Pearson-type I Distribution Function for Polydisperse Polymer Systems. Molar Mass Distribution[†,§]

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This paper presents an attractive feature of the distribution function, which uses a relatively simple expression for approximating probability density. The Pearson-type I distribution function is used to represent the molar mass distribution (MMD) function for polymers for which the number average ($\bar{M}_n$), mass average ($\bar{M}_w$), z-average ($\bar{M}_z$), and (z+1)-average ($\bar{M}_{z+1}$) values are available. In continuation, the Pearson-type I distribution is applied as the model MMD function in which model parameters ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$) are fitted from experimentally determined MMD. As the result, different molar mass averages are estimated with satisfactory agreement with experimental data.

INTRODUCTION

By definition all polymeric molecules, whether natural or synthetic, consist of large numbers of simple repeat units derived from small molecules and joined together by covalent bonds to form the polymer structure. In the simplest polymer structure, the linear homopolymer, only one type of repeat unit is present and the units are joined end-to-end to form linear chains. Although the number of repeat units in a given mass of such a polymer is determined by the molar mass of the repeat unit, it is very rare indeed for the repeat units to be distributed equally between the polymer molecules. The occurrence of random processing during polymer synthesis produce polymer molecules containing varying numbers of repeat units, so that the polymer contains a distribution of chain lengths and is said to be polydisperse. It is not possible to characterize the polymer by a single molar mass and the mass of the polymer molecules can only be completely characterized by molar mass distribution. Since the molar mass distribution for any polymer depends on the mechanism and conditions in synthesis, the measurements of molar mass distribution provides an important tool for studying polymerization mechanism. In addition, polymer samples, which are identical in terms of chemical techniques, such as elemental analysis, IR and NMR spectroscopy, may differ in molar mass distribution, with consequent differences in physical and mechanical properties. For example, a small proportion of chains of very high molar mass present in a polymer of moderate molar mass will produce a marked increase of melt viscosity which may lead to changes in processing behavior. Conversely, small proportions of very low molar mass species can exert a plasticizing effect on an amorphous, solid polymer, leading to a reduction of glass transition temperature. This suggests that the estimation of the molar mass distribution (MMD) is important in studying and controlling the physical properties of polymers, which in turn creates the need for mathematical description of the distribution.

This paper originated from the need to mathematically reproduce MMD on the basis of its moments measured by GPC or other methods and to provide information needed for the development and engineering of the polymerization process and operating conditions.

The most common distribution functions employed to describe polymer MMD can be found in the literature.[1−6] As Peebles[1] gives a detailed description of many equations and graphs showing the interrelationship among various distributions in his review of MMD, we have limited our presentation accordingly.

The Pearson-type functions have only recently been proposed for the description of MMD in polydisperse polymer systems.[7] This almost forgotten function[8−11] turned out to be useful in various fields. Several authors used it for various purposes, for example, to describe the potential energy distribution function,[12,13] modeling the ion implantation for silicon technology,[14−16] etc.

The aim of this paper is to present a model based on the Pearson-type I distribution function,[8−11,17−21] developed to describe MMD relying on the moments' data. It describes also the estimation procedure of the number average ($\bar{M}_n$), mass average ($\bar{M}_w$), z-average ($\bar{M}_z$), and (z+1)-average ($\bar{M}_{z+1}$) values from experimentally obtained MMD curves, when the Pearson-type I distribution is proposed as the model MMD function. The model parameters ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$) are fitted using nonlinear regression.

GENERAL FORMULATION OF THE PEARSON-TYPE DISTRIBUTION FUNCTION

The problem of approximating a distribution function from a finite number of its moments is an old one, dating back to the late 19th and early 20th century. Some of the earliest

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[§] Abbreviations: PA-6,6 = nylon-6,6; PIB = polyisobutylene; PS = polystyrene; PMMA = poly(methyl methacrylate); PPO = poly(2,6-diphenyl-1,4-phenylene oxide); PVAL = poly(vinyl alcohol).

PEARSON-TYPE I DISTRIBUTION FUNCTION

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works in this area are the classical investigations by K. Pearson.[8–11] Pearson's model contained many of the best known continuous distribution functions (see for example refs 17−21).

