Molecular Weight Distributions of Industrially-Produced Poly-(ε-Caprolactams) by Gel Permeation Chromatography

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Abstract

Gel permeation chromatography with differential refractometry is used to obtain molecular weight distributions (MWD) of poly-(ε-caprolactams). Elution is carried out using an *m*-cresol–chlorobenzene mixture (50:50, v/v) at 50°C. MW values are obtained by a Hamielec-based calibration method, using broad-MWD poly-(ε-caprolactam) standards with the same chemical nature and similar MWD to the samples. Relative errors for the number-average MW (M_n) using this calibration method range from 0.4% (in the low polyamide MW range) to 20% (in the high polyamide MW range). These values are much lower than those obtained from narrow-MWD polystyrene calibration, which range from 39% to 78%. Similar values have been obtained for the other usual average MW parameters. The ability to obtain repeatability parameters for a given confidence interval and the utilization of statistical criteria for chromatogram rejection allow this method to be used in quality control for MWD of poly-(ε-caprolactams). Thus, production variables are related to polyamide-6 behavior in its ulterior treatment. Typical relative standard deviation percentages (for $n = 6$) of a polyamide sample range from 1.9% (for M_n) to 3.3% (for M_{z+1}).

Introduction

Gel permeation chromatography (GPC) with differential refractometry (DR) detection has become the most common analytical technique used to obtain the molecular weight distributions (MWD) of organic polymers (1–3). The GPC chromatograms or elution curves obtained contain the MWD information of the sample, and the task is to extract the sample with accuracy and precision using an adequate calibration method.

Although GPC has been used in some cases as an online quality control method, simpler and more rapid measures are normally used for this purpose, depending on the polymer under consideration (e.g., intrinsic viscosity in the case of polyamides). This fact, technical drawbacks associated with DR (e.g., difficulty for stabilizing chromatographic baseline), the excessive duration of chromatographic runs, and the inherent limitations of GPC from a resolution point of view have precluded an adequate study of repeatability of GPC of polymers in general. The use of GPC as a quality control method becomes even more complicated in the case of difficult-to-solve polymers (e.g., polyamides) because of the special working conditions required (1,2). In these cases, elution curves have usually been obtained for relatively rapid comparative analyses rather than for quality control-oriented methods.

Despite this, GPC has sometimes been used as a quality control method when a more detailed analysis of the polymer is required and when traditional methods are not sufficiently informative or sensitive and fail to yield values that correlate well with the observed variations in production processes.

Poly-(ε-caprolactams), also called nylon 6 or polyamide-6 (PA-6), are commercially produced polyamides used as fibers, films, and molding resins. This polymer has been characterized by GPC to a lesser extent than other polymers because its crystallinity and poor solubility in conventional high-performance liquid chromatography (HPLC) eluants make it necessary to use special and expensive solvents for elution (2, 4–13). Different strategies have been tried with regard to mobile phases used in the GPC of PA-6. The classical approach has been to use certain solvents at high temperatures to reduce their viscosity (e.g., *m*-cresol at 100°C). Likewise, viscosity reduction of these solvents has been obtained by mixing *m*-cresol (or other solvents used at high temperatures) with another that plays the role of diluant (4). Therefore, these mixtures decrease *m*-cresol viscosity while retaining PA-6 solubility, enabling the operating temperature of HPLC equipment to be lowered (e.g., *m*-cresol–chlorobenzene, 50:50, v/v, at 43°C). Derivatization using trifluoracetylation has also been used as another strategy for increasing PA-6 solubility in common HPLC solvents (5,6). More recently, fluorinated solvents, in particular 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), have been increasing in popularity as a mobile phase in GPC analysis owing to their easy solubilization of polyamides at room temperature (7–10).

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Despite its many potential advantages, the use of HFIP comes with a number of unresolved questions (9). It is toxic, and its cost precludes its use in quality control applications in which a large number of analyses are involved. In order to reduce its cost, a mixture of a Freon (HCFC225cb or 1,3-dichloro-1,1,2,2,3-pentafluoropropane) and HFIP (10%, v/v) has been proposed as a mobile phase for PA-6 (10). However, this type of Freon is not easily available at present.

