different laboratories were obtained. The higher inter-laboratory variations are a concern and need to be addressed within a particular calibration method.

At this stage it is difficult to conclude which variable (e.g sample preparation, detection method, etc) is responsible for the differences observed.

Phases two and three of the project will help in explaining were these variations are coming from.

6. Future Work

- Results will be communicated to the participants soon and some of the questions arising from the results submitted will be forwarded to the participants and cleared before the final report of the first phase is published. Also a discussion forum will be opened via e-mail for participants to make inputs on the results already submitted while other phases of the project will be going on.
- Second phase will commence soon and will involve standardisation of sample dissolution time and temperature as well as column temperature
- Since the results are also analyst dependant with regard to integration method, an attempt should be made to standardise the manner in which chromatograms are integrated. For example, a low Mw limit could be defined (e.g. no integration below 500 g/mol).
- The results and the recommendations following the completion of the project will be communicated in various scientific forums in the form of posters, oral presentations or publications in international peer review journals.
- Using experimental conditions applied in the first phase of the project, participants using Universal calibrations will be asked to swap Polystyrene or vice versa. K and alpha could be defined for a specific column temperature. Then PS relative (type a) and PS conventional (type b) could be converted into each other using the Mark Houwink equation.

7. Acknowledgements

I would like to thank Dr Christian Piel, Prof. Harald Pasch and Prof Taihyun Chang for their invaluable inputs and guidance.

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	Basell Polyolefine, Germany		Dr. Dieter Lilge	Dieter.Lilge@lyondellbasell.com

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	Prof. Taihyun Chang	**Pohang University, Korea**
	Nyambeni Luruli	**Sasol Polymers**

Selected Experimental Conditions

Company	Instr.	No. of Col.	Type of Col.	Col. Temp	Sample prep Temp (oC)	Sample prep Time (h)	Conc. (g/ml)	Shake	Method
Sasol	Waters 2000	4	HT1, 2, 3, 4	145	150	3	1	Y	PS
Institut fur Chemie der Kunststoffe (ICK)	PL220	2	Mixed bed	135	160	2	1.6 - 2.1	Y	PS
Nomer Inovation_AS	Waters 2000	3	Mixed bed	140	140(3) 160(1)	4	0.33 - 0.8	Y	PS
Polymer Standards Service (PSS), Germany	Waters 150	4 + 1 prec	A2, 3, 5, 6	150	160	1	2 - 7	Y	PS & Univ
Dow Chemical Company	Waters 150	4	Mixed bed	150	160	4	2	Y	PS
Polymer Laboratories	PL220	3	Mixed bed	160	160	4	2	Y	PS/LS
Basell Polyolefins	Waters 150	4	Mixed bed	150	140	2	6	Y	Univ
Korea Petrochemical Ind	Waters 2000	2	Mixed bed	150	160	3	1	Y	PS&PE
DSM Resolve	PL210	2	Mixed bed	160	150	4	1.5	Y	LS
DKI	PL 220	4	HT1, 2, 3, 4	150	160	4-5	0.7	no	PS

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Appendix 1: Graphical representation of the molecular weight values from different laboratories

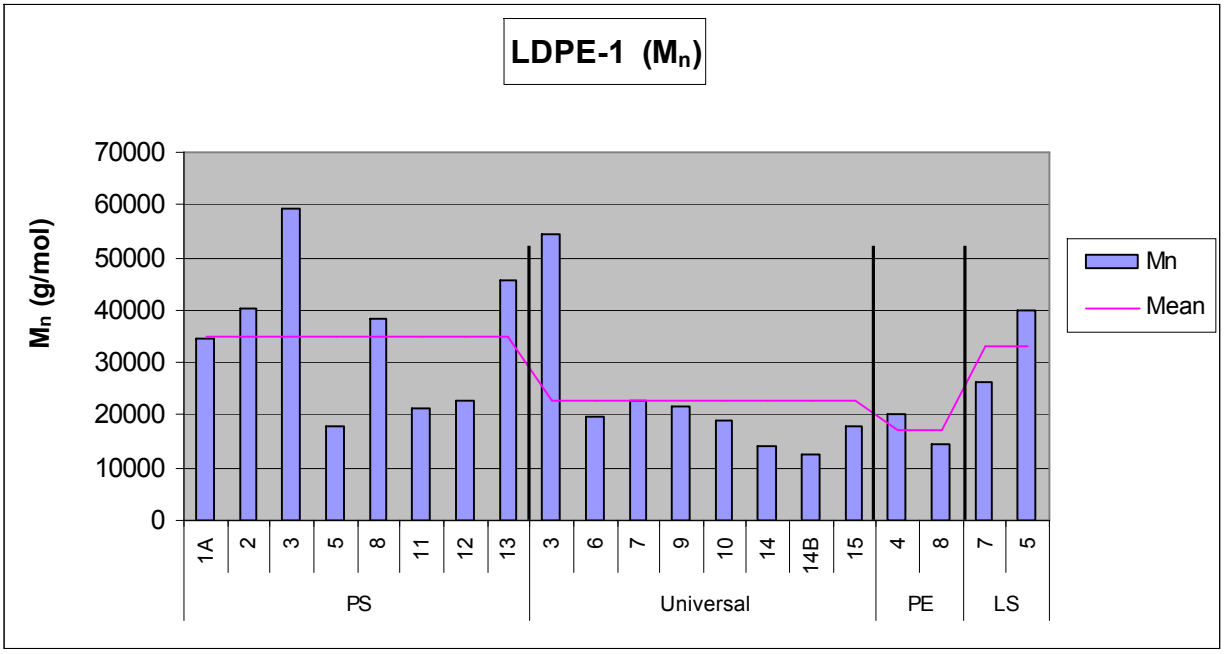

Figure 1: M_n average values for LDPE-1 from different laboratories

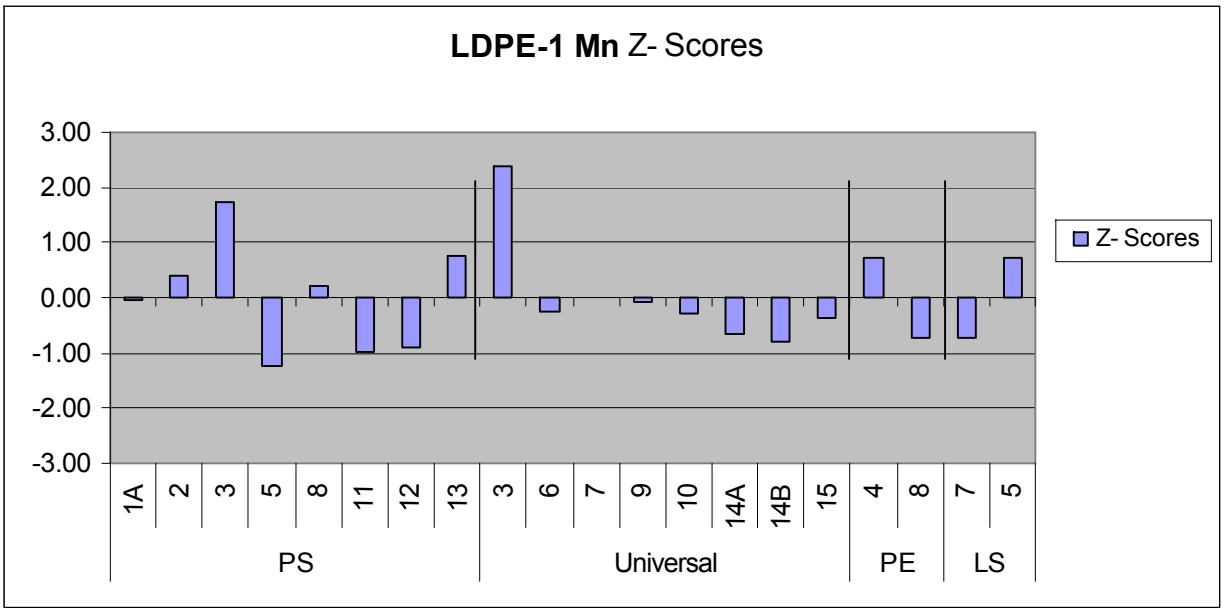

Figure 2: Z scores associated with M_n average values for LDPE-1 from different laboratories

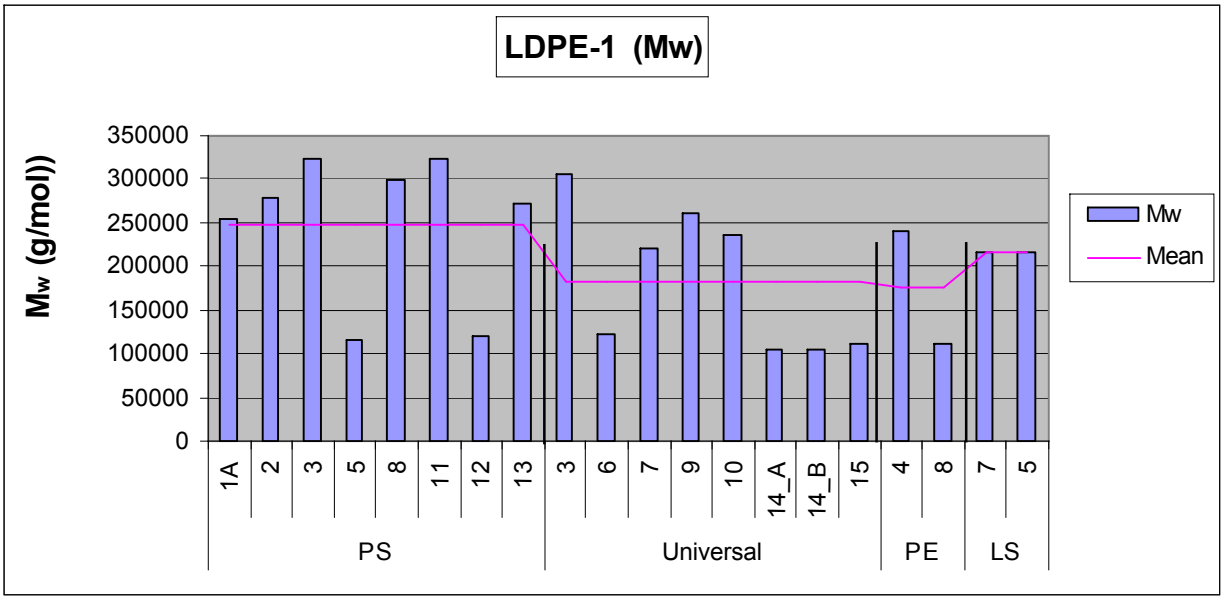

Figure 3: M_w average values for LDPE-1 from different laboratories

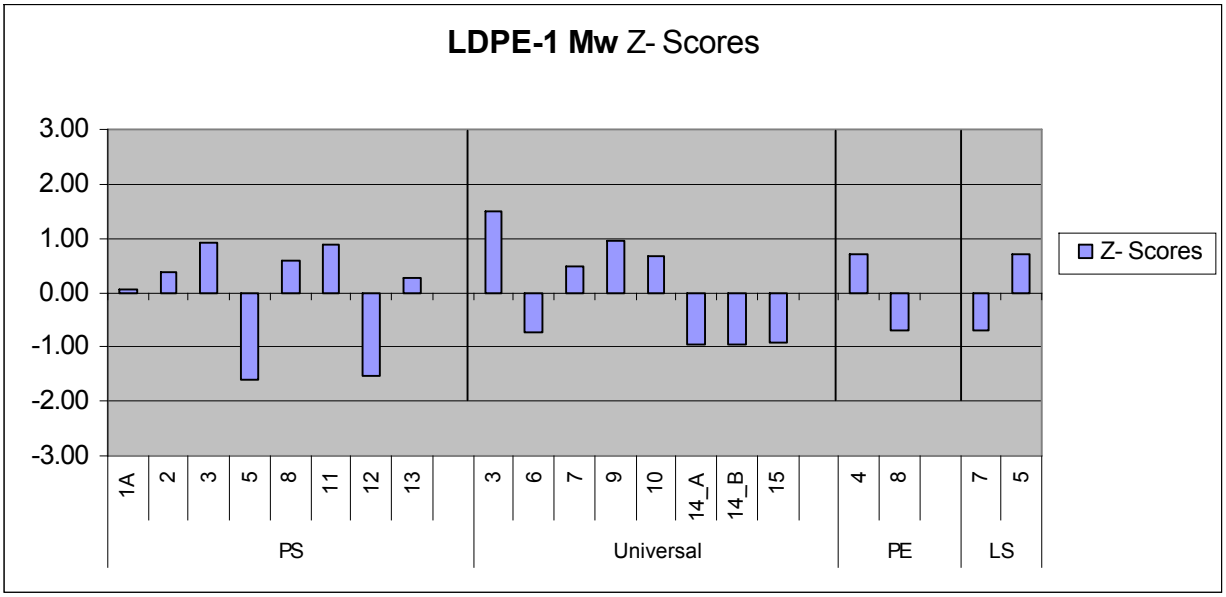

Figure 4: Z scores associated with M_w average values for LDPE-1 from different laboratories

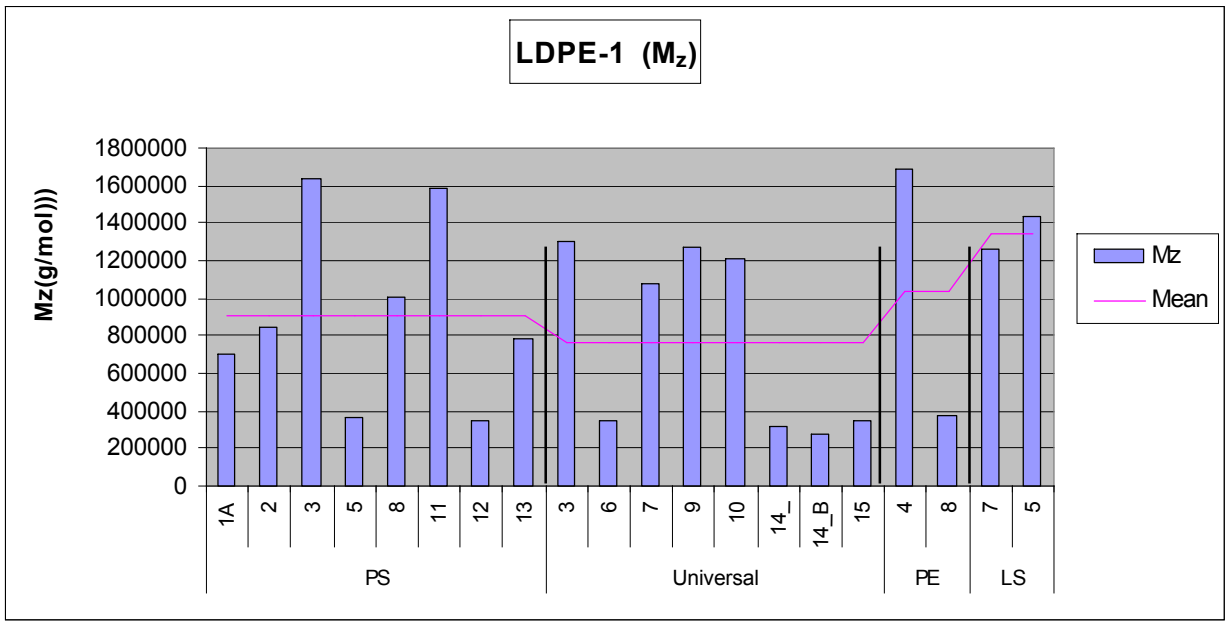

Figure 5: M_z average values for LDPE-1 from different laboratories

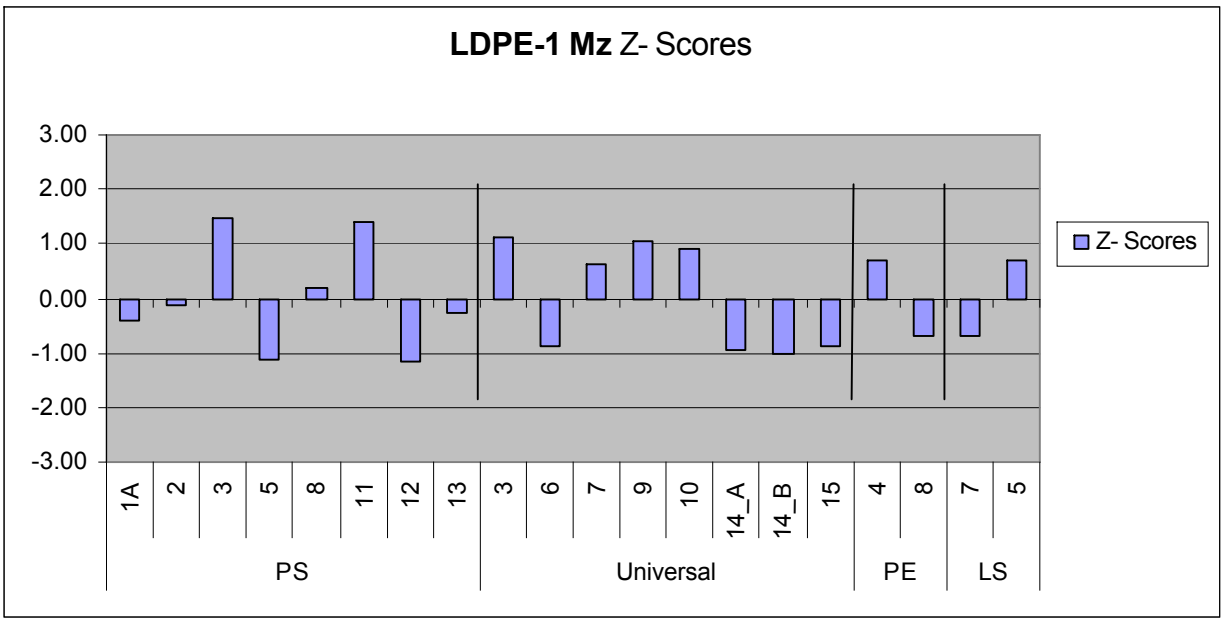

Figure 6: Z scores associated with M_z average values for LDPE-1 from different laboratories

