

# ESTIMATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF LINEAR HOMOPOLYMER BLENDS FROM LINEAR VISCOELASTICITY FOR BIMODAL AND HIGH POLYDISPERSE SAMPLES

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**Abstract--** This work is concerned with the approximate solution of the problem generated by the integral of first kind relating the shear relaxation modulus of entangled, linear and flexible homopolymer blends and the molecular weight distribution (MWD). Procedures are proposed to estimate the density distribution function (DDF) of the MWD from numerical solutions of the theoretical model composed by the double reptation mixing rule and a law for the relaxation time of chains in polydisperse matrixes. One procedure uses the expansion of the DDF through orthogonal polynomial functions. This expansion is formulated for two cases: a) Hermite polynomials associated with the normal-DDF and b) Laguerre polynomials associated with the gamma-DDF. The other procedure uses the mean value theorem of continuum functions, which turns out the integral problem into a differential form. Calculations are carried out with dynamic rheometric data of linear viscoelasticity for samples of polydimethylsiloxane, polypropylene and polybutadiene. High values of polydispersity are considered. The predictions of the DDF through these procedures compare well with experimental data of size exclusion chromatography (SEC).

**Keywords--** Bimodal Molecular Weight Distribution, High Polydispersity, Hermite and Laguerre Series, Double Reptation Model, Linear Flexible Homopolymer Blends.

## I. INTRODUCTION

The relation between the linear viscoelastic functions and the molecular weight distribution (MWD) involving linear and flexible homopolymer blends is a subject of intensive research at present, because several theoretical and numerical aspects must be still elucidated. This work considers one aspect, which consists on finding an approximate solution for the density distribution function (DDF)  $f_w(M)$  from the double reptation-mixing rule (Tsenoglou, 1991; des Cloizeaux, 1990a, 1990b and 1992) where data of the relaxation modulus  $G(t)$  are required. This problem is ill-posed in the sense

that many solutions of the DDF can be found satisfying this mixing rule expressed through an integral of first kind (see, for example, de Hoog, 1980 and Baker, 1977). From a practical point of view, one has to observe that the processability of polymeric compounds and the mechanical properties of final crosslinked products are significantly affected by the macromolecular statistics. Therefore, the knowledge of the DDF of a polymeric network obtained via dynamic rheometry can be useful as far as one can choose the physical solution from many ones available from this method of determination.

In this section, we define first the problem found in the determination of the DDF from dynamic rheometry, to propose then procedures for its numerical evaluation. The theoretical model is basically composed by the double reptation mixing rule (see also Anderssen and Mead, 1998),

$$\sqrt{\frac{G(t)}{G_N^o}} = \int_{\ln M_c}^{\infty} [\sqrt{f(t, \lambda)}]_{\lambda=\lambda(M)} f_w(M) d \ln M \quad (1)$$

and a relaxation law  $\lambda = \lambda(M, f_w(M)) \equiv \lambda(M)$  for the maximum relaxation time  $\lambda$  of a monodisperse fraction expressed as function of both  $M$  and DDF. In Eqn. (1),  $G_N^o$  is the plateau modulus of the blend. In addition, the relaxation modulus of the flexible, linear and monodisperse polymer is designated  $g(t, \lambda)$ , and the reduced relaxation function  $f(t, \lambda)$  is approximated by a single exponential as follows,

$$\sqrt{f(t, \lambda)} = \left( \frac{g(t, \lambda)}{g_N^o} \right)^{\frac{1}{2}} = \exp \left\{ -\frac{t}{2\lambda} \right\} \quad (2)$$

where  $g_N^o$  is the rubbery plateau value of the monodisperse fraction that is independent of the molecular weight  $M_w$  when  $Po=1$  and for an ideal network where  $M_c/M_n \ll 1$ . The critical molecular weight required to form a network is  $M_c = 2M_e$ , and hence,  $f_w(M)=0$  for  $M < M_c$  is a constrain of the DDF. Also,  $M_e = \rho RT/G_N^o$  is the average molecular weight between entanglements,  $\rho$  is the polymer

density,  $T$  is the absolute temperature and  $R$  is the universal gas constant.