Another problematic aspect in the GPC of PA-6 is calibration. Calibration of PA-6 samples has been usually performed by peak position using narrow polystyrene (PS) or polymethylmetachrylate (PMMA) standards (11). This provides GPC elution curves that can be qualitatively compared to different samples under the same conditions but that give inaccurate MWD values. Another approach is to perform calibration with PMMA or PS standards using a combination of several detectors [e.g., radioactivity detection (RD) and light scattering or viscometry). Thus, quantitation can be carried out using "artificial" calibration curves, which are obtained by correcting the standard calibration curve (with RD) with polyamide molar mass data from light scattering (12,13).

As calibration relates retention volume or time to the MW of a standard, the latter should be of the same chemical structure as the polymer sample in order to minimize inaccuracy in determinations caused by the effects of adsorption, which is of importance in elution of polyamides. Thus, an accurate calibration should be possible thanks to the relatively recent commercial availability of PA-6 standards. However, in spite of this possibility, studies dealing with the use of polyamide standards for a direct broad MWD calibration using RD detection have not been found.

The purpose of this work is to develop a quality control-oriented GPC–RD method for obtaining repeatable and accurate MWD of industrially-produced poly-(ε-caprolactams) that has the following characteristics: (*i*) the use of a mobile phase with a reasonable cost for quality control purposes; (*ii*) the use of a Hamielec-based calibration method, using broad MWD poly-(ε-caprolactam) standards, with the same chemical nature and an MWD similar to that of the samples; and (*iii*) a statistical treatment of data with repeatability studies for a given confidence interval.

An assessment of the broad MWD poly-(ε-caprolactam) calibration used is discussed. This calibration method and that of peak position using polystyrene standards have also been compared.

The developed method has been used in this work to relate production variables to the behavior of poly-(ε-caprolactams) in their ulterior treatment. Thus, some examples of alterations in properties that can be caused by batch-to-batch variations in produced poly-(ε-caprolactams) and that cannot be explained by a single parameter have been studied.

Table I. Characteristics of Broad-MWD poly-(ε-caprolactam) Standards

Standard	M_n	M_w	M_p	IV*
STD1	11300	17200	14500	1.08
STD2	19400	41000	33000	2.17

* Intrinsic Viscosity (dl/g) in HCOOH at 25°C (a = 0.70; k = 0.00145).

Experimental

Samples

Poly-(ε-caprolactams) were produced by NUREL S.A. (Zaragoza, Spain). Samples were selected from different batches and from two different plants of production. These samples were sorted by their intrinsic viscosity and their behavior in ulterior treatment.

Samples S1, S2, S4, S6, S7, S8, S13, S14, S15, and S17 have a low intrinsic viscosity with a normal behavior in processing; samples S9, S10, S13, and S16 have a high intrinsic viscosity; and samples S3, S5, and S11 have a low intrinsic viscosity and anomalous behavior in processing.

The intrinsic viscosity of the samples was measured in concentrated sulfuric acid at 25°C

Tests for selecting the PA-6 solvent and the mobile phase

The dissolution of PA-6 was tested in several mixtures of possible eluants, which consisted of a solvent and a diluant, to select the GPC mobile phase. The solvent and the diluant were mixed at room temperature in a closed, stirred vessel. After the sample was added, the mixture was further heated at 50°C. The solvent used was either *m*-cresol or *o*-chlorophenol. $CHCl_3$, tetrahydrofuran (THF), and chlorobenzene were each studied as a diluant of the solvent in proportions of 10%, 30%, 50%, and 90% diluant–solvent (v/v, %). Polyamide concentration used was between 0.25% and 5% (w/v, %).

Sample preparation

The sample preparation for the chromatographic injection was carried out by dissolving the corresponding PA-6 (0.4%, w/v) in a freshly prepared mixture (50:50, v/v) of *m*-cresol and chlorobenzene. Dissolution was carried out in a closed, stirred vessel at 50°C for 1 h. The solution was further diluted up to 1 mg/mL using the previously mentioned mixture. Before injection, samples were filtered through a Teflon 0.45-µm filter (Micron Separations).