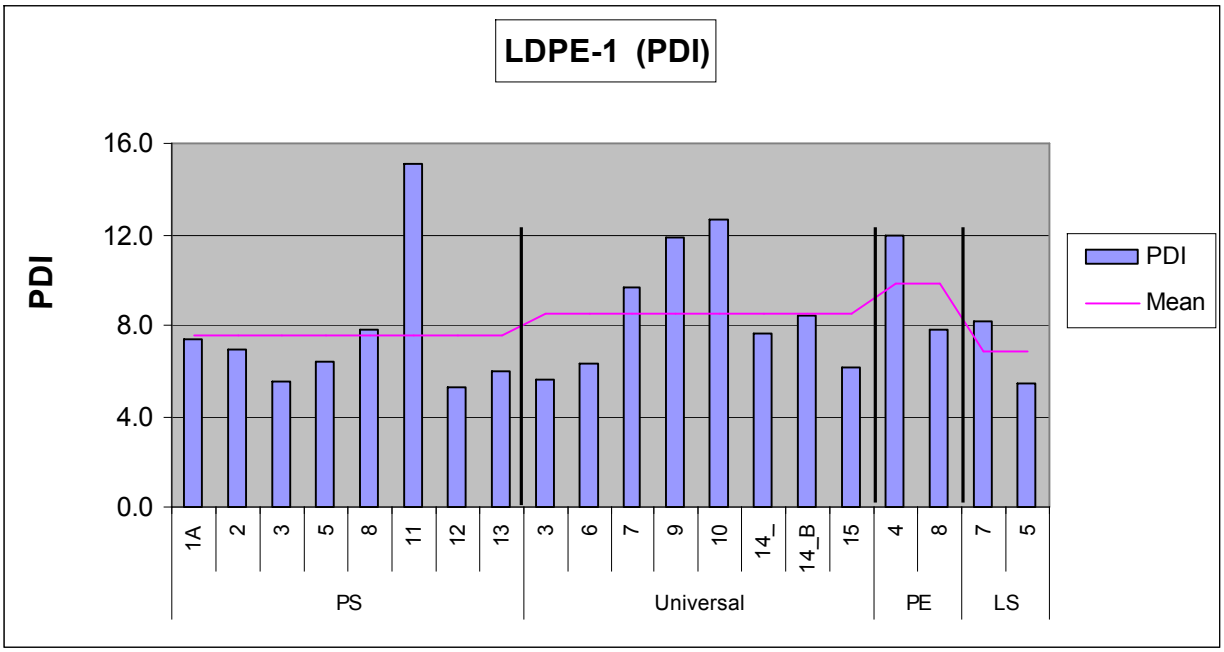

Figure 7: Polydispersity average values for LDPE-1 from different laboratories

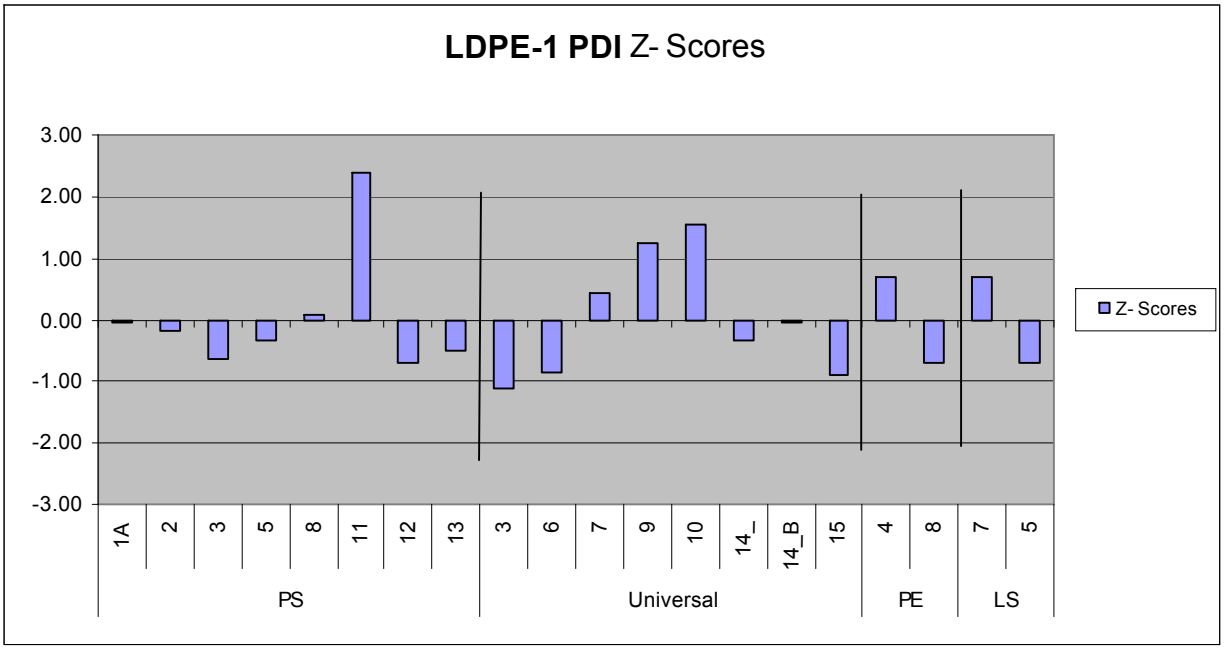

Figure 8: Z scores associated with Polydispersity average values for LDPE-1 from different laboratories

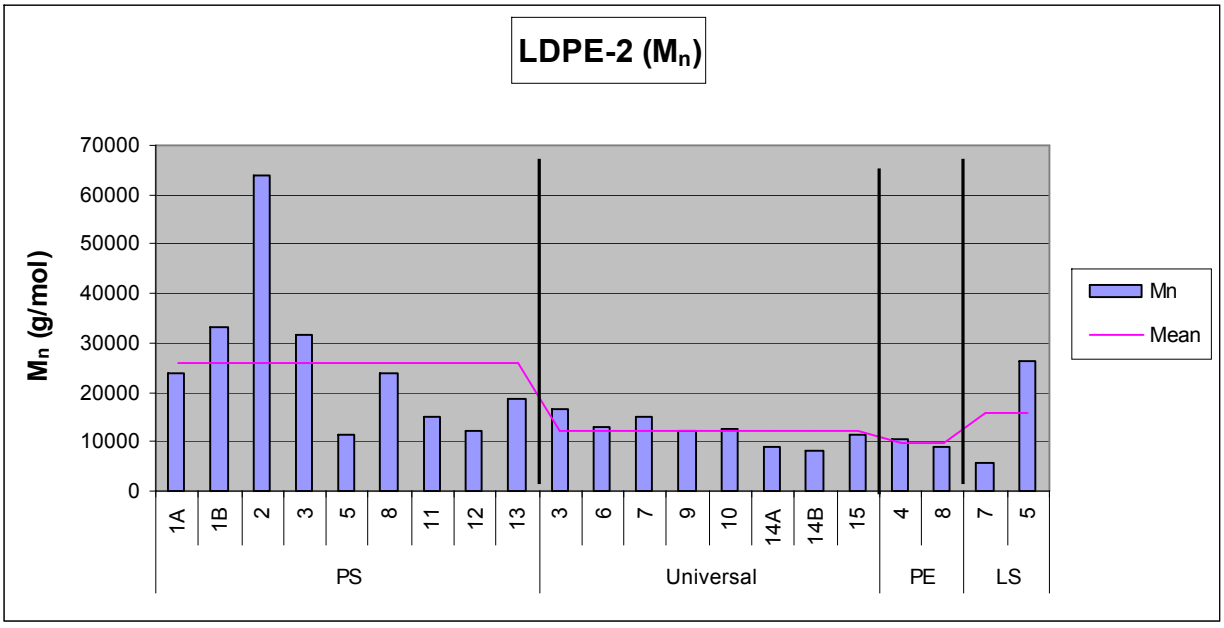

Figure 9: M_n average values for LDPE-2 from different laboratories

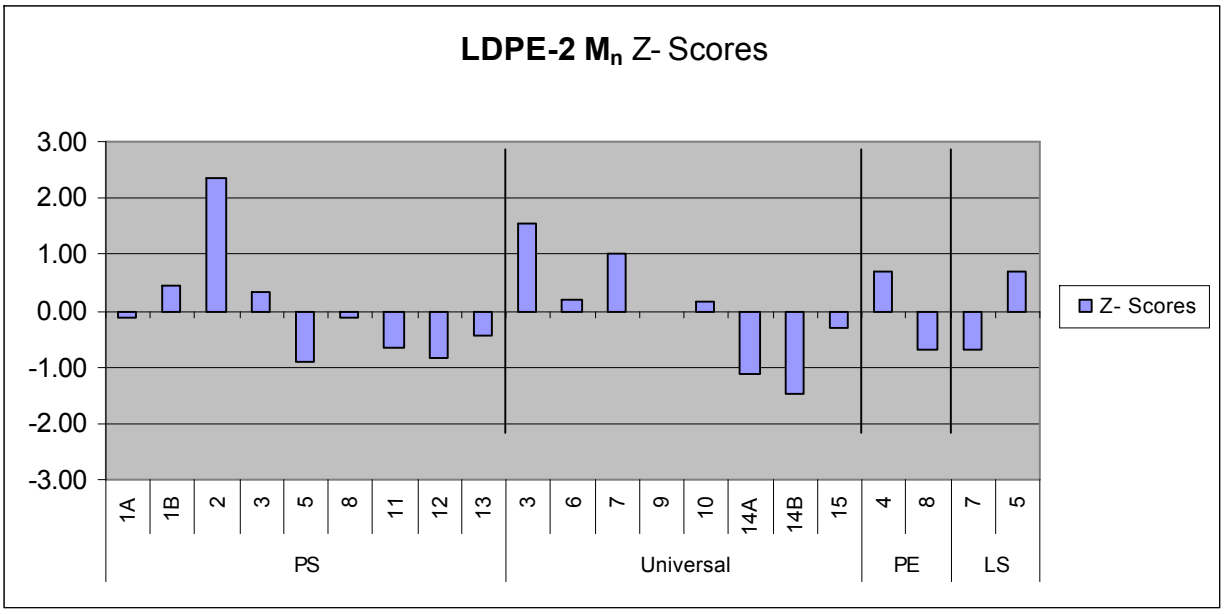

Figure 10: Z scores associated with M_n average values for LDPE-2 from different laboratories

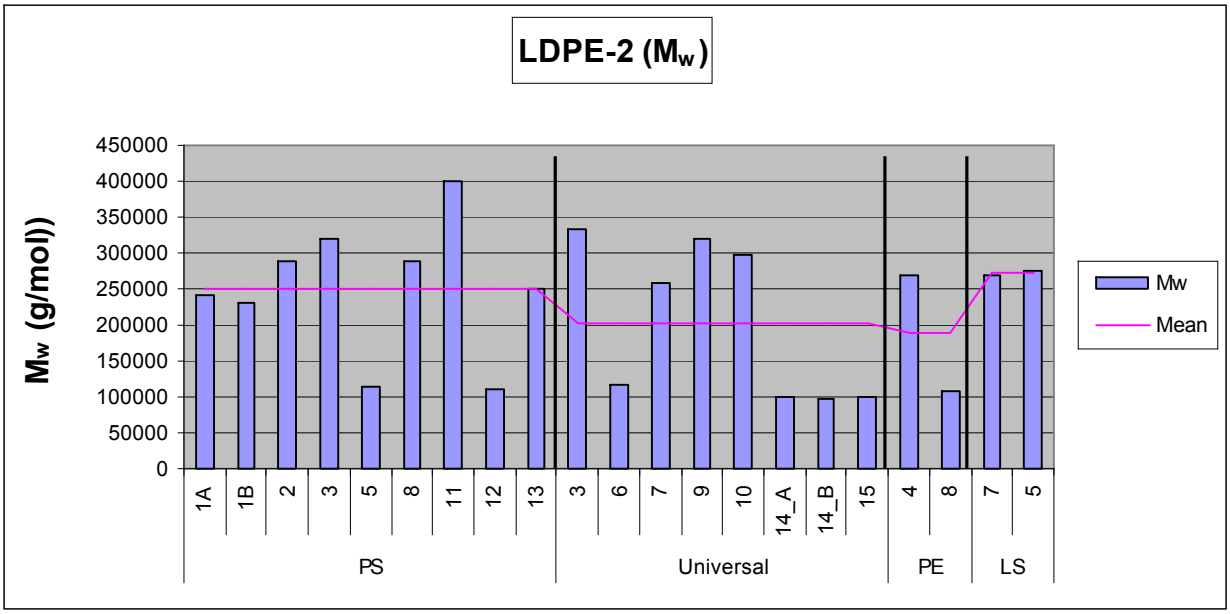

Figure 11: M_w average values for LDPE-2 from different laboratories

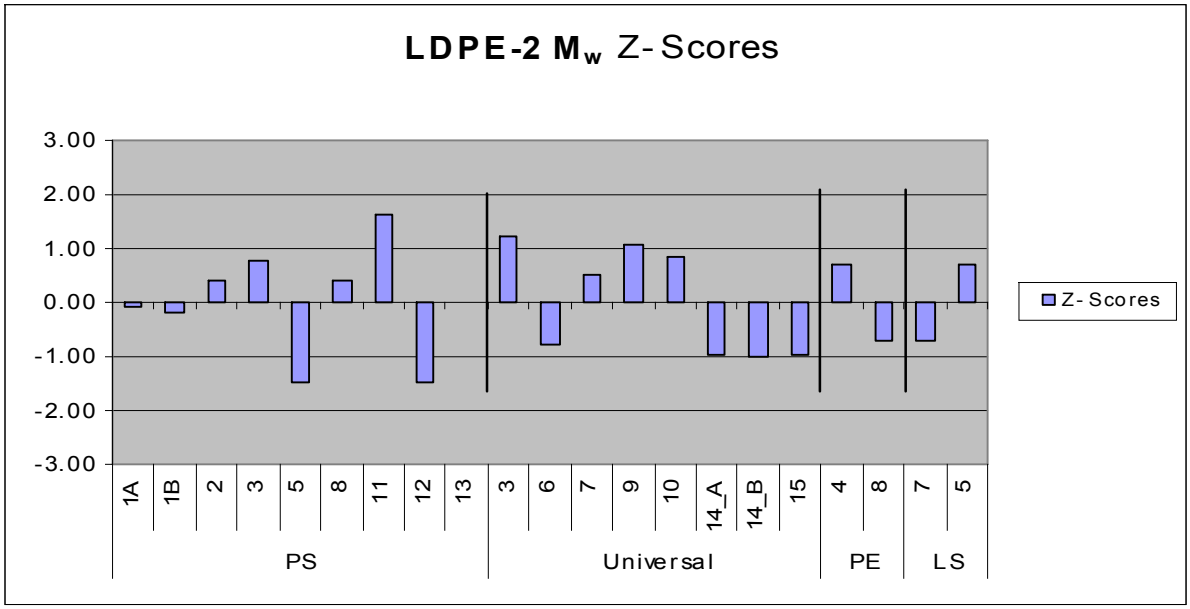

Figure 12: Z scores associated with M_w average values for LDPE-2 from different laboratories

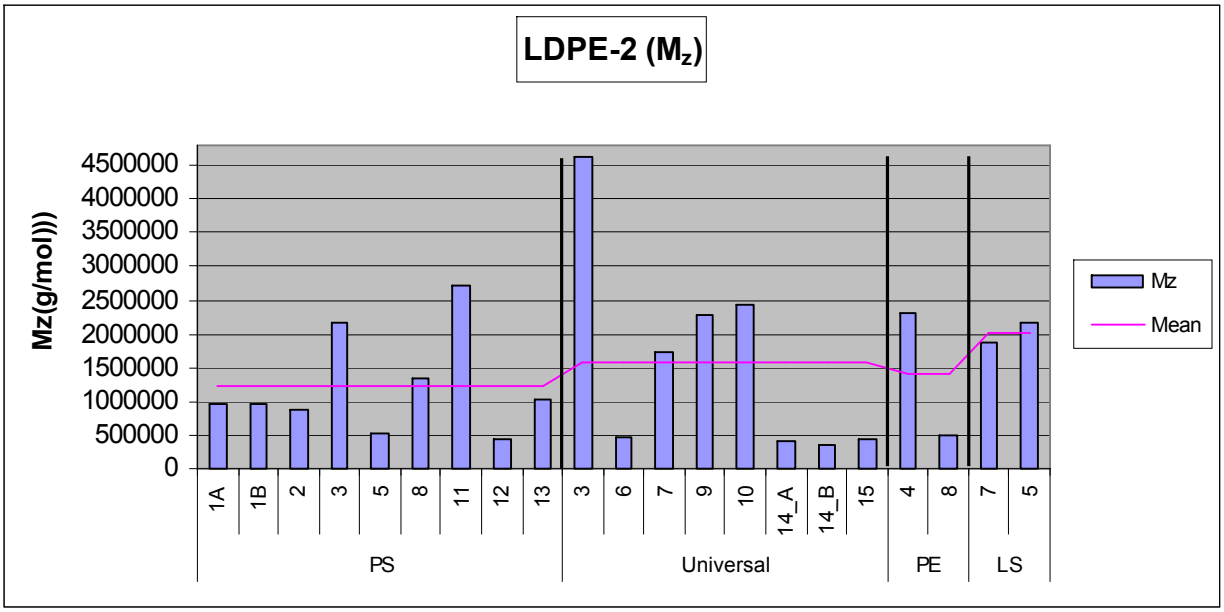

Figure 13: M_z average values for LDPE-2 from different laboratories

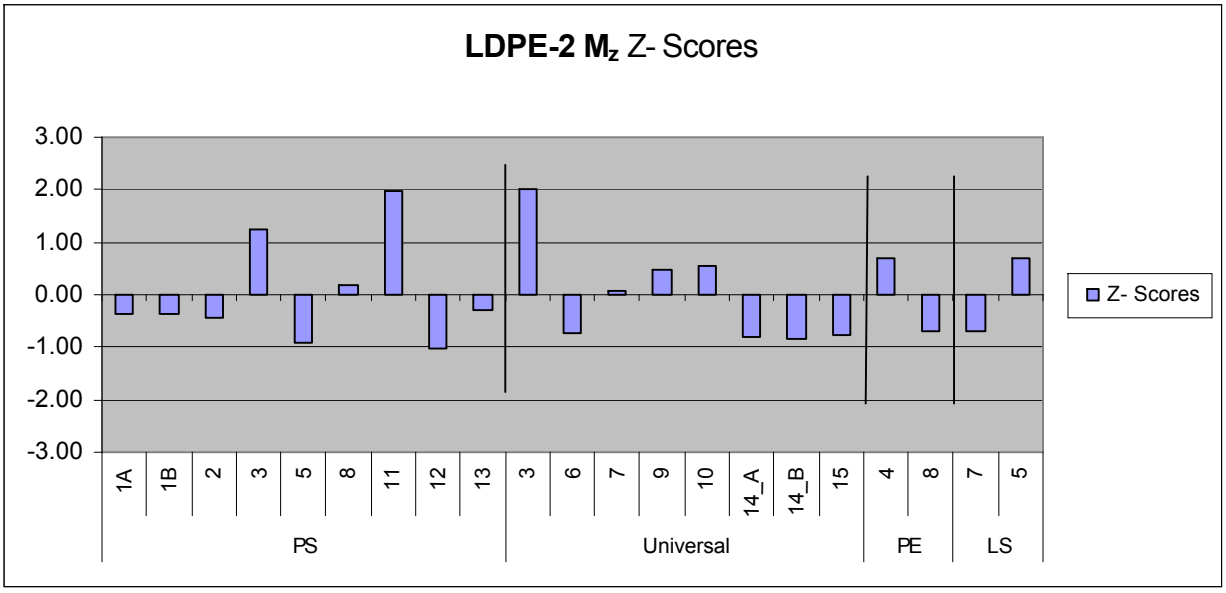

Figure 14: Z scores associated with M_z average values for LDPE-2 from different laboratories