The general Pearson-type distribution function is an approximation for the hypergeometric distribution and can be defined through differential equations[17]

$$\frac{df(x)}{f(x)} = \frac{(x - a)dx}{(b_0 + b_1 x + b_2 x^2)} \quad (1)$$

where a, b_0, b_1, and b_2 can be expressed through the moments about the mean, μ_2, μ_3, and μ_4:

$$a = -\mu_3(\mu_4 + 3\mu_2^2)/A$$

$$b_0 = -\mu_2(4\mu_2\mu_4 - 3\mu_3^2)/A$$

$$b_1 = -\mu_3(\mu_4 + 3\mu_2^2)/A$$

$$b_2 = -(2\mu_2\mu_4 - 3\mu_3^2 - 6\mu_2^3)/A$$

where

$$A = 10\mu_4\mu_2 - 18\mu_2^3 - 12\mu_3^2$$

The moments about the mean can further be expressed through the moments about the origin

$$\mu_r' = \int x^r f(x)dx$$

where $r = 1, 2, 3,$ and 4, i.e.:

$$\mu_2 = \mu_2' - \mu_1'^2$$

$$\mu_3 = \mu_3' - 3\mu_1'\mu_2' + 2\mu_1'^3$$

$$\mu_4 = \mu_4' - 4\mu_1'\mu_3' + 6\mu_1'^2\mu_2' - 3\mu_1'^4$$

A given set of moments defines a unique distribution curve. The measure of the asymmetry or skewness, Sk, of a Pearson type distribution function[17] is defined as

$$Sk = \frac{\beta_1^{1/2}(\beta_2 + 3)}{2(5\beta_2 - 6\beta_1 - 9)}$$

while the "departure" from the normal distribution called kurtosis[17] is given by

$$\gamma = \beta_2 - 3$$

where β_1 and β_2 are dimensionless quantities, i.e.:

$$\beta_1 = \frac{\mu_3^2}{\mu_2^3}$$

and

$$\beta_2 = \frac{\mu_4}{\mu_2^2}$$

The kurtosis of the normal distribution equals to zero.

It is more convenient to rewrite eq 1 in the following form

$$\frac{df(x)}{f(x)} = \frac{x \, dx}{B_0 + B_1 x + B_2 x^2} \quad (2)$$

where B_0, B_1, and B_2 are given by the expressions

$$B_0 = b_0 + (1 + b_2)a^2$$

$$B_1 = a(1 + 2b_2)$$

$$B_2 = b_2$$

Equation 2 can be solved analytically.

Various Person-type functions can be obtained depending on the nature of the roots of the expressions[17,18] in the denominator and eventually on the values of B_0, B_1, and B_2. The Pearson-type function commonly called Type I, is obtained when the denominator of eq 2 has two real roots, α_1 and α_2:

$$f(x) = (x - \alpha_1)^{\alpha_1/B_2(\alpha_1 - \alpha_2)} (x - \alpha_2)^{-\alpha_2/B_2(\alpha_1 - \alpha_2)} \quad (3)$$

where

$$\alpha_{1,2} = \frac{-B_1 \pm (B_1^2 - 4B_0B_2)^{1/2}}{2B_2}$$

It was found[22] that some of the ratios

$$\frac{\mu_r'}{\mu_{r-1}'}$$

are related to the experimentally measurable quantities $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ as follows:

$$\bar{M}_n = \frac{\mu_1'}{\mu_0'}$$

$$\bar{M}_w = \frac{\mu_2'}{\mu_1'}$$

$$\bar{M}_z = \frac{\mu_3'}{\mu_2'}$$

$$\bar{M}_{z+1} = \frac{\mu_4'}{\mu_3'}$$

Therefore, knowing the values of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$, the corresponding distribution function (MMD) is directly obtained, what means that, with Pearson-type functions the reality is embedded into the function through empirical parameters ($\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$, respectively) via the first four moments.

RESULTS AND DISCUSSION

The purpose of this section is to demonstrate the capability of the Pearson-type I distribution function to represent MMD for polymers whose number average, mass average, z-average, and (z+1)-average values are available. In addition, proposing the Pearson-type I function as a model MMD

function makes it possible to estimate different molar mass average values (i.e. $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$) from experimentally determined MMD.