GPC equipment and conditions

The solvent delivery system consisted of a Waters model 515 HPLC pump (Waters, Milford, MA). The sample was injected (1 mg/mL, 50-µL loop) by using a 7725i Rheodyne injector (Rohnert Park, CA). GPC separation was performed by connecting, in series, two polystyrene-divinylbenzene based, Waters µ-styragel columns (7.8 × 300 mm): a HT4 (10^4 Å pore size) and a HT2 (500 Å pore size) (Waters). The columns were heated at 50°C in an oven. Nominal separation range for this system of columns is 600000-100 of equivalent PS.

A mixture (50:50, v/v) of *m*-cresol and chlorobenzene was used as the mobile phase. Prior to its use, the mixture was filtered through a Teflon 0.5-µm pore size filter and degassed by

sonication. The flow rate was 0.4 mL/min. The eluant was continuously pumped through the columns. When GPC runs were being not performed, eluant was flowing at 0.1 mL/min.

A 2414 Waters differential refractometer was used for detection. The working detector temperature and sensitivity were 50°C and 128×, respectively.

Control of the system, and data acquisition and treatment were performed using Millenium^{32} software (Waters).

Calibration and standards

A polystyrene standard (M_w = 1290000) (Polymer Laboratories, Shropshire, UK) was used as exclusion standard. Styrene (M_w = 104; Aldrich, Madrid, Spain) was used as permeation standard.

Molecular weight average values (M_n, M_w, M_p, M_z, M_{z+1}) of each sample were obtained through broad-MWD standard calibration according to Hamielec method (14), by application of GPC-Millenium^{32} software (Waters). They are defined as follows (1):

$$M_n = \frac{\sum_i W_i}{\sum_i W_i/M_i} \; ; \; M_w = \frac{\sum_i W_i M_i}{\sum_i M_i}$$

$$M_z = \frac{\sum_i W_i M_i^2}{\sum_i W_i/M_i} \; ; \; M_{z+1} = \frac{\sum_i W_i M_i^3}{\sum_i W_i M_i}$$

where W_i is the weight of molecules having molecular weight M_i.

M_p is the molecular weight corresponding to that of the maximum of the chromatographic peak.

For calibration, two poly-(ε-caprolactam) standards (STD1 and STD2) (American Polymer Standards Co., Mentor, Ohio) were used to obtain calibration curves. MW data of these standards as furnished by the provider are shown in Table I.

The calibration curve was performed daily, after injection of the two standards and before the sample injection. All data were accumulated to improve the calibration curves. These were obtained under the same conditions as the samples to minimize errors in the accuracy of MWD determination.

Before selecting the previously mentioned calibration method, STD1 and STD2 were alternatively used as the unknown samples to assess its application.

Peak-position calibration using narrow MWD polystyrene standards (PS) of different molecular weights was also performed. The MW of polystyrene standards were 210500, 28500, 10850, 5460, and 2050 (Polymer Laboratories). The polydispersity was in all cases lower than 1.03.

Statistical treatment of data

Chromatograms with baseline drift and noise higher than 15 and 0.1 AU, respectively, were not considered for data treatment. This criterion was defined using the previously mentioned poly-(ε-caprolactam) standards and adopted to avoid subjective interpretation of chromatograms.

The relative standard deviations (RSD) of GPC chromatograms (retention times and MW values) for each sample at the conditions used were calculated as:

$$RSD = \frac{SD \times 100}{\bar{x}} \qquad \text{Eq. 1}$$

where SD is the sample standard deviation, and $\bar{x}$ is the average from at least eight GPC runs of a given sample.

Intervals of repeatability for retention times (min) and the different MW parameters (M_n, M_w, M_p, M_z, and M_{z+1}) were calculated for a 95% confidence interval. Runs for all samples were randomly injected.