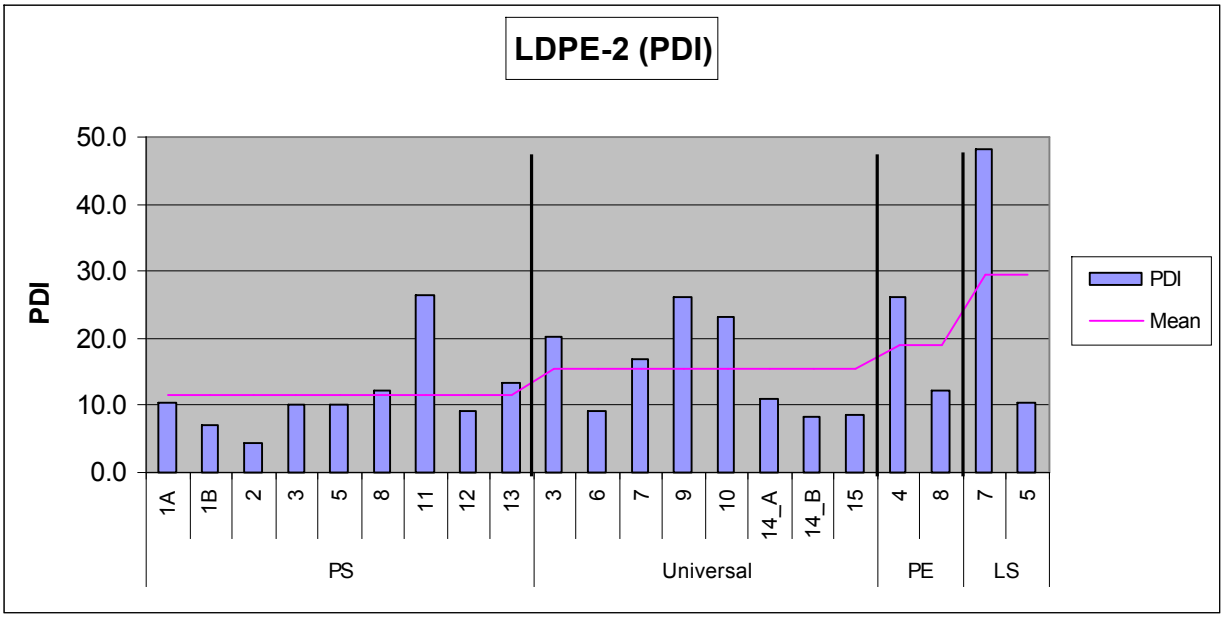

Figure 15: Polydispersity average values for LDPE-2 from different laboratories

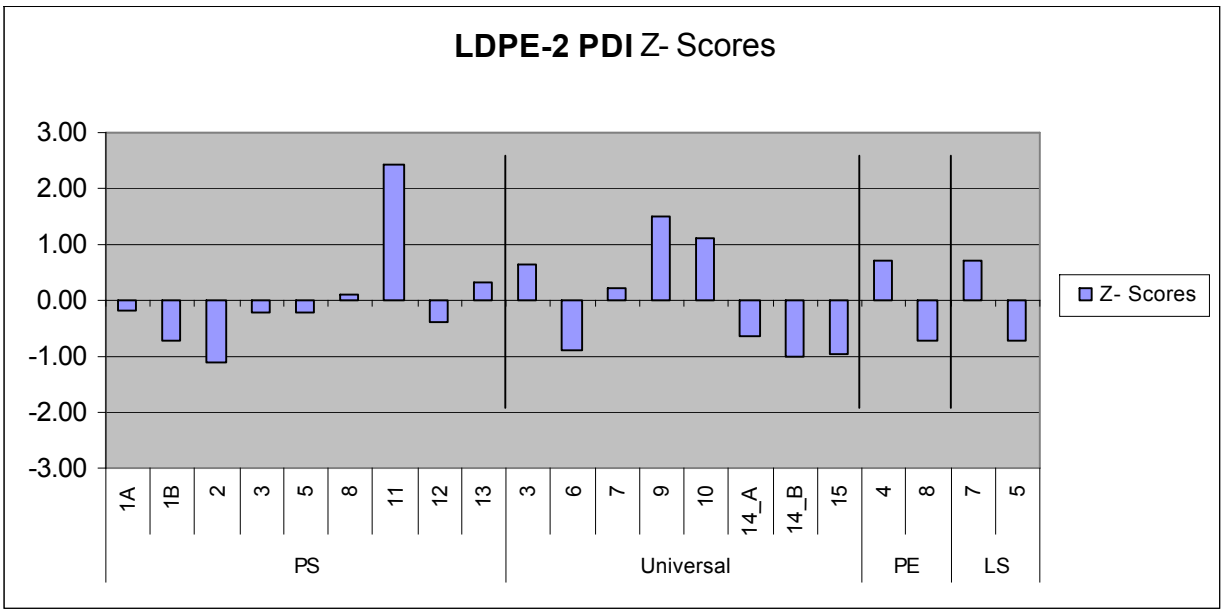

Figure 16: Z scores associated with Polydispersity average values for LDPE-2from different

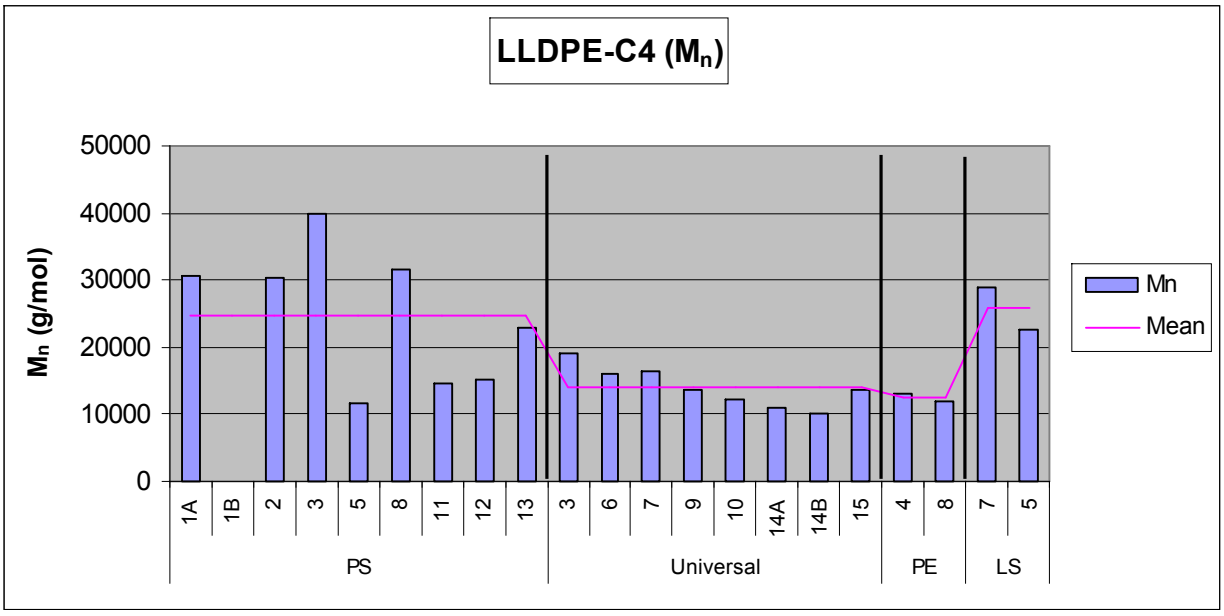

Figure 17: M_n average values for LLDPE-C4 from different laboratories

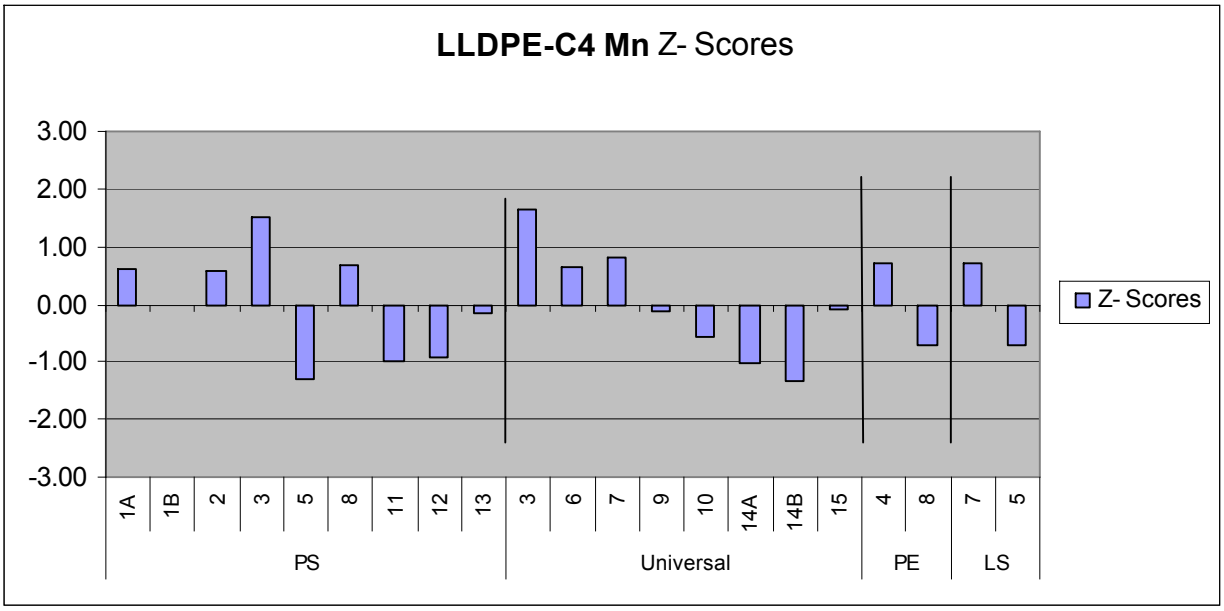

Figure 18: Z scores associated with M_n average values for LLPE-C4 from different laboratories

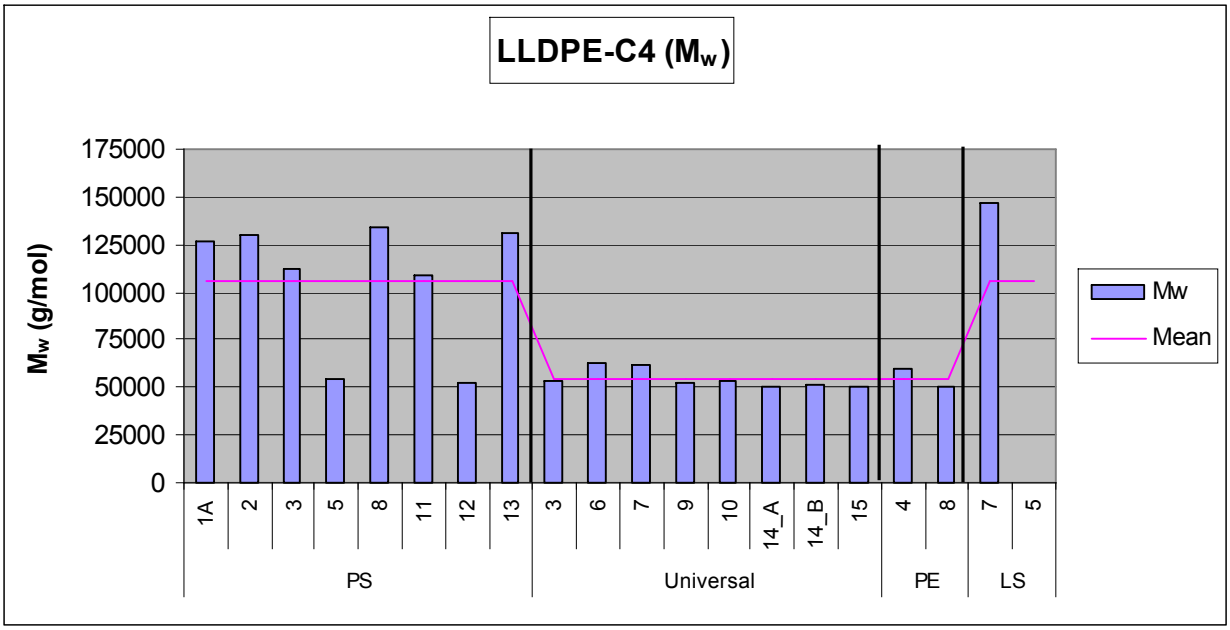

Figure 19: M_w average values for LLPE-C4 from different laboratories

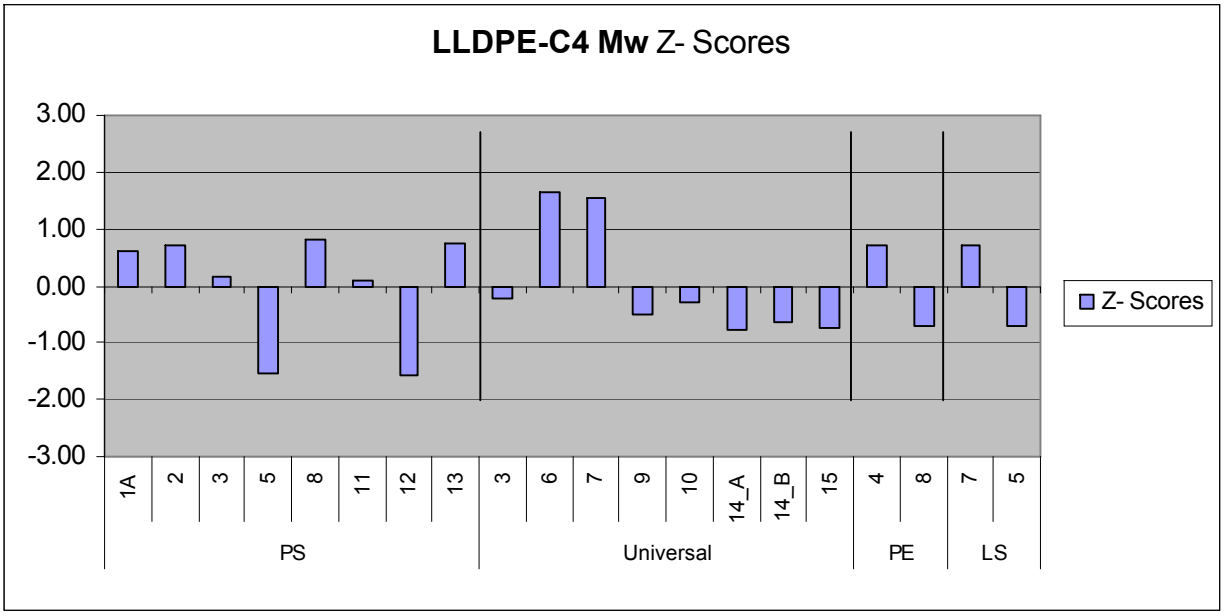

Figure 20: Z scores associated with M_w average values for LLPE-C4 from different laboratories