For a polydisperse homopolymer blend, the prediction of the relaxation time  $\lambda = \lambda(M, f_w(M))$  is required and it is a matter of research at present (see, for example, Cassagnau *et al.*, 1993). In particular,  $\lambda = K_r M^b$  with  $b \cong 3.4$  is only valid for near monodisperse polymers (see also, Daoud and de Gennes, 1979; Green *et al.*, 1984; Montfort *et al.*, 1984 and 1986; Green and Kramer, 1986; Klein, 1986; Marin *et al.*, 1987; Wasserman and Graessley, 1996). In a wider context of analysis, the relaxation law  $\lambda(M, f_w(M))$  of chains in the melt network for the case of relatively high polydispersity,  $Po = M_w / M_n > 1$ , has been approximated as follows (Deiber *et al.*, 1997),

$$\lambda(M, f_w(M)) = \frac{K_r M^b}{1 + \frac{K_r}{K_t} M^{b-\alpha} \int_{-\infty}^{\infty} \frac{f_w(S) d \ln S}{S^{b-b_k}}} \quad (3)$$

where  $K_t \cong K_r / z M_e^\alpha$ . This equation indicates that the confined M-chain in the molecular tube may follow the tube constraint release through Rouse or Zimm modes of relaxation, which are proportional to  $M^\alpha$  with  $1 \leq \alpha \leq 2$ . Additionally the S-chains forming the tube of the M-chain cannot reptate independently, and hence, a correction factor  $0 \leq b_k \leq 1$  is introduced (Klein, 1986; Montfort *et al.*, 1984 and 1986; Marin *et al.*, 1987).

With the DDF, the basic macromolecular weight averages are readily defined,

$$M_w = \int_{-\infty}^{\infty} M f_w(M) d \ln M \quad (4)$$

$$\frac{1}{M_n} = \int_{-\infty}^{\infty} \frac{1}{M} f_w(M) d \ln M \quad (5)$$

and the moment  $\mu_n$  of order  $n$  of the DDF is expressed through the following equation,

$$\mu_n = \int_{-\infty}^{\infty} (\ln M - \langle \ln M \rangle)^n f_w(M) d \ln M \quad (6)$$

where,

$$\langle \ln M \rangle = \int_{-\infty}^{\infty} \ln M f_w(M) d \ln M \quad (7)$$

These last equations will be used later for further calculations.

Two practical situations emerge from the above theory. In fact, it is clear that the mixing rule with the single exponential-reduced relaxation function and the relaxation law have to be solved to obtain either  $G(t)$  (direct problem) or  $f_w(M)$  (inverse problem). In the direct problem (see, for example, Wasserman and Graessley, 1992; Carrot *et al.*, 1996) experimental data of  $f_w(M)$  from SEC are introduced into Eqn. (1) to evaluate  $G(t)$ ; then this function is compared with rheometric values obtained from the mechanical spectrometer to visualize consistency of the results. We

will not consider this situation because it does not provide us the DDF. In the inverse problem, however, one uses rheometric data  $G(t)$  in Eqn. (1) to evaluate  $f_w(M)$ , which may be compared with SEC data to analyze the accuracy of both the relaxation theory and the DDF obtained from this method. In this last aspect, there exist several proposals in the literature to invert the mixing rule to predict the DDF function. Unfortunately, this task leads one to a non-unique shape of the DDF. In this sense, it is generally concluded that the inverse problem requires further research to assure that a reliable DDF is predicted. This situation is even more complicated when the DDF may present more than one peak (multimodal DDF). Additionally, for relatively high polydispersity (say  $Po > 2$ ) the ill-posed problem placed by the integral of first kind also requires the complete knowledge of the relaxation law  $\lambda = \lambda(M, f_w(M))$  that relates the relaxation time  $\lambda$  of a polymer chain with its molecular weight  $M$ , including necessarily the effect of  $f_w(M)$  in this expression.

In a wider context of analysis, it should be established that either the direct as well as the inverse problems lead one to important conclusions concerning the different mechanisms of chain relaxation in polydisperse melts. In fact, we have shown previously that the prediction of polydispersity of polymer samples through the inverse problem was a severe test for the validation of molecular theories (Deiber *et al.*, 1997) although the DDF could not be uniquely defined.