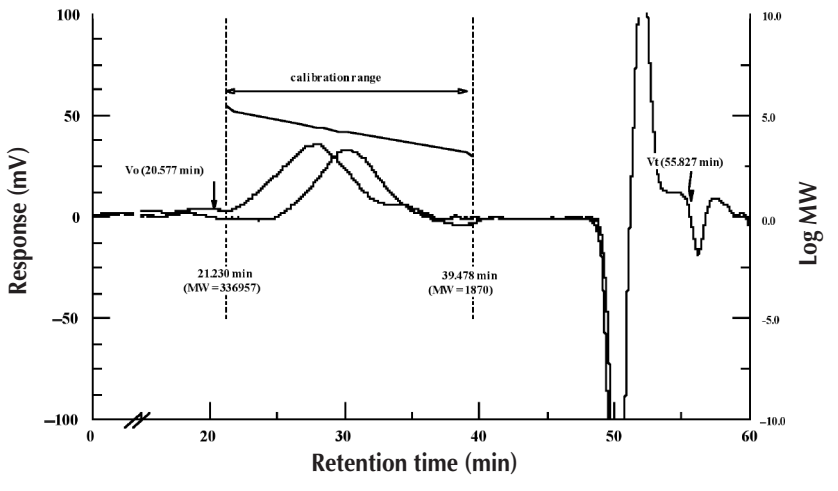

Figure 1. Chromatograms of STD1 and STD2 poly-(ε-caprolactam) standards with details of exclusion and permeation times, and calibration range. Working conditions as indicated in the Experimental section.

Results and Discussion

In polyamide analysis, the choice of standards and solvent systems are related. The calibration of polyamides with PMMA in HFIP is currently used for determining their relative molecular weight in the comparison of different polyamides (2,12). Either viscosity or light-scattering coupling (12) allows determination of absolute molecular weights to be carried out. For obtaining absolute molecular weight values, an "artificial" curve has been obtained in HFIP by correcting the PMMA calibration curve with the MWD of polyamide obtained, in turn, from light-scattering measurements (12). Even in this case, this correction depends on the mobile phase used because hydrody-

namic volume and association effects of PMMS and polyamide are different in different solvents. Nevertheless, an ideal calibration for absolute MWD should be done using broad MW standards with an identical chemical composition to the analyzed sample for a given solvent.

In this work, polyamide-based standards have been used rather than PMMA in a system, which is compatible with differential refractometry. An elution system (a solvent plus a diluant) has been selected that has a low viscosity, provides stable baseline, is not as expensive as HFIP, and can be used at mild temperature. This approach is preferred to the solubilization of polyamides through derivatization reactions [e.g., trifluoroacetylation (5,6)] because they involve several delicate experimental steps, a difficult control and evaluation of reactions, and, as a result, the possibility of creating artifacts.

This discussion is undertaken under the basis of the determination of relative MWD. However, even if our purpose is not to obtain absolute molecular weight distributions of polyamides, these values should be more accurate and closer to the absolute values than those obtained from PMMA or other calibrants in HFIP.

According to our solvent tests, all of the studied combinations of solvents and diluants may be adequate for their use as a mobile phase in GPC of PA-6. From the possibilities, *m*-cresol–chlorobenzene (50:50, v/v) had been previously used and referenced in the literature (4). When used as an *m*-cresol diluant, chlorobenzene has a higher boiling point than THF or $CHCl_3$. This avoids loss of the diluant during degassing as well as bubble formation during GPC runs, thus maintaining the solvent-mixture composition.

Figure 1 shows GPC elution curves corresponding to the poly-(ε-caprolactam) standards of Table I under working conditions described in the Experimental section, as well as the MW range in which broad MW calibration has been applied.

Before selecting the previously mentioned calibration method, and once a calibration curve had been generated using STD1 and STD2 broad MWD standards, each one of them was alternatively used as unknown samples to evaluate calibration applicability.

Table II shows that reference MW values are, in general, in good agreement with those obtained from the application of broad MWD calibration. MW values seem to fit better in the lower MW range (STD1) than in the higher one (STD2). As will be shown later, the MWD of all the analyzed polycaprolactams are very similar to STD1, especially in the lower MW zone.