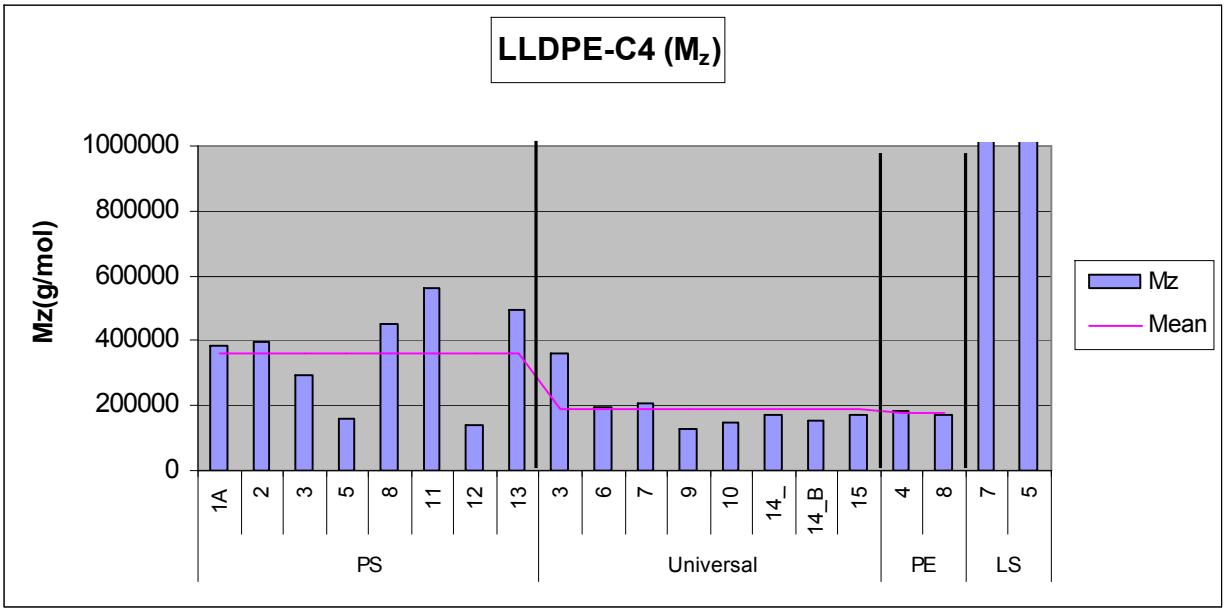

Figure 21: M_z average values for LLDPE-C4 from different laboratories

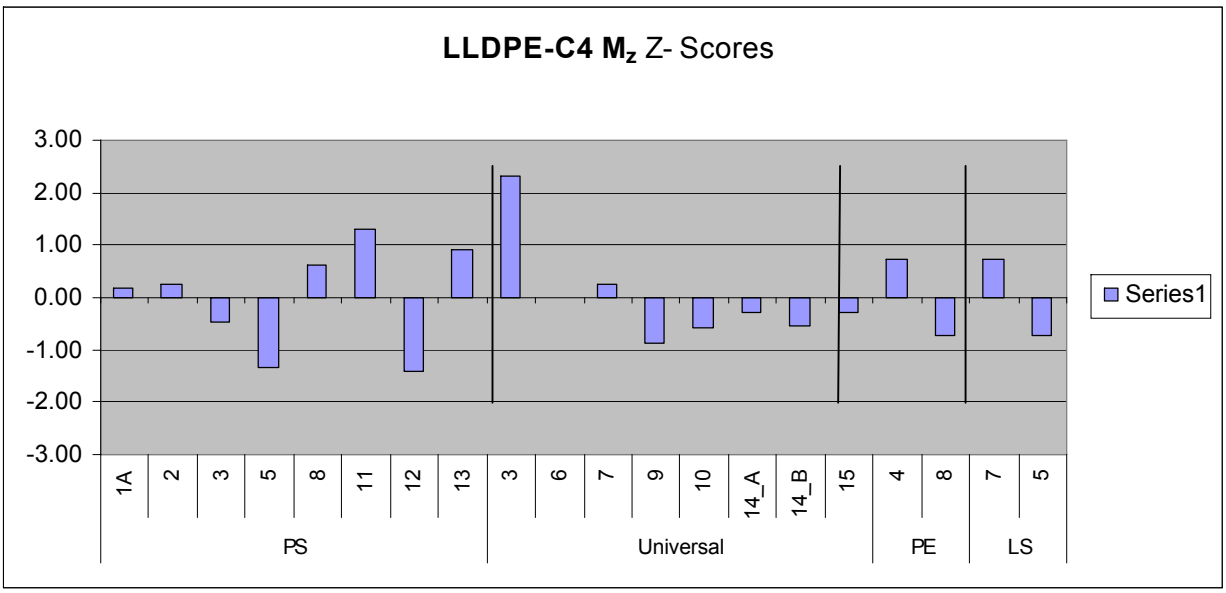

Figure 22: Z scores associated with M_z average values for LLDPE-C4 from different laboratories

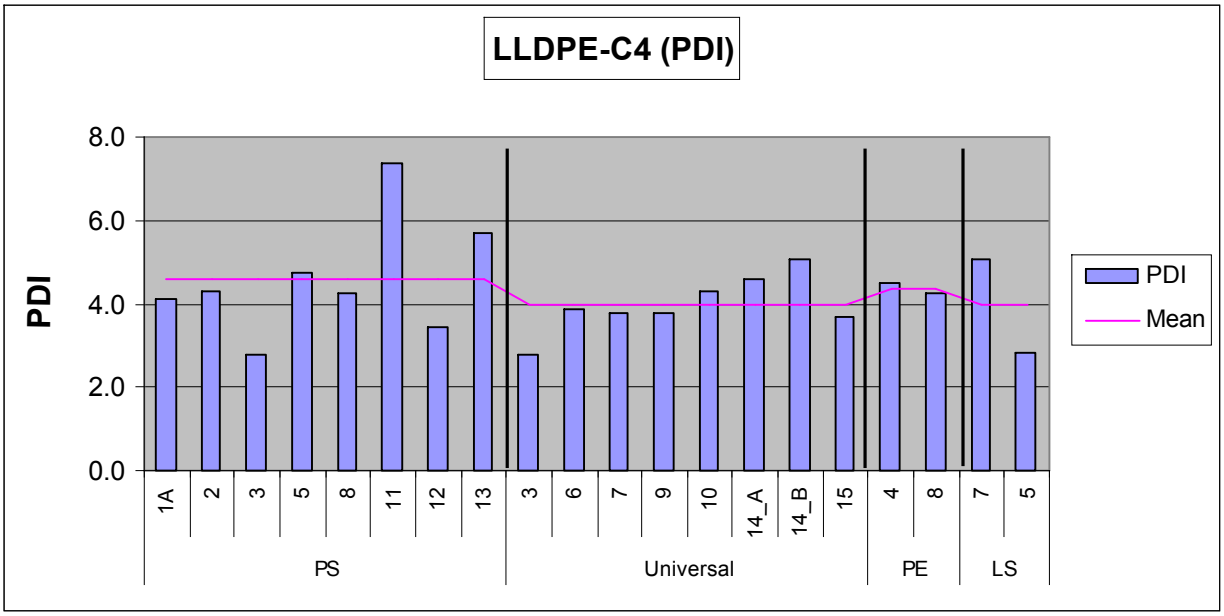

Figure 23: Polydispersity average values for LLDPE-C4 from different laboratories

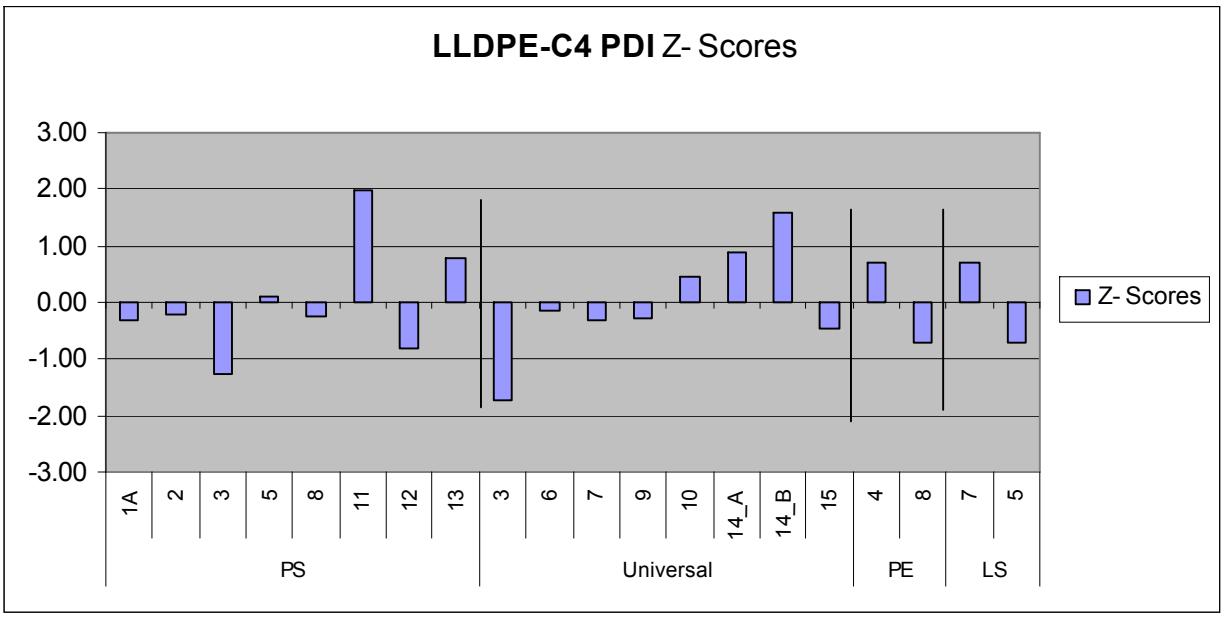

Figure 24: Z scores associated with Polydispersity average values for LLDPE-C4 from different

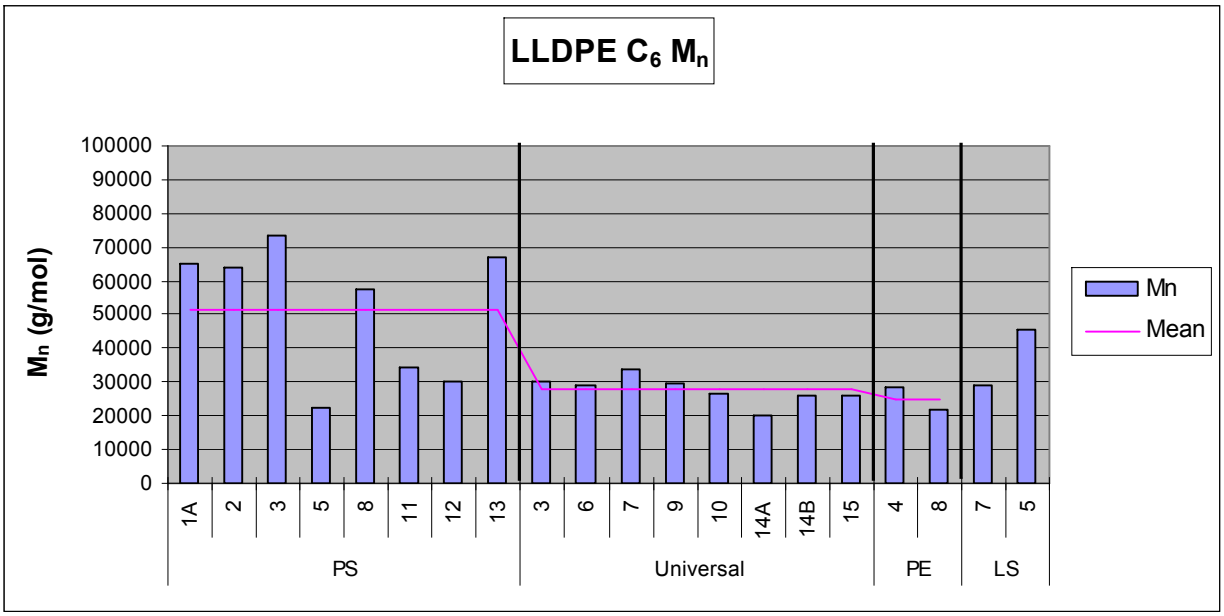

Figure 25: M_n average values for LLDPE-C6 from different laboratories

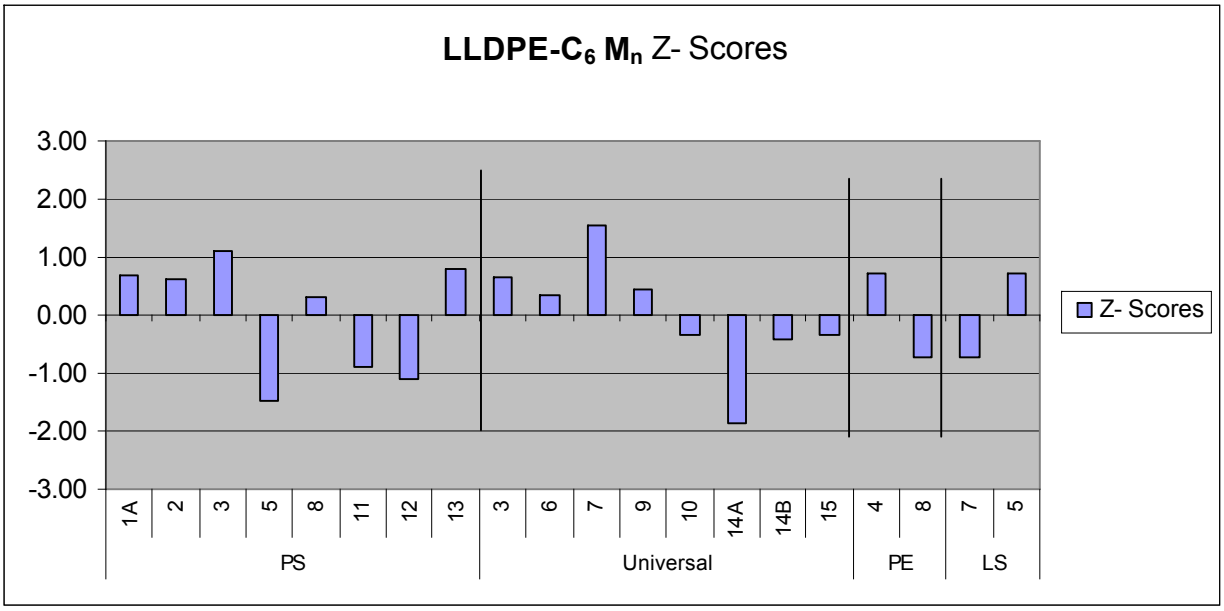

Figure 26: Z scores associated with M_n average values for LLDPE-C6 from different laboratories

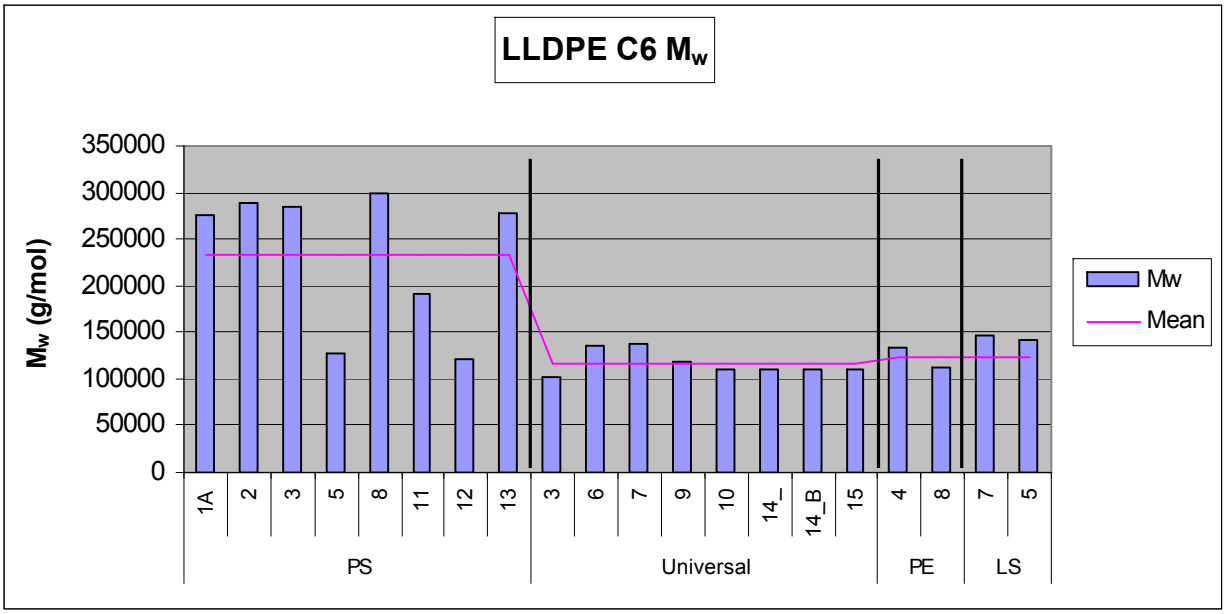

Figure 27: M_w average values for LLDPE-C6 from different laboratories

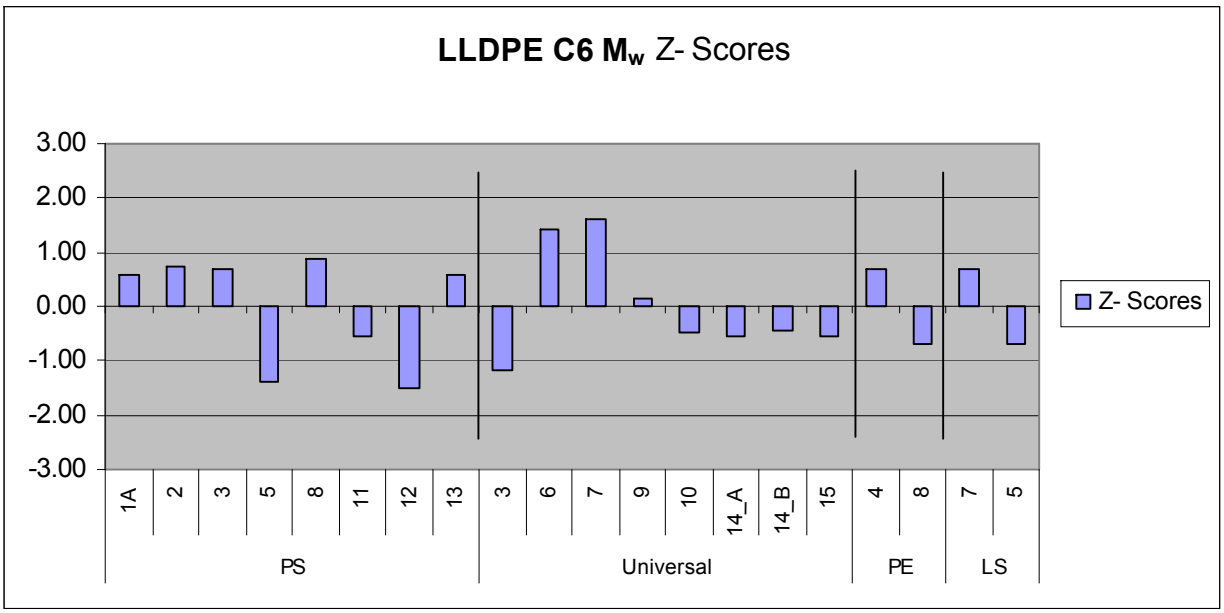

Figure 28: Z scores associated with M_w average values for LLDPE-C6 from different laboratories