The first step was to determine the capability of the Pearson-type I distribution function to compute MMD for polymers, whose $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ are known. There where the values of $\bar{M}_z$ and $\bar{M}_{z+1}$ are missing, they can be satisfactorily determined using van Krevelen's, Goedhart's, and Hoftyzer's approximate relationships. The experimentally determined "universal ratios" of MM-averages after van Krevelen et al.[23] are listed below:

$$\frac{\bar{M}_w}{\bar{M}_n} = Q$$

$$\frac{\bar{M}_z}{\bar{M}_w} \approx Q^{0.75}$$

$$\frac{\bar{M}_{z+1}}{\bar{M}_z} \approx Q^{0.56}$$

$$\frac{\bar{M}_z \bar{M}_{z+1}}{\bar{M}_w^{\,2}} \approx Q^{2.06}$$

$$\frac{\bar{M}_z}{\bar{M}_n} \approx Q^{1.75}$$

$$\frac{\bar{M}_{z+1}}{\bar{M}_n} \approx Q^{2.31}$$

$$\frac{\bar{M}_z \bar{M}_{z+1}}{\bar{M}_n^{\,2}} \approx Q^{4.06}$$

MMD functions of polymeric molecules of size $M(i)$ for different polymers were calculated using eq 3:

$$f[M(i)] = [M(i) - \alpha_1]^{\alpha_1/B_2(\alpha_1-\alpha_2)} [M(i) - \alpha_2]^{-\alpha_2/B_2(\alpha_1-\alpha_2)}$$

MMD was calculated for many examples using experimental values of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ from Table 1 in ref 23. It was found that MMD function for all listed polymers in ref 23 except PMMA and PPO can be described by the Pearson-type I distribution function. Figures 1 and 2 show the MMD for PS and PVAL. The average molar masses of the polymers are given in the caption.

The second step was to use the Pearson-type I function to estimate different molar mass averages of polymers, i.e., $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$, from the experimentally obtained MMD. The problem of fitting the Pearson-type I function to experimental MMD is reduced to finding the values of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ that will correlate MMD to the experimental data as close as possible. There are many ways to get an objective function for $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ estimation. We tried several of them and estimated the parameters that would minimize the following expression

$$O.F. = \sum_j \sum_i \left[\frac{Y_{ji}^{\exp} - Y_{ji}^{\mathrm{cal}}}{Y_{ji}^{\exp}} \right]^2$$
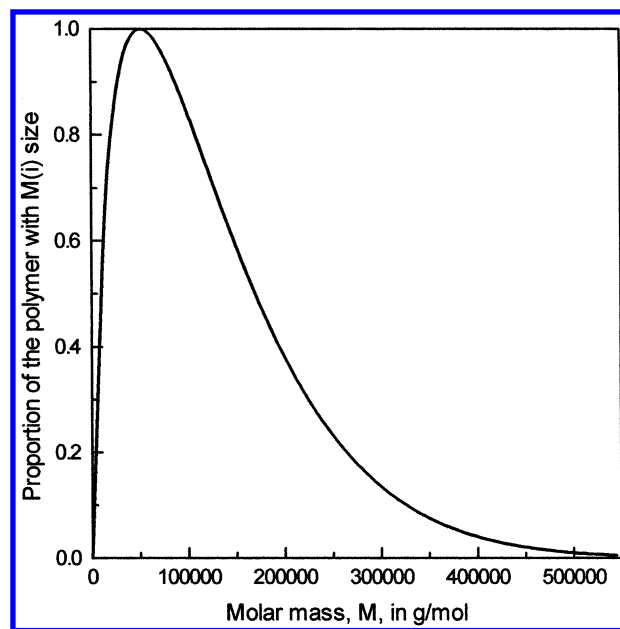