The main requirements of the applicability of this calibration technique for PA-6 samples have been fulfilled (15), and the MWD of the standards span most of the sample dynamic range. In addition, two moments of the distribution of the standard (e.g., M_n and M_w) must be accurately known as an external measurement.

Table II. MW Averages of STD1 and STD2 as Unknown Samples Obtained Using Two Calibration Techniques

	M_n	M_p	M_w	Polydispersity
STD1 specifications*	11300	14500	17200	1.52
STD1 by Broad-MWD-PA6 calibration†	11347	13777	16054	1.42
STD1 by Narrow-MWD-PS calibration‡	55564	82519	105183	1.89
STD2 specifications*	19400	33000	41000	2.11
STD2 by Broad-MWD-PA6 calibration†	23558	25736	31577	1.34
STD2 by Narrow-MWD-PS calibration‡	170378	192910	345718	2.02

* M_n, M_w, M_p as provided by the manufacturer.
† Broad-MWD- PA6 calibration was performed as detailed in Experimental, using STD1 and STD2 as broad standards.
‡ Narrow-MWD-PS calibration was performed as detailed in Experimental, using polystyrene standards.

Table III. Data of S9 Poly-(ε-Caprolactam) Sample*

Sample		M_p	M_n	M_w	M_z	M_{z+1}	Polydispersity	Area	t_R(min)
S9	Day 3	19384	18402	22695	28147	34356	1.23	8761129	29.43
S9	Day 3	19941	18039	21934	26677	32034	1.22	9562641	29.32
S9	Day 4	19537	18178	22237	27325	33236	1.22	8345405	29.40
S9	Day 5	19941	18918	23098	28026	33346	1.22	8414792	29.32
S9	Day 5	19750	18048	21844	26545	31954	1.21	8618167	29.36
S9	Day 5	19265	18056	21974	26603	31564	1.22	8335531	29.46
C.I.†	$\overline{x}$	19636	18274	22297	27221	32745	1.22		
(95%)	SD	286	345	499	728	1073	0.01		
	RSD (%)	1.46	1.89	2.24	2.67	3.28	0.82		
	±	300	362	524	764	1126	0.01		

* After applying rejection criteria (baseline < 15; noise < 0.1).
† The confidence interval (C.I. = $x \mp tSD\sqrt{n}$) is defined here as the interval in which the true value lies with a given probability, 95% in this case, where x is the molecular weight average, t is the Student's distribution, SD is the standard deviation, and n is the number of measurements.

Because the precision of Hamielec method increases with the difference between the two MW values used in the calibration (14), standards were selected with the greatest difference in MW values among those available, taking into account the MWD distribution range of samples. As previously mentioned, samples are similar to STD1 in MWD.

The MW values from peak position calibration using narrow MWD polystyrene standards have been compared to those from broad MWD poly-(ε-caprolactam) standard calibration. Table II shows that peak position calibration using narrow MWD polystyrene standards results in a high amount of inaccuracy in determining MW values.

A characteristic example GPC chromatogram, showing samples S9, S5, and S2 with their most typical MW values, is given in Figure 2.

Baseline and noise stabilization of RD detection is crucial for method application. This detection system is highly sensitive to the surrounding effects. Baseline drift can produce errors in MW determination, and noise may interfere with integration limits selection.