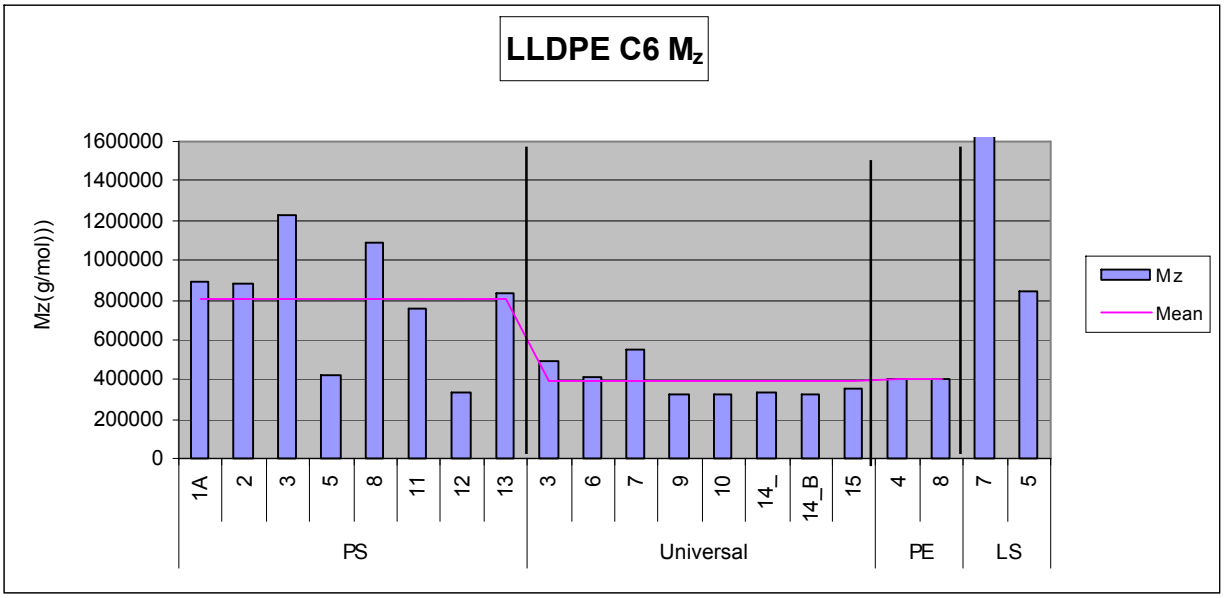

Figure 29: M_z average values for LLDPE-C6 from different laboratories

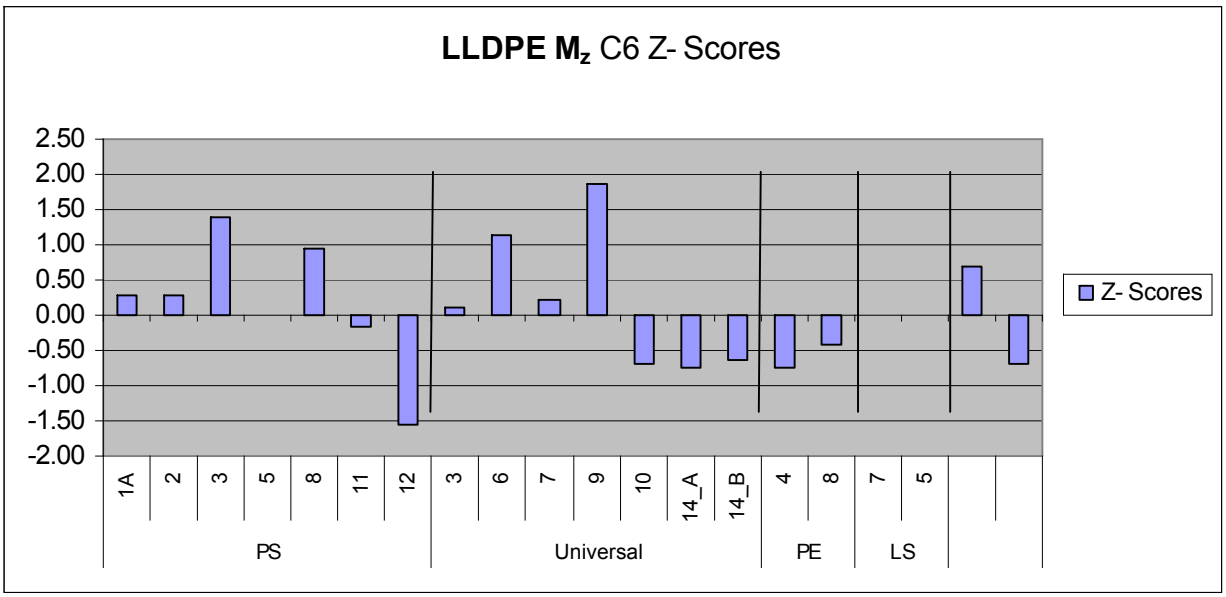

Figure 30: Z scores associated with M_z average values for LLDPE-C6 from different laboratories

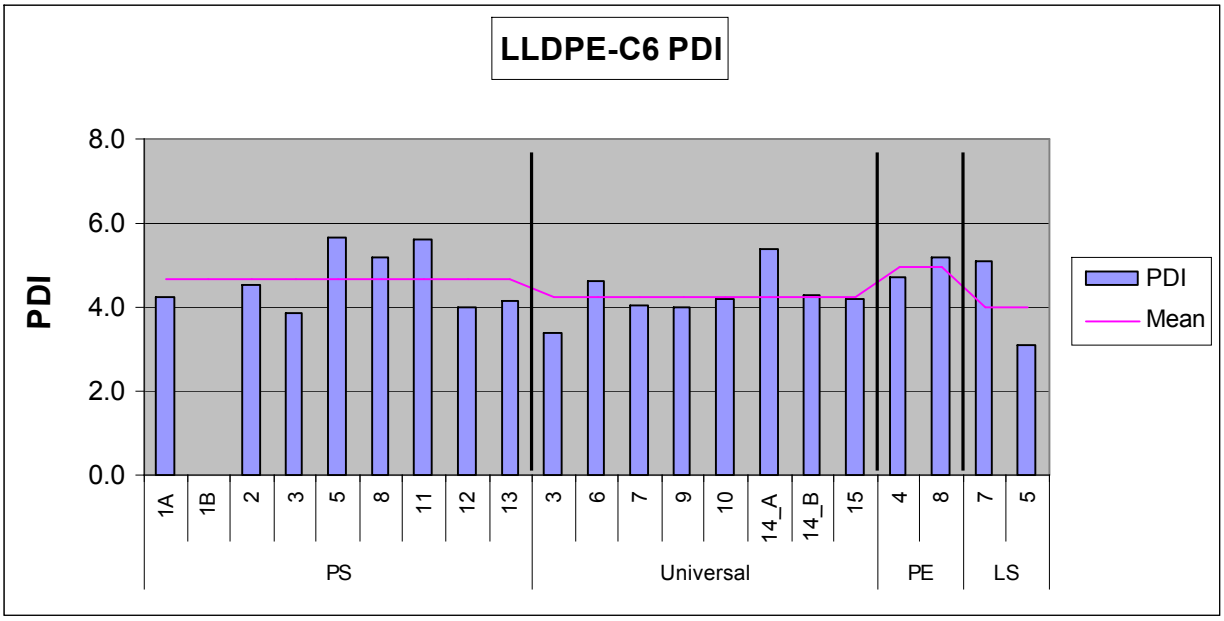

Figure 31: Polydispersity average values for LLDPE-C6 from different laboratories

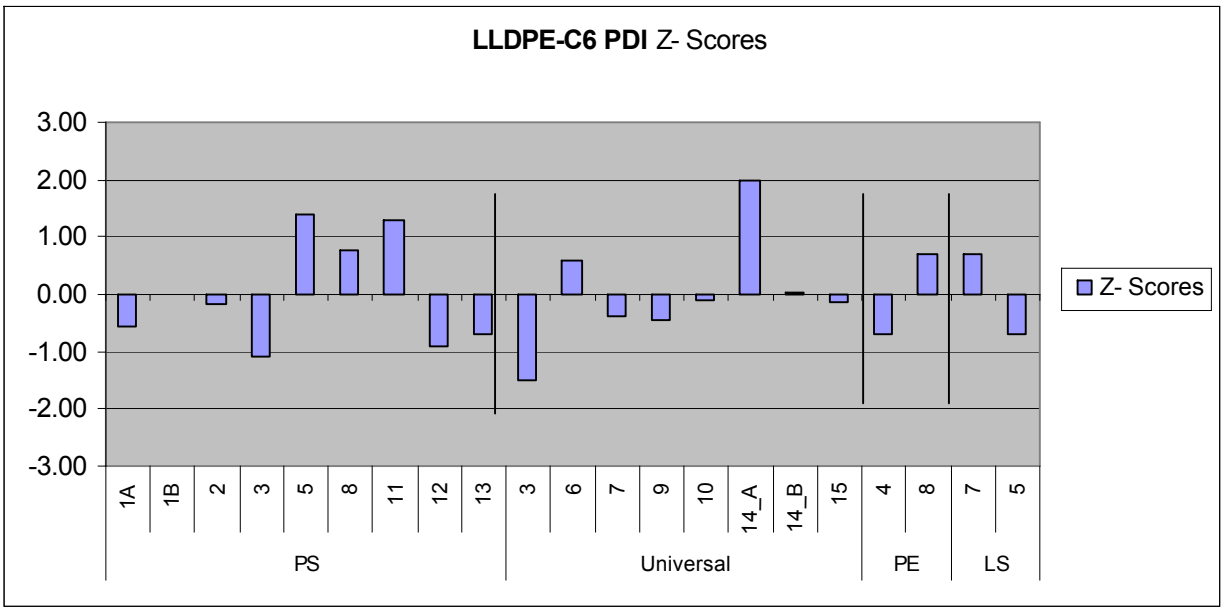

Figure 32: Z scores associated with Polydispersity average values for LLDPE-C6 from different

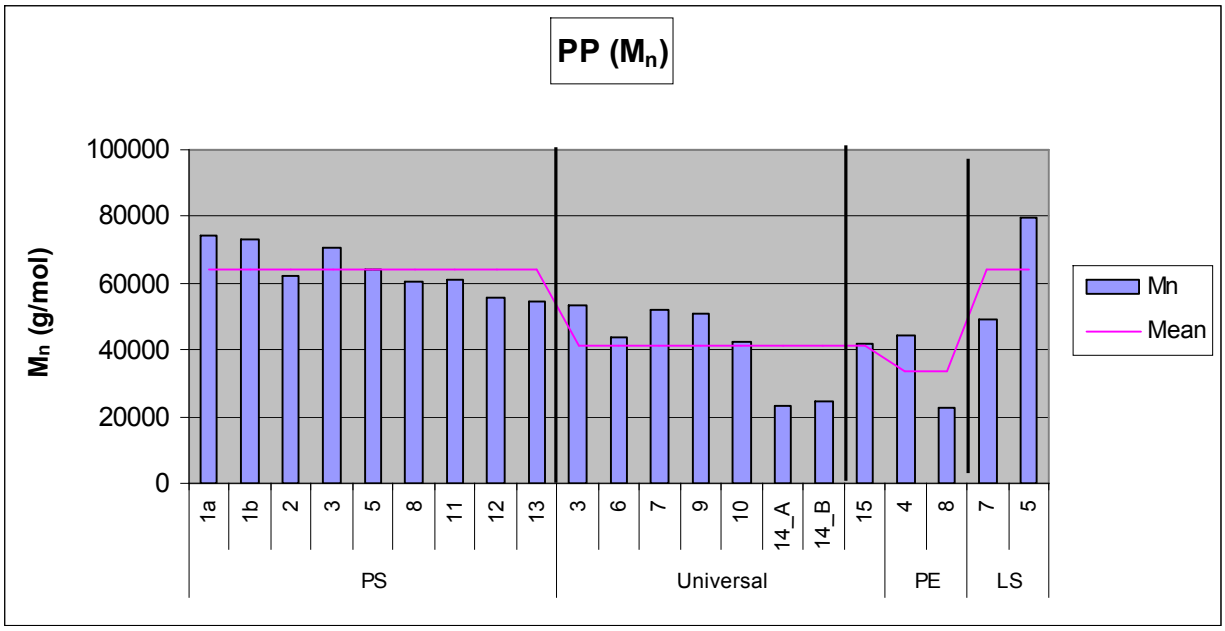

Figure 33: M_n average values for Polypropylene from different laboratories

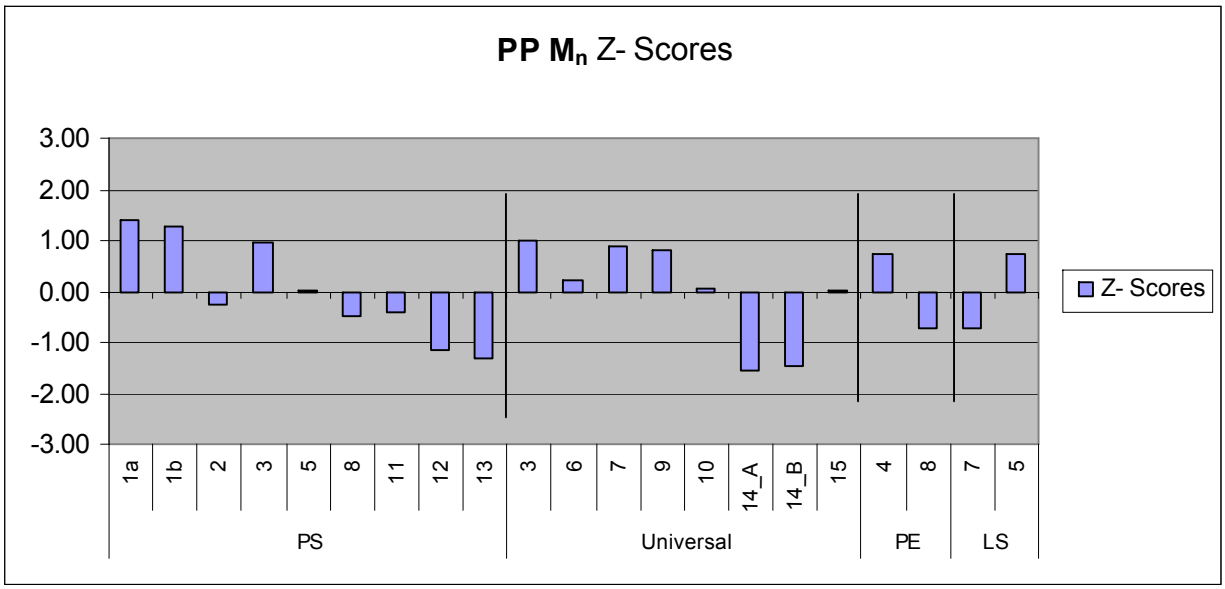

Figure 34: Z scores associated with M_n average values for Polypropylene from different laboratories

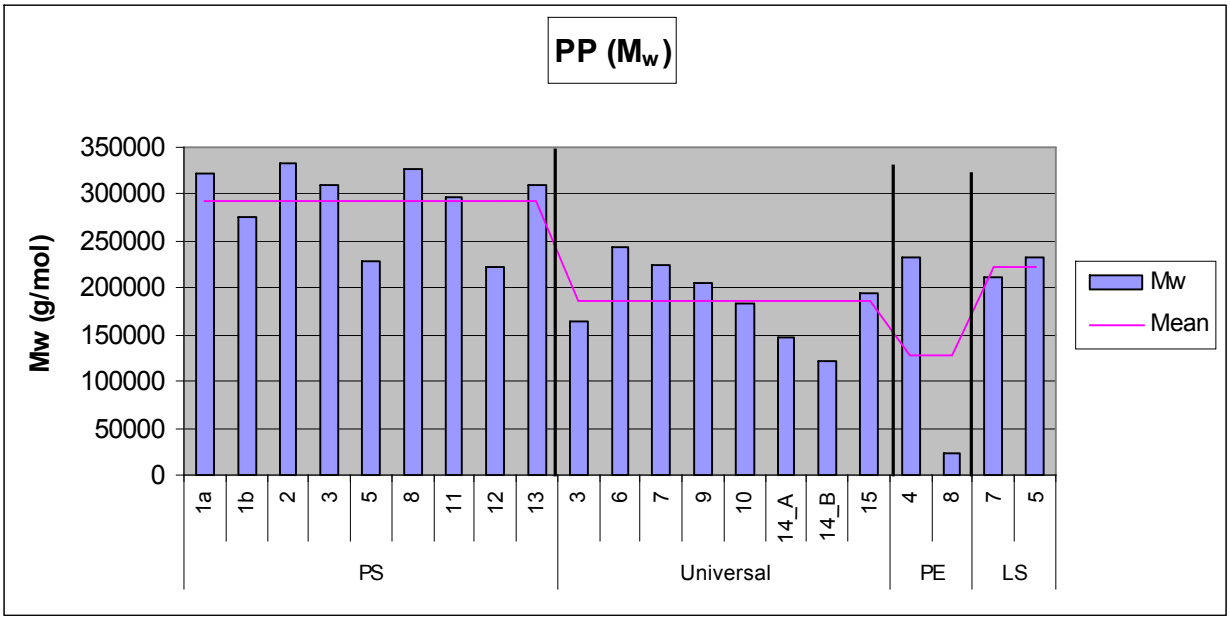

Figure 35: M_w average values for Polypropylene from different laboratories

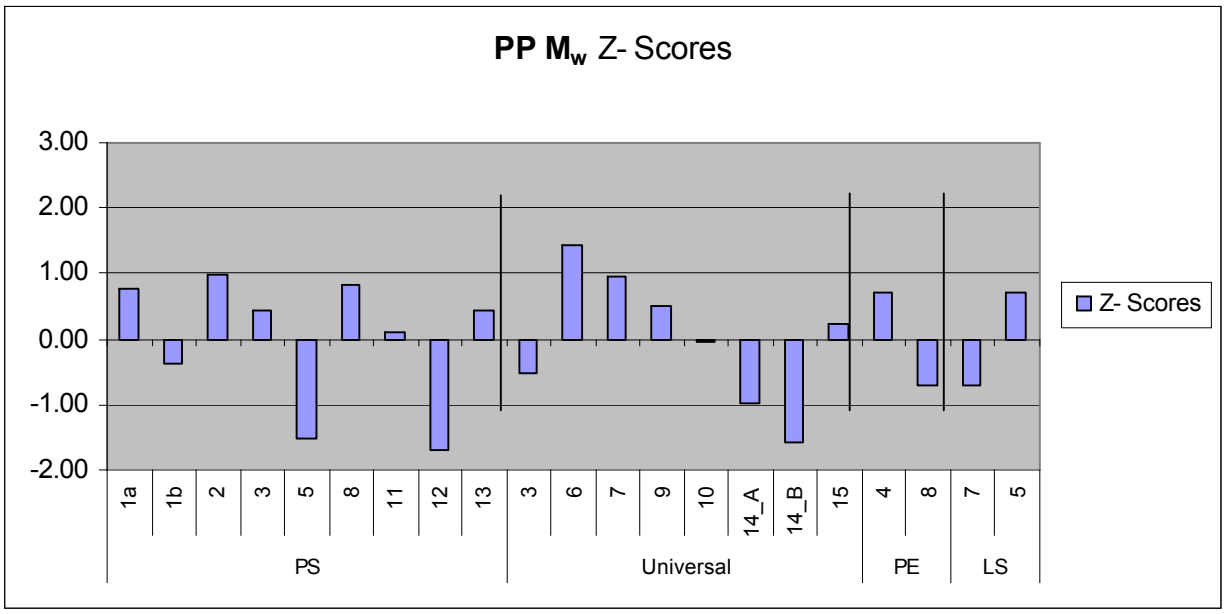

Figure 36: Z scores associated with M_w average values for Polypropylene from different laboratories