Therefore, the purpose of this work is specifically to find numerically an approximate solution of the ill-posed problem generated by the integral of first kind relating the shear relaxation modulus of entangled, linear and flexible homopolymer blends and the molecular weight distribution (MWD). Procedures are presented here to evaluate the DDF of the MWD from the model composed by the double reptation mixing rule and the law for the relaxation time of chains in polydisperse matrixes. One procedure uses the expansion of the DDF through orthogonal polynomial functions. This expansion is formulated for two cases: a) Hermite polynomials associated with the normal-DDF and b) Laguerre polynomials associated with the gamma-DDF. The other procedure uses the mean value theorem of continuum functions, which turns out rigorously the integral problem to a differential form. Calculations are carried out with dynamic rheometric data of linear viscoelasticity for samples of polybutadiene, polypropylene and polydimethylsiloxane. The predictions of the DDF are compared with experimental data of size exclusion chromatography (SEC). Its application to binary blends will allow us to show the quality of the procedures proposed here to evaluate the DDF. The calculations are also extended to high polydisperse polymer melts. For practical reasons, Table 1 summarizes the description of the samples studied in this work, with the codes to designate them.

**Table 1.** Polymer samples studied and references cited.

Code	Sample Composition (wt %)	Reference
PB3	Polybutadiene binary mixture: 63.8% of $M_w = 355000$ and 26.2% of $M_w = 70900$ .	Rubinstein and Colby (1988)
PB4	Polybutadiene binary mixture: 76.8% of $M_w = 355000$ and 23.2% of $M_w = 70900$ .	
B50	Polydimethylsiloxane binary mixture: 50% of $M_w = 343800$ and 50% of $M_w = 100300$ .	
D75	Polydimethylsiloxane binary mixture: 75% of $M_w = 343800$ and 25% of $M_w = 183600$ .	Peirotti <i>et al.</i> (1998)
L4	Near monodisperse Polydimethylsiloxane of $M_w = 276400$ .	
PP1	Polydisperse Polypropylene of $M_w = 348500$ .	Cassagnau <i>et al.</i> (1993)
C1	Polydisperse Polypropylene of $M_w = 165000$ .	
D1	Polydisperse Polypropylene of $M_w = 212000$ .	Carrot <i>et al.</i> (1996)

## II. BASIC SOLUTION OF THE INVERSE PROBLEM

A DDF  $f_w(M)$  that satisfies the ill-posed problem (Eqns (1) to (3)) is designated here a basic solution in the sense that it fits Eqn. (1) for numerical data  $G(t)$ , within an acceptable error that is intrinsic to any numerical algorithm used. In this work we take as the basic solution that one already described in our previous work (Deiber *et al.*, 1997), where the solution of the inverse problem involved in Eqn. (1) is obtained with the following density distribution function,

$$f_w(M) = \sum_{i=1}^N a_i \delta_i(M - M_i) \quad (8)$$

In Eqn. (8),  $\delta_i(M - M_i)$  are Dirac delta functions and  $a_i$  are constant coefficients to be determined in the inversion process of Eqn. (1).

Since the density distribution function must be normalized, from Eqn. (8) it is simple to show that,

$$\int_{-\infty}^{\infty} f_w(M) d \ln M = \sum_{i=1}^N \frac{a_i}{M_i} = 1 \quad (9)$$

By combining Eqns (1), (2) and (8), the result is,

$$\sqrt{\frac{G(t)}{G_N^o}} = \sum_{i=1}^N \left( \frac{a_i}{M_i} \exp\left(-\frac{t}{2\lambda_i}\right) \right)_{\lambda_i(M_i)} \quad (10)$$

where  $\lambda_i = \lambda_i(M_i)$  is given by Eqn. (3).

Therefore, Eqn. (10) can be solved when numerical data of  $G(t)$  versus  $t$  are available as they are obtained from experimental data of moduli  $G'(\omega)$  and  $G''(\omega)$  of dynamic rheometry and the use of Fourier transform to convert frequency  $\omega$  to time  $t$ . With the above formulation of the double reptation mixing rule (Eqns (3) and (10)) numerical values for the spectrum  $\{a_i\} - \{M_i\}$  with  $i = 1..W$  can be found. The numerical problem thus generated is nonlinear and it has to be solved iteratively. In this sense, one defines a set of values  $\{M_i\}$  with dimension  $N$ , where the molecular weights are equally spaced in the decimal logarithmic scale, and calculate the set  $\{a_i\}$  by using a fitting algorithm with the constraint that  $a_i > 0$  for  $i = 1..W$  (see details in the work of Peirotti *et al.*, 1998). Here,  $W \leq N$  is the resulting number of modes that minimizes the fitting error in Eqn. (10) and keeps  $a_i > 0$ . In our calculations, this error is less than around 0.5 % when the numerical prediction of  $\sqrt{G(t)/G_N^o}$  and its value obtained from rheometry are compared. In this numerical algorithm, the prediction of polydispersity  $Po = \sum_{i=1}^N a_i \sum_{i=1}^N a_i / M_i^2$  and mass average molecular weight  $M_w = \sum_{i=1}^N a_i$  shall approximate the values of  $Po = M_w / M_n$  and  $M_w$  obtained from SEC or absolute measurements like membrane osmometry for  $M_n$  and low angle light scattering (LALLS) for  $M_w$  (see also Steeman, 1998).