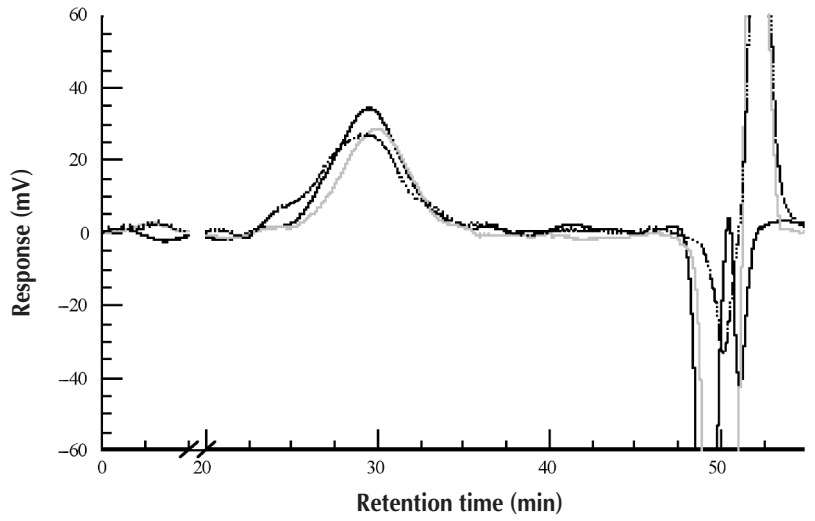

Figure 2. GPC Chromatograms of three poly-(ε-caprolactam) samples. Working conditions as indicated in Experimental. A high intrinsic viscosity sample, S9, (dark solid line). A low intrinsic viscosity sample, S2, (solid grey line). A low intrinsic viscosity sample, S5, having an anomalous behavior in its ulterior treatment (broken line).

The combined utilization of statistical criteria for chromatogram rejection, a relatively high number of injections per sample, and injection randomness allow adequate repeatability parameters of retention time and MW values to be obtained for a chosen confidence interval. Run-to-run and day-to-day results showed adequate repeatability. Table III provides analytical data for an example (the S9 sample) according to the selected criteria.

The described technique has allowed the characterization of MWD of industrially-produced poly-(ε-caprolactams) to be obtained. Although exclusion time and permeation time are 20.577 and 55.827 min, respectively, the range in which calibration is applicable for obtaining accurate MW values is given by the standards and goes from 336957 to 1857 (Figure 1). Under this MW value, no eluted material was found in our samples.

Although detection of low-concentrated, low-sized PA-6 oligomers was out of the

Table IV. %RSD and Semi-intervals of Molecular Weights for a 95% Confidence Interval in Several Industrial Samples

	S1		S2		S3		S4		S5		S6	
	% RSD	±	% RSD	±	% RSD	±	% RSD	±	% RSD	±	% RSD	±
M_n	3.96	508	1.46	223	5.70	859	4.05	666	2.24	454	4.90	731
M_w	3.70	595	1.41	271	3.45	743	4.33	962	5.43	1498	4.06	759
M_z	4.35	866	3.02	720	6.65	1089	9.51	2791	9.63	3558	3.88	890
	S7		**S8**		**S9**		**S10**		**S11**		**S12**	
	% RSD	±	% RSD	±	% RSD	±	% RSD	±	% RSD	±	% RSD	±
M_n	4.49	683	3.10	470	1.89	362	7.06	1379	4.18	750	4.98	777
M_w	2.90	587	4.58	887	2.24	524	6.73	1643	2.99	861	5.03	1063
M_z	4.90	1274	6.56	1596	2.67	764	6.47	1945	3.79	1654	5.96	1679
	S13		**S14**		**S15**		**S16**		**S17**			
	% RSD	±	% RSD	±	% RSD	±	% RSD	±	% RSD	±		
M_n	4.66	573	6.72	1296	5.52	855	3.53	536	7.21	810		
M_w	5.32	883	7.46	1315	3.95	832	4.43	848	8.61	1345		
M_z	5.74	1252	6.92	1545	3.97	1094	4.91	1164	8.91	1865		

scope of this work, some attempts were made to qualitatively detect the caprolactam monomer. For this purpose, a processed monomer-rich sample was subjected to GPC. The presence of low concentrations of low-MW oligomers in poly-(ε-caprolactams) has been traditionally considered to be related to some anomalies in the production process, although their influence has not been unequivocally established. The elution of the caprolactam monomer interferes with that of the eluant, which also provides the DR response. However, indirect evidence of the presence of caprolactam monomer was found through the qualitative variation in the DR response of peaks in the solvent/monomer zone (results not shown here). In general, RD detection under GPC conditions is not sensitive enough to detect them. Recently, a number of linear and cyclic PA-6 oligomers have been separated, identified, and quantified using other techniques (16). They open the possibility of an in-depth study of these compounds, although they are still not oriented to a quality control analysis and are labor-intensive. They involve a preparative isolation by HPLC at critical conditions; further identification of the separated fraction by mass spectrometry techniques as LC–electrospray ionization-MS and matrix-assisted laser desorption/ionization-time of flight; and quantitation of oligomers in each separated fraction by HPLC with evaporative light-scattering detection.