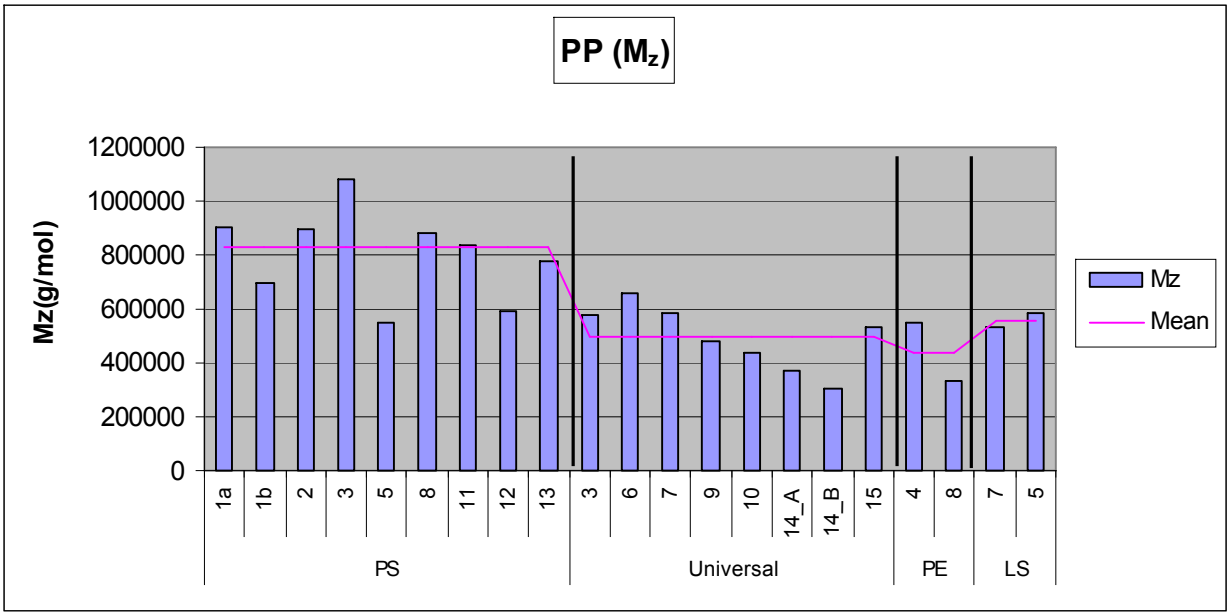

Figure 37: M_z average values for Polypropylene from different laboratories

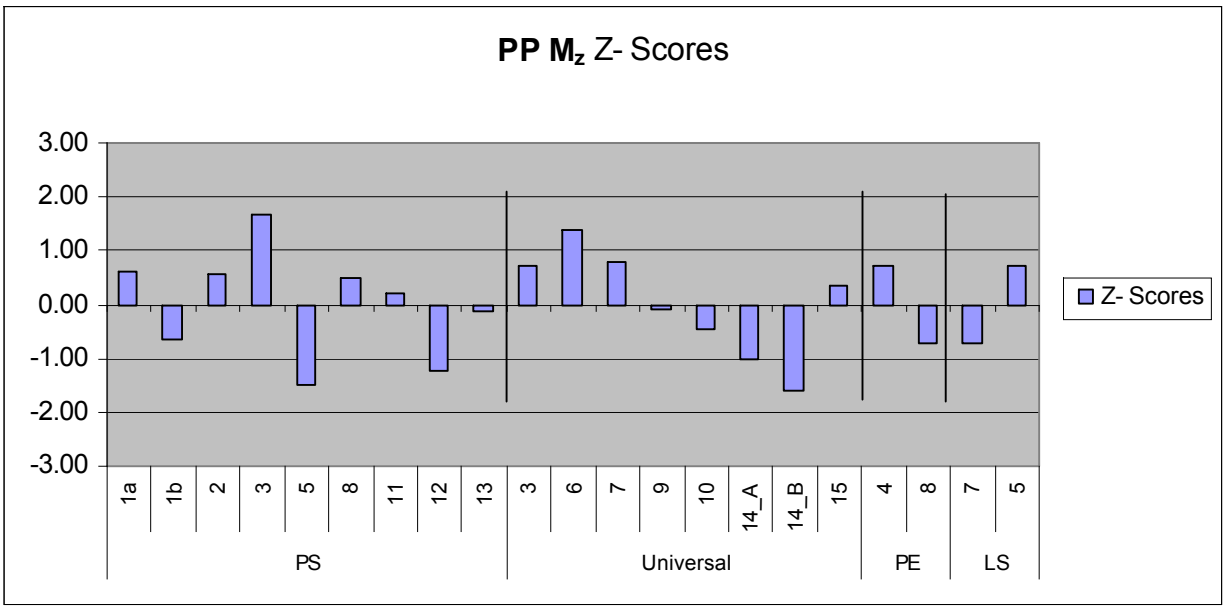

Figure 38: Z scores associated with M_z average values for Polypropylene from different laboratories

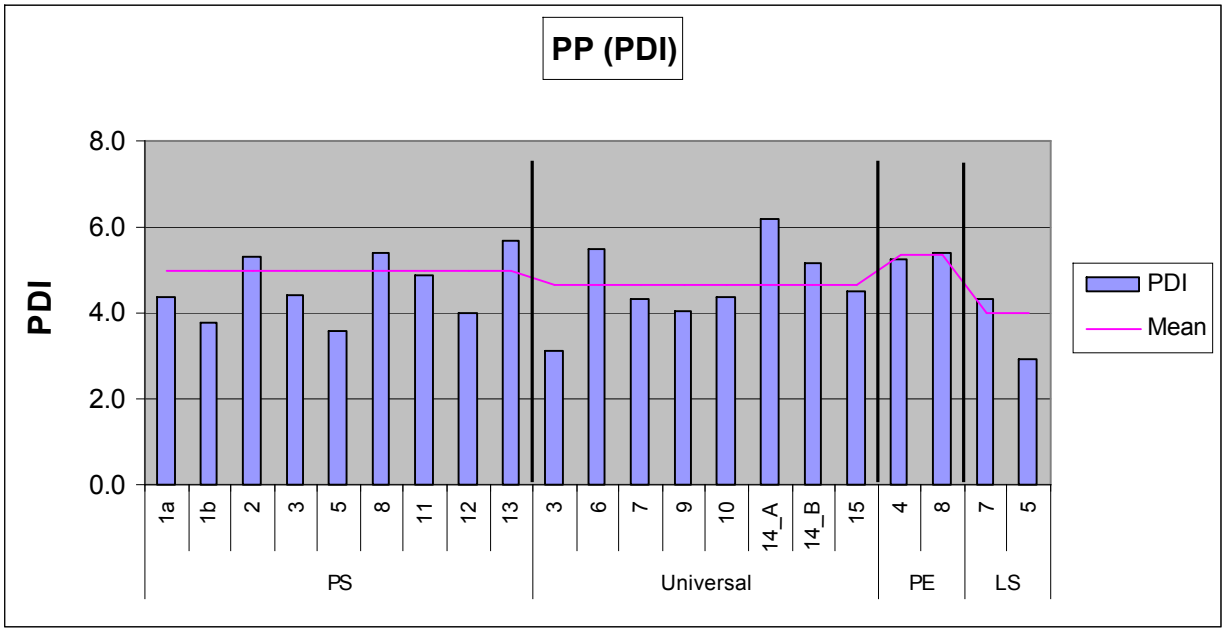

Figure 39: M_z average values for Polypropylene from different laboratories

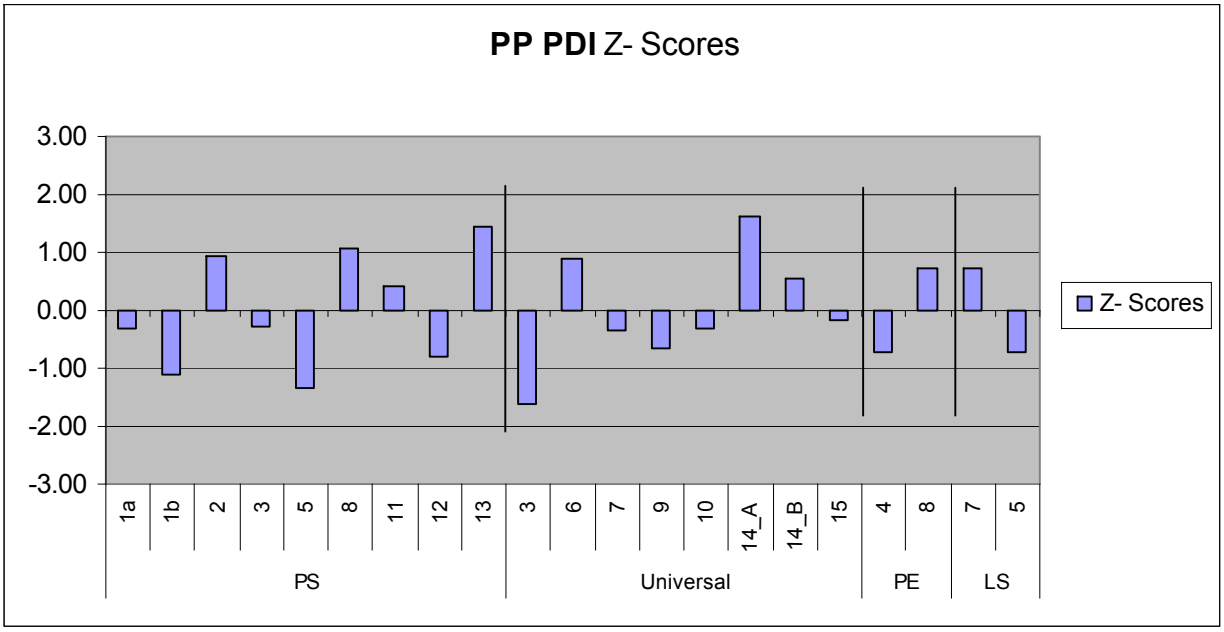

Figure 40: Z scores associated with Polydispersity average values for Polypropylene from different

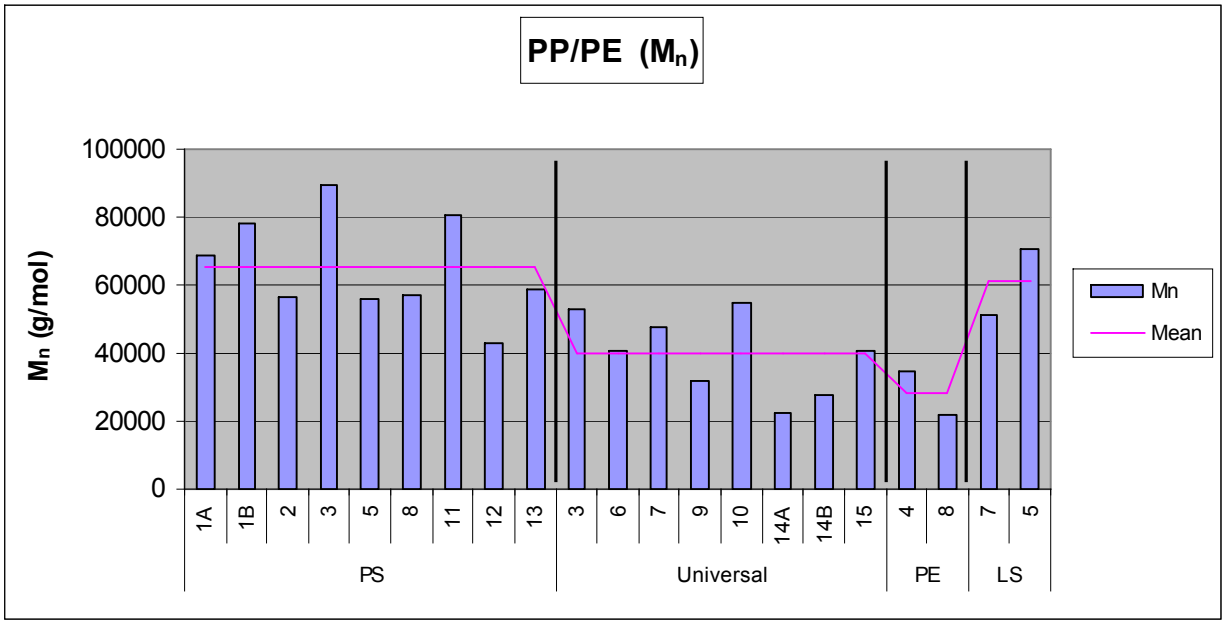

Figure 41: M_n average values for Polypropylene/ethylene copolymer from different laboratories

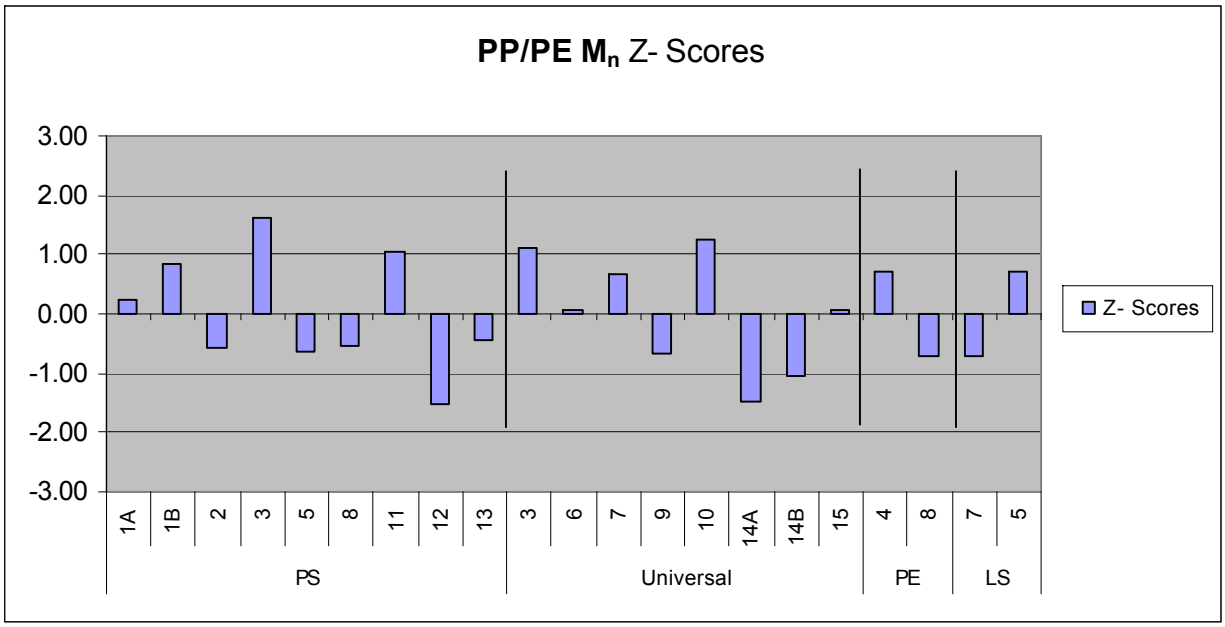

Figure 42: Z scores associated with M_n average values for Polypropylene/ethylene copolymer from different laboratories

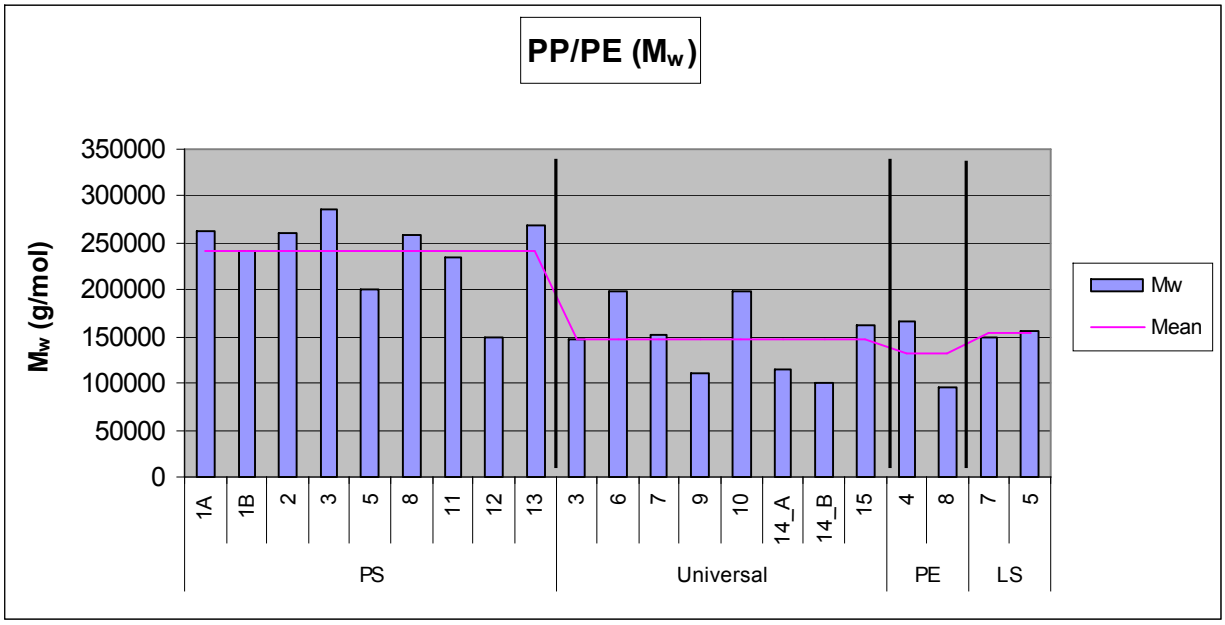

Figure 43: M_w average values for Polypropylene/ethylene copolymer from different laboratories