Figure 1. Distribution of molar mass in PS as calculated by the Pearson-type I MMD function [experimental values as given in ref 23: $\bar{M}_n = 74000$; $\bar{M}_w = 165000$; $\bar{M}_z = 304000$; $\bar{M}_{z+1} = 479000$].
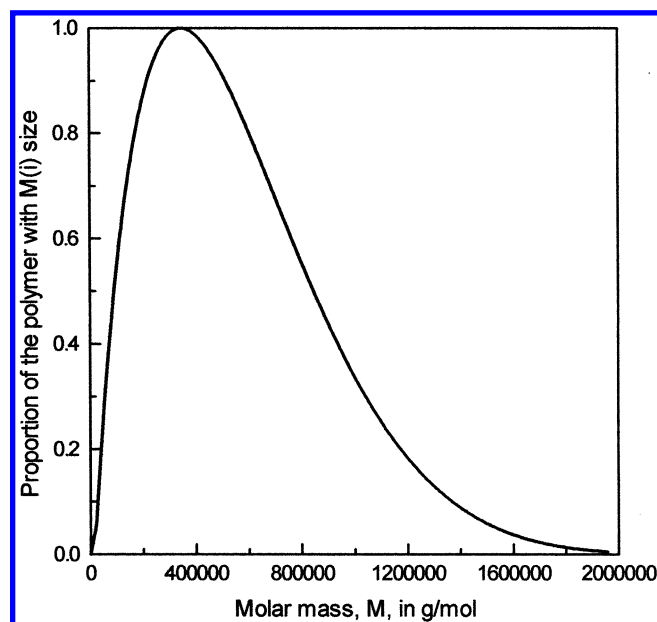

Figure 2. Distribution of molar mass in PVAL as calculated by the Pearson-type I MMD function [experimental values as given in ref 23: $\bar{M}_n = 66000$; $\bar{M}_w = 294000$; $\bar{M}_z = 941000$; $\bar{M}_{z+1} = 184600$].

where Y is a measured and calculated quantity (proportion of the polymer with $M(i)$ mass), i is summed over the number of measured variables in a data point, and j is summed over the total number of data points. The optimization algorithm used in the parameter estimation program is a modified Levenberg-Marquard algorithm[24] from the IMSL program library.

Figures 3−5 compare correlated MMD with experimental data for PA-6,6, PS, and PIB. Figure 3 refers to PA-6,6, for which the experimentally obtained information are fitted within 11% errors (the absolute mean deviations expressed in % between experimental and calculated MMD of polymer) in the MMD of polymer. The estimated average molar masses are $\bar{M}_n = 12993$, $\bar{M}_w = 25987$, $\bar{M}_z = 30877$, and
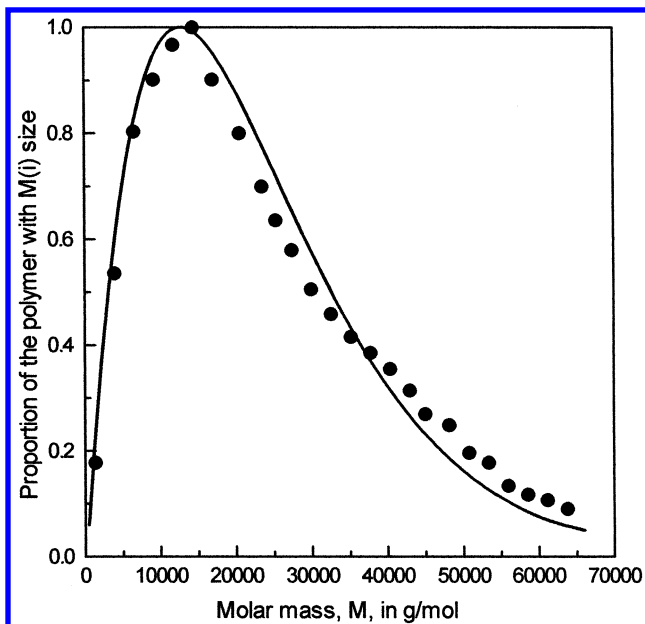
Figure 3. Distribution of molar mass in PA-6,6 (—) as correlated by the Pearson-type I MMD function, • experimental data (ref 25).