Figure 3 and Table IV summarize the MW average values of analyzed samples (M_{z+1}, M_z, M_w, M_p, and M_n) and their repeatability, respectively. MWs of PA-6 samples fall between those of used standards, being more similar to MWD of STD1 as previously mentioned. For the PA-6 samples analyzed, the eluted material with the highest value of MW was 115369 and the lowest was 2537. Both values were within the calibration zone.

According to the results, three zones or types of MWD distributions can be distinguished that are related to different specifications of produced poly-(ε-caprolactams) (Figure 3): (*i*) those having low MW average moments in all MWD, which correspond to products with an intrinsic viscosity value of 2.4 dl/g in specifications; (*ii*) those having high MW average moments in all MWD, which correspond to products with intrinsic viscosity values of 2.7 dl/g in specifications; and (*iii*) those having low values of intrinsic viscosity (2.4 dl/g) but having a different MWD shifted towards high MW moments with an increase in the ponderation of heaviest ones (M_z, M_{z+1}). Some of these poly-(ε-caprolactams) have been identified as behaving anomalously in their ulterior processing.

Conclusion

In summary, although GPC–RD has intrinsic limitations for quality control of PA-6 on a routine, high-sample throughput basis, the proposed method can be efficiently used at a reasonable cost as a special control technique for detecting some anomalies in the production process or for evaluating the influence of selected variables.

Acknowledgments

Authors thank the Spanish Ministerio de Ciencia y Tecnología (PPQ2000-0173-P4-02 project) and NUREL, S.A. for financial support. Thanks to Dr. M. Matt for the gift of some PS standards. E.M. acknowledges CSIC and NUREL, S.A. for a grant.

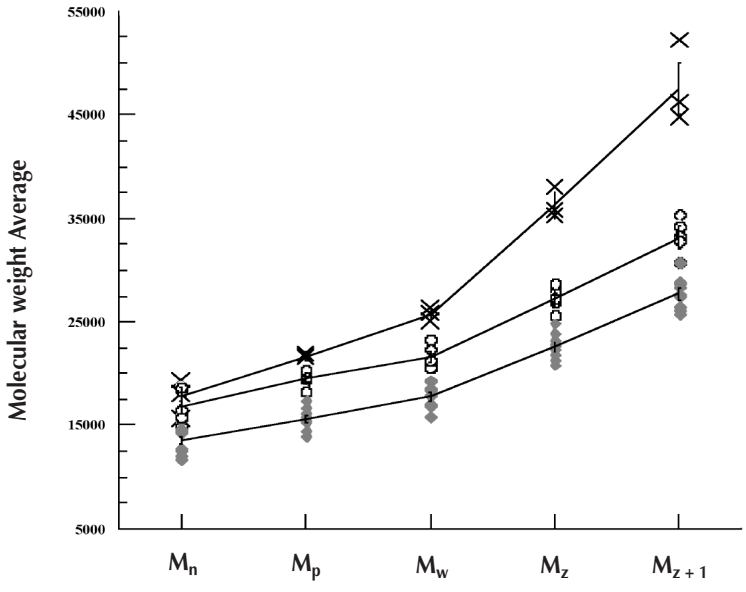

Figure 3. Values of MW averages (M_n, M_w, M_p, M_z, and M_{z+1}) for poly-(ε-caprolactam) analyzed samples. Working conditions as indicated in Experimental. Three types of samples are shown: Group of samples (S1, S2, S4, S6, S7, S8, S13, S14, S15, and S17) of low intrinsic viscosity with a normal behavior in processing (®); Group of samples (S9, S10, S13, and S16) of high intrinsic viscosity (o); and Group of samples (S3, S5, S11) of low intrinsic viscosity with anomalous behavior in processing. Solid lines show confidence intervals and mean values of each group of samples (X).

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Manuscript received November 16, 2005;
revision received March 21, 2007.