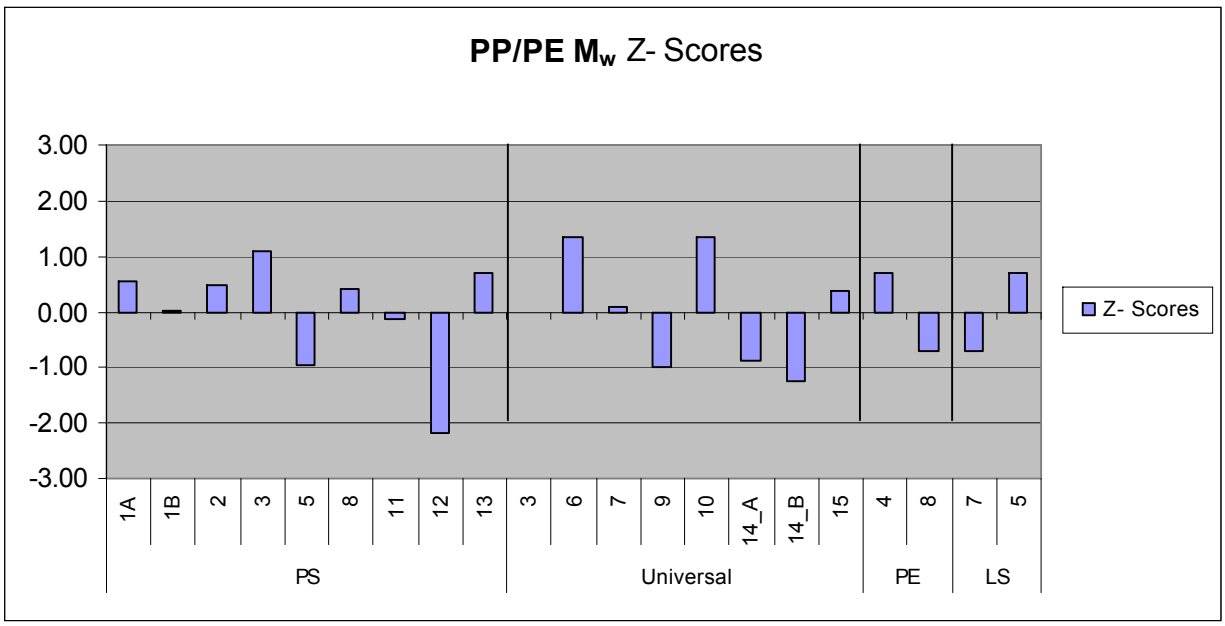

Figure 44: Z scores associated with M_w average values for Polypropylene/ethylene copolymer from different laboratories

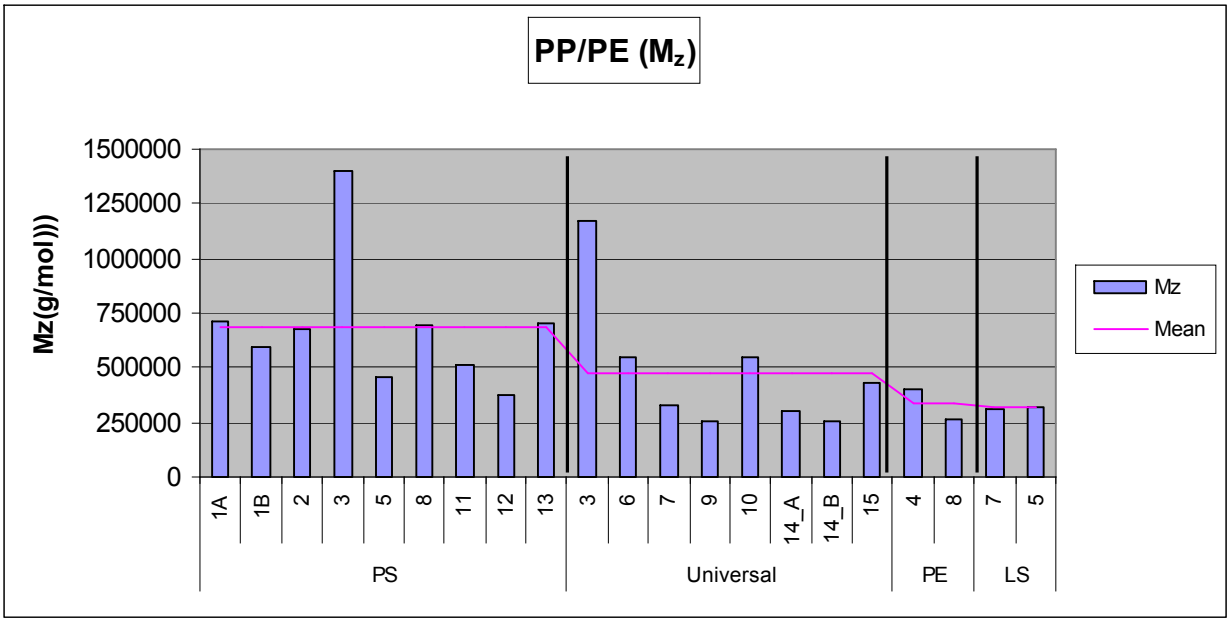

Figure 45: M_z average values for Polypropylene/ethylene copolymer from different laboratories

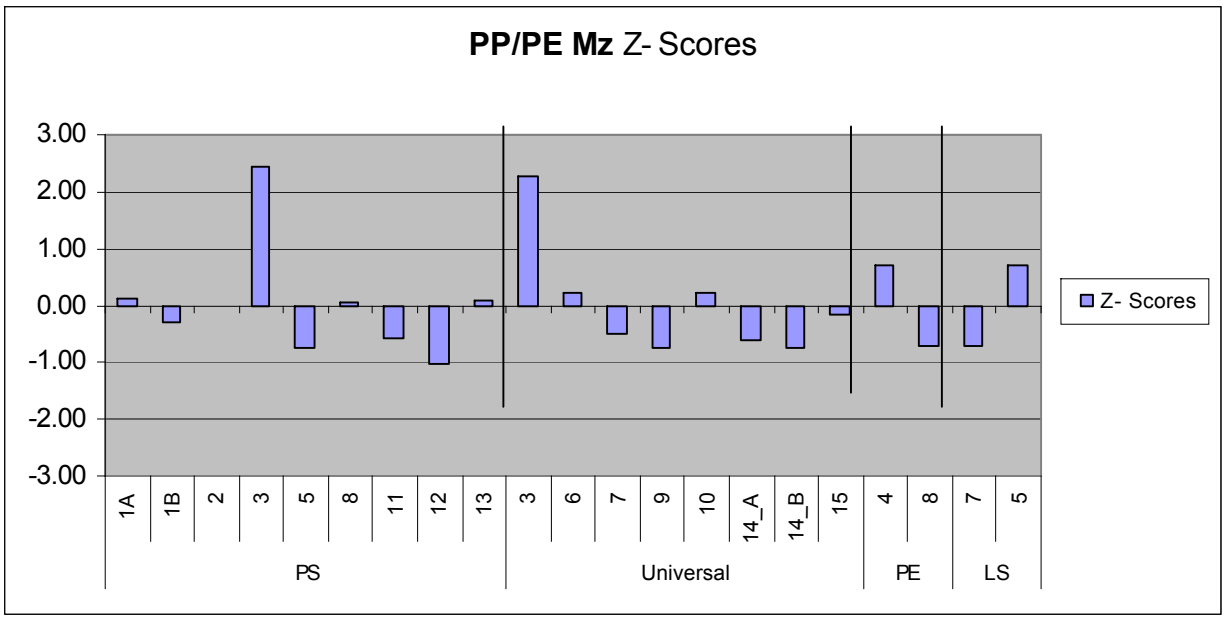

Figure 46: Z scores associated with M_z average values for Polypropylene/ethylene copolymer from different laboratories

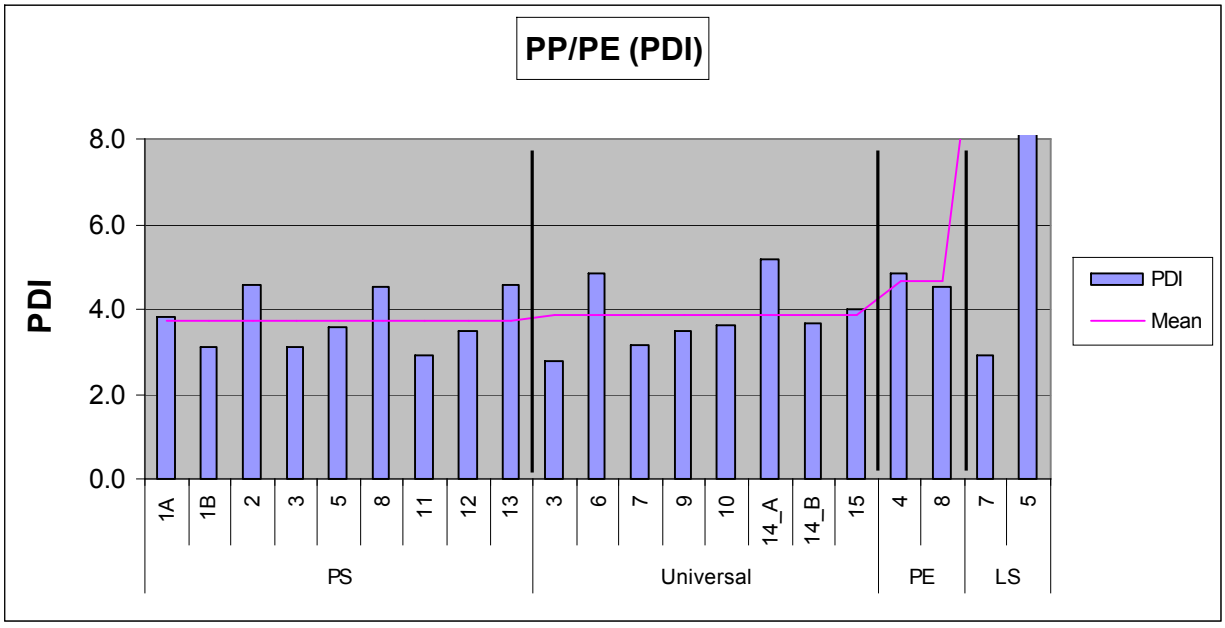

Figure 47: Polydispersity average values for Polypropylene/ethylene copolymer from different laboratories

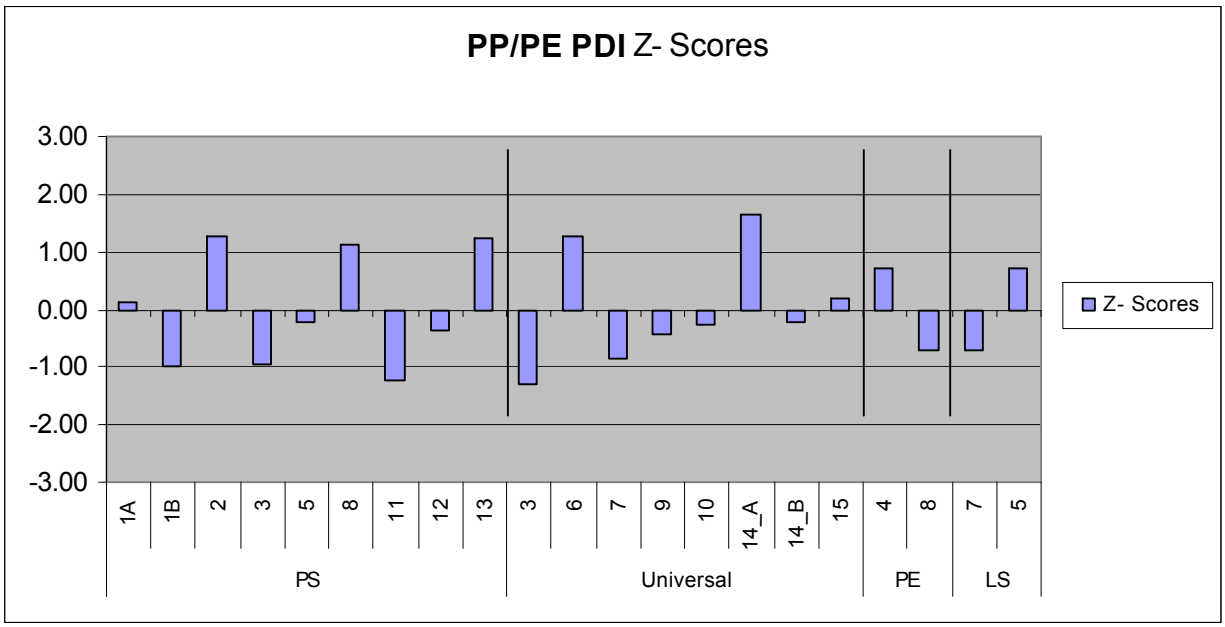

Figure 48: Z scores associated with Polydispersity average values for Polypropylene/ethylene copolymer from different

Appendix 2: Data of the molecular weight values from different laboratories

Table 1: Number average Molecular weight (Mn) data from participants using Polystyrene (PS) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
1A	Mean	34662	23898	30610	65149	73981	69077
	RSD	5.5	1.1	3.6	1.8	2.5	1.6
	Z-Score	0.0	-0.1	0.6	0.7	1.4	0.2
1B	Mean	na	33000	na	na	73000	78100
	RSD	na	0.3	na	na	5.2	2.0
	Z-Score	na	0.4	na	na	1.3	0.9
2	Mean	40349	63938	30339	63938	62207	56710
	RSD	4.1	5.2	5.0	5.2	3.0	2.2
	Z-Score	0.4	2.3	0.6	0.6	-0.2	-0.6
3	Mean	59200	31467	39900	73567	70867	89233
	RSD	9.6	11.8	5.4	4.7	9.1	3.5
	Z-Score	1.7	0.3	1.5	1.1	1.0	1.6
5	Mean	18033	11351	11545	22417	64006	55740
	RSD	1.8	1.5	1.1	2.2	5.1	0.3
	Z-Score	-1.2	-0.9	-1.3	-1.5	0.0	-0.7
8	Mean	38270	23700	31450	57587	60333	57330
	RSD	2.0	0.1	0.3	3.0	3.4	2.6
	Z-Score	0.2	-0.1	0.7	0.3	-0.5	-0.5
11	Mean	21400	15000	14700	34300	60900	80700
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-1.0	-0.7	-1.0	-0.9	-0.4	1.0
12	Mean	22657	12321	15217	30012	55441	42674
	RSD	0.0	0.0	0.0	0.0	na	0.0
	Z-Score	-0.9	-0.8	-0.9	-1.1	-1.2	-1.5
13	Mean	45690	18539	22845	67107	54520	59063
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	0.8	-0.5	-0.2	0.8	-1.3	-0.4
Overall	**Mean Average**	**35033**	**25913**	**24576**	**51760**	**117856**	**65403**
	RSD	**2.9**	**2.2**	**1.9**	**2.1**	**3.6**	**1.3**
	Overall RSD	**39.9**	**66.0**	**41.0**	**38.0**	**146.2**	**23.0**

Table 2: Weight average Molecular weight (Mw) data from participants using Polystyrene (PS) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
1A	Mean	254353	242185	126451	276650	323005	263372
	RSD	0.4	0.4	1.2	0.6	4.1	2.0
	Z-Score	0.1	-0.1	0.6	0.6	0.6	0.5
1B	Mean	na	230600	na	na	275500	241250
	RSD	na	1.2	na	na	0.4	1.2
	Z-Score	na	-0.2	na	na	0.0	0.2
2	Mean	279653	288180	129973	288180	332227	260060
	RSD	2.2	1.8	1.5	1.8	0.7	2.3
	Z-Score	0.4	0.4	0.7	0.7	0.7	0.4
3	Mean	324000	319333	112000	284333	309667	287000
	RSD	5.1	5.4	3.3	3.2	4.1	4.0
	Z-Score	0.9	0.8	0.2	0.7	0.4	0.8
5	Mean	115535	114162	54642	126759	229285	200388
	RSD	0.2	0.8	1.5	0.9	0.3	0.8
	Z-Score	-1.6	-1.5	-1.5	-1.4	-0.5	-0.4
8	Mean	298070	288130	133737	299643	325487	257520
	RSD	0.5	0.8	1.0	1.5	0.5	0.7
	Z-Score	0.6	0.4	0.8	0.9	0.6	0.4
11	Mean	322600	398800	109500	191000	295700	234700
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	0.9	1.6	0.1	-0.6	0.3	0.1
12	Mean	121464	111853	52644	119922	221551	269779
	RSD	na	0.0	0.0	0.0	na	na
	Z-Score	-1.5	-1.5	-1.6	-1.5	-1.7	0.7
13	Mean	271219	250851	130757	277699	309450	269779
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	0.3	0.0	0.7	0.6	0.4	0.6
Overall	**Mean**	**248362**	**249344**	**106213**	**233023**	**291319**	**253761**
	Average RSD	**1.2**	**1.2**	**1.1**	**1.0**	**1.3**	**1.4**
	Overall RSD	**33.7**	**39.4**	**31.6**	**32.4**	**14.9**	**10.5**