Figure 5. Distribution of molar mass in PIB (—) as correlated by the Pearson-type I MMD function, • experimental data (ref 27).
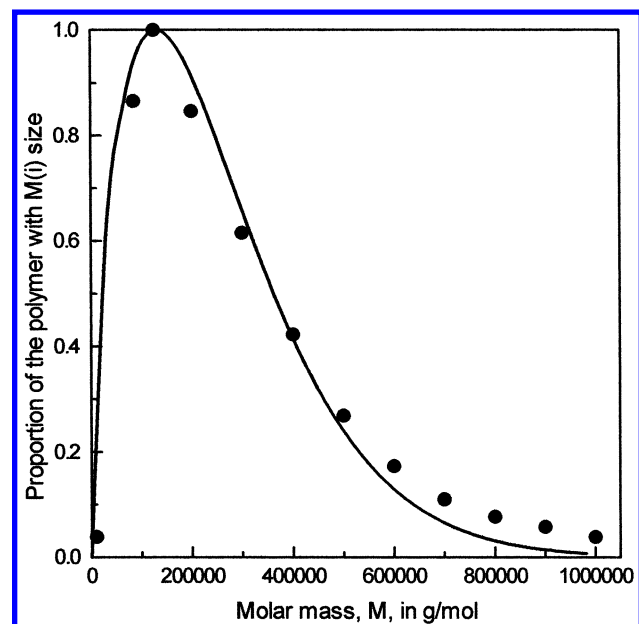

Figure 4. Distribution of molar mass in PS (—) as correlated by the Pearson-type I MMD function, • experimental data (ref 26).

$\bar{M}_{z+1} = 49486$, which is in excellent agreement with ref 25 ($\bar{M}_n = 13000$, $\bar{M}_w = 26910$). Figure 4 refers to PS for which the experimentally obtained information are fitted within 18% errors in the MMD of polymer. The estimated average molar masses are $\bar{M}_n = 100009$, $\bar{M}_w = 280000$, $\bar{M}_z = 366751$, and $\bar{M}_{z+1} = 605043$, which is in agreement with ref 26 ($\bar{M}_n = 104000$, $\bar{M}_w = 280000$, $\bar{M}_z = 455900$). Figure 5 refers to PIB for which the experimentally obtained information are fitted within 13% errors in the MMD of polymer. The estimated average molar masses are $\bar{M}_n = 21993$, $\bar{M}_w = 40099$, $\bar{M}_z = 54689$, and $\bar{M}_{z+1} = 91038$, which is in excellent agreement with ref 27 ($\bar{M}_n = \sim20000$, $\bar{M}_w = \sim46000$).

CONCLUSIONS

We developed a Pearson-type I based model, which is capable of approximating the molar mass distribution (MMD)
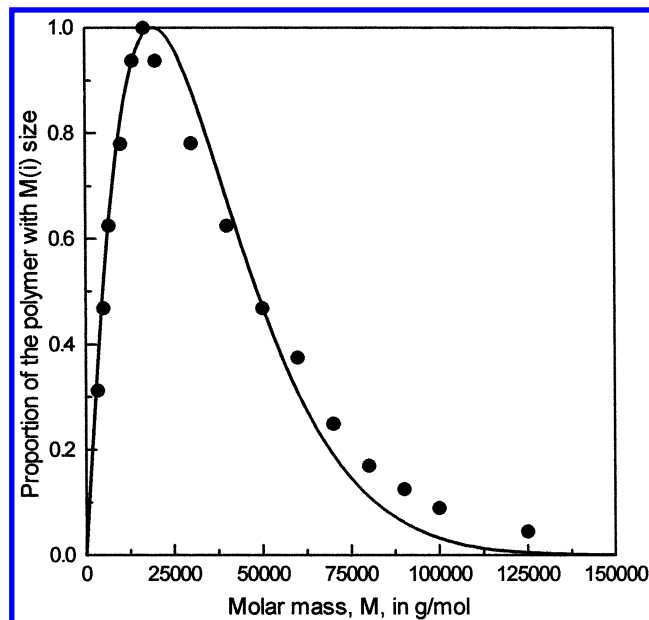
functions on the basis of its moments. In principle, a distribution function can be determined if there is sufficient input on the distribution average values. In practice, however, only the number, mass, and perhaps *z*-averages can be found, which is not enough to define the Pearson-type I distribution without making further assumptions. In this work, we have shown that the Pearson-type I distributions can be computed even though M_z and M_{z+1} values are missing, calculating them by van Krevelen et al.[23] relationships. Correlation of experimentally obtained MMD was tested on many examples, and the model was provided capable of estimating average molar masses with good agreement with experimentally obtained information. This model is quite versatile, as shown in Figures 1−5.

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