Table 3: Mz Molecular weight (Mz) data from participants using Polystyrene (PS) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
1A	Mean	705818	951720	385634	889897	900968	713660
	RSD	1.3	1.1	8.7	2.8	5.0	4.1
	Z-Score	-0.4	-0.4	0.2	0.3	0.5	0.0
1B	Mean	na	951450	na	na	693350	590650
	RSD	na	2.2	na	na	0.8	3.0
	Z-Score	na	-0.4	na	na	-0.9	-0.4
2	Mean	840575	887163	398810	887163	897537	680733
	RSD	0.8	4.0	4.4	4.0	1.6	5.1
	Z-Score	-0.1	-0.4	0.2	0.3	0.4	-0.1
3	Mean	1640000	2156666	290333	1223333	1080000	1403333
	RSD	25.9	16.2	9.1	18.7	11.2	11.3
	Z-Score	1.5	1.2	-0.5	1.4	1.7	2.3
5	Mean	363211	526208	156624	420928	549457	459655
	RSD	0.4	1.8	4.9	2.6	2.0	2.3
	Z-Score	-1.1	-0.9	-1.3	na	-1.51	-0.7
8	Mean	1008100	1351033.333	451933	1087567	882700	697233
	RSD	1.6	1.0	4.4	6.7	1.3	1.8
	Z-Score	0.2	0.2	0.6	0.9	0.3	0.0
11	Mean	1590000	2718000	562300	754800	835500	508700
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	1.4	2.0	1.3	-0.2	0.0	-0.7
12	Mean	349533	449020	142282	336683	595197	376429
	RSD	na	0	0	0	0	na
	Z-Score	-1.1	-1.0	-1.4	-1.5	-1.6	-1.1
13	Mean	781079	1013990	496783	837144	776814	706146
	RSD	0	0	0	0	0	0
	Z-Score	-0.3	-0.3	0.9	0.1	-0.4	0.0
Overall	**Mean**	**909790**	**1222806**	**360587**	**804689**	**832758**	**681838**
	Average RSD	**4.3**	**2.9**	**3.9**	**4.3**	**2.5**	**3.5**
	Overall RSD	**53.9**	**65.0**	**42.4**	**37.6**	**17.6**	**46.2**

Table 4: Polydispersity (PDI) data from participants using Polystyrene (PS) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
1A	Mean	7.4	10.3	4.1	4.3	4.4	3.8
	RSD	5.6	2.8	4.7	1.6	2.9	3.6
	Z-Score	-0.1	-0.2	-0.3	-0.6	-0.3	0.1
1B	Mean	na	7.0	na	na	3.8	3.1
	RSD	na	1.4	na	na	4.0	0.8
	Z-Score	na	-0.7	na	na	-1.1	-1.0
2	Mean	6.9	4.5	4.3	4.5	5.3	4.6
	RSD	1.9	6.5	3.7	6.5	1.9	2.7
	Z-Score	-0.2	-1.1	-0.2	-0.2	0.9	1.3
3	Mean	5.5	10.3	2.8	3.9	4.4	3.1
	RSD	12.7	11.5	2.9	7.4	13.0	2.6
	Z-Score	-0.6	-0.2	-1.3	-1.1	-0.3	-1.0
5	Mean	6.4	10.1	4.7	5.7	3.6	3.6
	RSD	1.9	1.7	2.3	1.4	5.2	0.9
	Z-Score	-0.4	-0.2	0.1	1.4	-1.3	-0.2
8	Mean	7.8	12.2	4.3	5.2	5.4	4.5
	RSD	2.4	0.9	1.2	1.6	2.9	3.3
	Z-Score	0.1	0.1	-0.2	0.8	1.1	1.1
11	Mean	15.1	26.6	7.4	5.6	4.9	2.9
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	2.4	2.4	2.0	1.3	0.4	-1.2
12	Mean	5.3	9.1	3.5	4.0	4.0	3.5
	RSD	0.0	0.0	0.0	na	0.0	na
	Z-Score	-0.7	-0.4	-0.8	-0.9	-0.8	-0.4
13	Mean	5.9	13.5	5.7	4.1	5.7	4.6
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-0.5	0.3	0.8	-0.7	1.4	1.2

Overall	**Mean**	**8**	**12**	**5**	**5**	**5**	**4**
	Average RSD	**3.1**	**2.7**	**1.8**	**2.7**	**3.3**	**1.7**
	Overall RSD	**42.1**	**55.9**	**30.8**	**15.6**	**15.9**	**17.9**

Table 5: Number average Molecular weight (Mn) data from participants using Universal calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
3	Mean	54400	16600	19000	30300	53300	53000
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	2.4	1.4	1.7	0.6	0.9	1.1
6	Mean	19605	12807	15973	29080	43966	40651
	RSD	1.0	1.7	0.6	0.9	1.7	1.2
	Z-Score	-0.2	0.1	0.6	0.3	0.1	0.0
7	Mean	22884	15116	16479	33986	52117	47791
	RSD	3.8	0.3	3.2	1.7	7.8	2.6
	Z-Score	0.0	0.9	0.8	1.6	0.8	0.6
9	Mean	21867	12200	13733	29533	51000	31967
	RSD	5.5	1.2	2.1	1.8	1.4	2.8
	Z-Score	-0.1	-0.1	-0.1	0.4	0.7	-0.7
10	Mean	19000	12667	12333	26333	42333	54667
	RSD	8.6	9.8	10.1	6.5	4.5	7.4
	Z-Score	-0.3	0.0	-0.6	-0.3	0.0	1.2
14_A	Mean	13900	9100	11000	20300	23600	22300
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-0.7	-1.2	-1.0	-1.8	-1.6	-1.5
14_B	Mean	12400	8200	10100	26000	24300	27500
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-0.8	-1.5	-1.3	-0.4	-1.5	-1.1
15	Mean	17798	11466	13763	26298	42032	40489
	RSD	0.3	8.7	0.5	0.5	1.2	2.0
	Z-Score	-0.4	0.5	-0.1	-0.4	0.0	0.1

Overall	**Mean**	**22732**	**12269**	**14048**	**27729**	**41581**	**39796**
	Average RSD	**2.7**	**3.1**	**2.4**	**1.6**	**2.4**	**2.3**
	Overall RSD	**17.1**	**19.2**	**17.0**	**15.1**	**27.9**	**28.6**

Table 6: Weight average Molecular weight (Mw) data from participants using Universal calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
3	Mean	305000	334000	53400	102000	164000	147000
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	1.5	1.1	-0.2	-1.2	-0.6	-0.1
6	Mean	123438	117703	62440	134961	242780	198039
	RSD	1.1	2.4	0.5	0.8	1.8	3.1
	Z-Score	-0.7	-1.0	1.6	1.4	1.3	1.2
7	Mean	221484	258661	61980	136976	223659	151419
	RSD	0.6	1.0	0.4	1.4	1.1	0.2
	Z-Score	0.5	0.4	1.5	1.6	0.8	0.0
9	Mean	260000	318333	51967	118333	205000	111333
	RSD	2.5	1.0	1.8	0.4	0.7	1.1
	Z-Score	0.9	0.9	-0.5	0.1	0.4	-1.0
10	Mean	236000	296333	53000	110667	184000	198000
	RSD	1.0	2.1	3.1	1.9	1.2	10.5
	Z-Score	0.6	0.7	-0.3	-0.5	-0.1	1.2
14_A	Mean	105400	99700	50700	109900	146300	115200
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-1.0	-1.2	-0.8	-0.5	-1.0	-0.9
14_B	Mean	104800	95900	51300	111100	122500	101000
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-1.0	-1.3	-0.6	-0.4	-1.6	-1.3
15	Mean	110354	100182	50815	109727	194052	161636
	RSD	0.3	30.9	0.9	0.6	0.3	0.2
	Z-Score	-0.9	0.4	-0.7	-0.6	0.2	0.4
Overall	**Mean**	**183310**	**202602**	**54450**	**116708**	**185286**	**147953**
	Average RSD	**0.8**	**5.3**	**1.0**	**0.7**	**0.7**	**2.2**
	Overall RSD	**38.0**	**50.4**	**9.7**	**10.4**	**22.7**	**27.4**

Table 7: Mz Molecular weight (Mz) data from participants using Universal calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
3	Mean	1300000	4610000	359000	491000	579000	1170000
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	1.0	2.0	2.3	1.1	0.6	2.2
6	Mean	350227	482041	193041	409435	657547	546673
	RSD	1.9	2.5	2.0	2.7	0.3	3.2
	Z-Score	-1.1	-0.9	0.0	0.2	1.3	0.2
7	Mean	1073704	1714329	210132	554046	586631	328981
	RSD	4.0	1.0	13.1	12.2	1.4	1.7
	Z-Score	0.5	-0.1	0.3	1.9	0.7	-0.6
9	Mean	1272000	2293333	129000	328667	482333	252333
	RSD	6.7	2.0	4.4	0.3	1.3	1.1
	Z-Score	0.9	0.3	-0.9	-0.7	-0.2	-0.8
10	Mean	1207333	2443333	149333	324667	438667	552000
	RSD	3.3	3.1	5.8	3.1	4.1	40.8
	Z-Score	0.8	0.4	-0.6	-0.7	-0.5	0.2
14_A	Mean	313800	396000	170600	334000	373800	298400
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-1.2	-1.0	-0.3	-0.6	-1.0	-0.7
14_B	Mean	279500	346000	152300	323600	306000	253300
	RSD	0.0	0.0	0.0	0.0	0.0	0.0
	Z-Score	-1.3	-1.0	-0.5	-0.8	-1.6	-0.8
15	Mean	341360	445181	171894	353174	535463	426753
	RSD	32.9	39.4	2.3	0.5	0.6	1.0
	Z-Score	0.3	0.2	-0.3	-0.4	0.3	0.2

Overall	**Mean**	**767240**	**1591277**	**191912**	**389823**	**494930**	**478555**
	Average RSD	**7.0**	**6.9**	**3.9**	**2.7**	**1.1**	**6.8**
	Overall RSD	**60.7**	**59.9**	**14.3**	**21.6**	**24.6**	**27.1**

Table 8: Polydispersity (PDI) data from participants using Universal calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
	Mean	5.60	20.10	2.80	3.40	3.10	2.80
3	RSD	0.00	0.00	0.00	0.00	0.00	0.00
	Z-Score	-1.11	0.65	-1.74	-1.51	-1.62	-1.30
	Mean	6.30	9.17	3.90	4.60	5.50	4.87
6	RSD	1.30	1.36	0.00	0.00	0.00	1.94
	Z-Score	-0.84	-0.89	-0.14	0.59	0.89	1.25
	Mean	9.69	17.11	3.77	4.03	4.31	3.17
7	RSD	4.40	1.32	3.66	3.06	6.68	2.46
	Z-Score	0.43	0.23	-0.33	-0.40	-0.35	-0.84
	Mean	11.87	26.07	3.80	4.00	4.03	3.50
9	RSD	3.25	1.58	2.15	2.04	1.17	2.33
	Z-Score	1.25	1.49	-0.28	-0.46	-0.64	-0.43
	Mean	12.67	23.33	4.30	4.20	4.37	3.63
10	RSD	9.85	8.81	6.85	5.14	4.71	9.08
	Z-Score	1.55	1.10	0.45	-0.11	-0.29	-0.27
	Mean	7.61	10.90	4.60	5.40	6.19	5.18
14_A	RSD	0.00	0.00	0.00	0.00	0.00	0.00
	Z-Score	-0.35	-0.65	0.89	1.99	1.62	1.64
	Mean	8.46	8.46	5.09	4.28	5.18	3.67
14_B	RSD	0.00	0.00	0.00	0.00	0.00	0.00
	Z-Score	-0.03	-0.99	1.60	0.03	0.56	-0.22
	Mean	6.18	8.74	3.69	4.17	4.50	3.99
15	RSD	0.45	1.27	0.63	0.04	1.83	2.11
	Z-Score	-0.89	-0.95	-0.44	-0.15	-0.16	0.17

Overall	**Mean**	**9**	**15**	**4**	**4**	**5**	**4**
	Average RSD	**2.7**	**2.0**	**1.9**	**1.5**	**2.1**	**2.6**
	Overall RSD	**30.1**	**47.8**	**13.1**	**11.5**	**16.7**	**19.3**

Table 9: Number average Molecular weight (Mn) data from participants using Polyethylene (PE) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
4	Mean	20200	10367	13167	28300	44400	34667
	RSD	4.6	6.0	0.9	0.9	0.8	7.5
	Z-Score	0.7	0.7	0.7	0.7	0.7	0.7
8	Mean	14387	8910	11827	21957	22687	21557
	RSD	2.0	0.1	0.3	2.1	3.4	2.6
	Z-Score	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7

Overall	**Mean**	**17293**	**9638**	**12497**	**25128**	**33543**	**28112**
	Average RSD	**3.3**	**3.0**	**0.6**	**1.5**	**2.1**	**5.0**
	Overall RSD	**23.8**	**10.7**	**7.6**	**17.9**	**45.8**	**33.0**

Table 10: Weight average Molecular weight (Mw) data from participants using Polyethylene (PE) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
4	Mean	240333	270000	59333	133333	232667	167000
	RSD	0.7	0.5	1.6	1.3	0.2	0.8
	Z-Score	0.7	0.7	0.7	0.7	0.7	0.7
8	Mean	112077	108337	50283	112130	22687	96827
	RSD	0.5	0.8	1.0	0.7	3.4	0.7
	Z-Score	-0.7	-0.7	-0.7	-0.7	-0.7	-0.7

Overall	**Mean**	**176205**	**189168**	**54808**	**122732**	**127677**	**131913**
	Average RSD	**0.6**	**0.7**	**1.3**	**1.0**	**1.8**	**0.8**
	Overall RSD	**51.5**	**60.4**	**11.7**	**12.2**	**116.3**	**37.6**

Table 11: Mz Molecular weight (Mz) data from participants using Polyethylene (PE) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
4	Mean	1687000	2317667	183667	399667	549457	406000
	RSD	2.5	0.4	5.1	2.3	2.0	3.0
	Z-Score	0.7	0.7	0.7	na	0.7	0.7
8	Mean	379033	507966	169933	399667	331900	262166
	RSD	1.5	1.0	4.3	3.4	1.3	1.8
	Z-Score	-0.7	-0.7	-0.7	na	-0.7	-0.7

Overall	**Mean**	**1033017**	**1412817**	**176800**	**399667**	**440678**	**334083**
	Average RSD	**2.0**	**0.7**	**4.7**	**2.8**	**1.6**	**2.4**
	Overall RSD	**89.5**	**90.6**	**5.5**	**0.0**	**34.9**	**30.4**

Table 12: Polydispersity (PDI) data from participants using Polyethylene (PE) calibration method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
4	Mean	11.9	26.1	4.5	4.7	5.3	4.8
	RSD	4.0	5.5	1.8	1.0	0.0	8.3
	Z-Score	0.7	0.7	0.7	-0.7	-0.7	0.7
8	Mean	7.8	12.2	4.3	5.2	5.4	4.5
	RSD	2.4	0.8	1.1	1.6	2.9	3.3
	Z-Score	-0.7	-0.7	-0.7	0.7	0.7	-0.7
Overall	**Mean**	**10**	**19**	**4**	**5**	**5**	**5**
	Average RSD	**3.2**	**3.1**	**1.5**	**1.3**	**1.4**	**5.8**
	Overall RSD	**29.7**	**51.5**	**4.0**	**6.7**	**1.3**	**5.1**

Table 13: Number average Molecular weight (Mn) data from participants using Light Scattering (LS) detection method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
7	Mean	26322	5612	28874	28874	48862	51219
	RSD	5.0	0.6	6.5	6.5	3.5	1.2
	Z-Score	2.2	-0.7	0.7	0.7	-0.7	-0.7
5	Mean	39820	26210.6667	22748	45760	79427	70644
	RSD	4.9	3.6	na	na	na	na
	Z-Score	0.7	0.7	-0.7	0.7	0.7	0.7
Overall	**Mean**	**33071**	**15911**	**25811**	**37317**	**64145**	**60932**
	Average RSD	**5.0**	**2.1**	**6.5**	**6.5**	**3.5**	**1.2**
	Overall RSD	**28.9**	**91.5**	na	na	na	na

Table 14: Weight average Molecular weight (Mw) data from participants using Light Scattering (LS) detection method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
7	Mean	215597	270666	146263	146263	211308	149482
	RSD	0.4	1.6	0.3	0.3	0.2	0.9
	Z-Score	0.4	-0.7	0.7	0.7	-0.7	-0.7
5	Mean	216542	274864	64633	141843	231926	156631
	RSD	0.9	0.4	na	na	na	na
	Z-Score	0.4	0.7	-0.7	-0.7	0.7	0.7
Overall	**Mean**	**216070**	**272765**	**105448**	**144053**	**221617**	**153056**
	Average RSD	**0.7**	**1.0**	**0.3**	**0.3**	**0.2**	**0.9**
	Overall RSD	**0.3**	**1.1**	na	na	na	na

Table 15: Mz Molecular weight (Mz) data from participants using Light Scattering (LS) detection method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
7	Mean	1260642	1868337	5024353	5024353	532420	314881
	RSD	3.4	3.3	32.7	32.7	2.0	2.8
	Z-Score	na	-0.7	0.7	0.7	-0.7	-0.7
5	Mean	1432868	2177695	1957000	846538	585531	320170
	RSD	9.6	5.9	na	na	na	na
	Z-Score	na	0.7	-0.7	-0.7	0.7	0.7
Overall	**Mean**	**1346755**	**2023016**	**3490677**	**2935446**	**558975**	**317525**
	Average RSD	**6.5**	**4.6**	**32.7**	**32.7**	**2.0**	**2.8**
	Overall RSD	**9.0**	**10.8**	na	na	na	na

Table 16: Polydispersity (PDI) data from participants using Light Scattering (LS) detection method

Laboratory	Sample Code	LDPE_1	LDPE_2	LLDPE_C4	LLDPE_C6	PP	PP_PE
7	Mean	8.2	48.2	5.1	5.1	4.3	2.9
	RSD	4.6	1.0	6.3	6.3	3.2	0.3
	Z-Score	0.7	0.7	0.7	0.7	0.7	-0.7
5	Mean	5.5	10.5	2.8	3.1	2.9	22.8
	RSD	4.8	3.9	na	na	na	na
	Z-Score	-0.7	-0.7	-0.7	-0.7	-0.7	0.7
Overall	**Mean**	**7**	**29**	**4**	**4**	**4**	**13**
	Average RSD	**4.7**	**2.4**	**6.3**	**6.3**	**3.2**	**0.3**
	Overall RSD	**28.6**	**90.8**	**41.0**	**34.3**	**28.0**	**109.3**