It must be pointed out here that with the basic solution, the molecular parameters  $(K_r, \alpha, b_k, z)$  of Eqn. (3) are determined, and hence, the expression for the relaxation time  $\lambda = \lambda(M, f_w(M))$  is available now for further calculations. Thus, by using Eqns (6), (7) and (8), the moments  $\mu_n$  of  $f_w(M)$  can be calculated because they are rather independent of the ill-posed problem associated to the evaluation of the DDF, as it is analyzed in the next section.

## III. MOMENTS OF THE DDF

The purpose of this section is to illustrate that the moments of any density distribution function satisfying the ill-posed problem of Eqn. (1) are determined by the numerical data  $G(t)$  placed at this equation (see Mead, 1994 and Anderssen *et al.*, 1997). In addition, one may infer that these moments can be directly calculated, as a first approximation, through a DDF obtained as a solution of Eqn. (1) within a small numerical error (Section II). This statement can be proved in particular if we assume that the relaxation law is  $\lambda = K_r M^b$  (relaxation by reptation corrected by contour length fluctuations only). Therefore, after successive

integration by parts of both sides of Eqn. (1), it is simple algebra to show that this equation can be expressed as follows:

$$\int_0^\infty dt_n \int_{t_n}^\infty dt_{n-1} \int_{t_{n-1}}^\infty dt_{n-2} \cdots \int_{t_2}^\infty \sqrt{\frac{G(t)}{G_N^o}} dt_1 dt_2 \cdots dt_n = \frac{1}{K_r^n} \int_{-\infty}^\infty M^{nb} f_w(M) d \ln M = \frac{\mu_{nb}^*}{K_r^n} \quad (11)$$

Equation (11) indicates that a DDF  $f_w(M)$  that is a solution of Eqn. (1) can be used to calculate the moments  $\mu_{nb}^*$ , since these moments are completely determined and defined by the  $G(t)$  data only. A similar and more general result can be obtained from the analysis presented by Mead (1994) where the Mellin transform is applied to Eqn. (1) with  $\lambda = K_r M^b$ . Thus, by multiplying Eqn. (1) by  $t^{\kappa-1}$  and integrating the time  $t$  in the domain  $[0, \infty)$ , one obtains,

$$\mu_n^* = \left\{ \text{MT} \left[ \sqrt{G(t)/G_N^o} \right] / \left( \Gamma(\kappa) [2K_r]^\kappa \right) \right\}_{\kappa = \frac{n}{b}} \quad (12)$$

where MT indicates the Mellin transform operator. Eqn. (12) shows us that the moments  $\mu_{bk}^*$  can be obtained from the Mellin transform of the numerical data  $G(t)$ , according to the choice of the arbitrary constant  $\kappa$ , to get integral and nonintegral moments. Concerning the moments  $\mu_n^*$ , it should be observed that the above demonstrations are valid for both asymptotic responses of the relaxation law, when  $\kappa = n/b$  and  $\kappa = n/\alpha$ . In fact, for low and high values of molecular weights one gets  $\lambda \propto M^b$  and  $\lambda \propto M^\alpha$ , respectively, as inferred from Eqn. (3). In this sense, a relevant work of Anderssen and Mead (1998) generalized the result expressed through Eqn. (12) by using a linear functional strategy to evaluate the moments  $\mu_n^*$ . In this strategy, these moments are rigorously calculated when the relaxation law (Eqn. (3)) can be inverted to give

$$M = \lambda^{-1}(\lambda) = \lambda^{-1} \left( \frac{1}{2\zeta} \right), \text{ where } \zeta \text{ shall be defined as}$$

variable in the Laplace transform. In particular, we use here the direct calculation of the moments having mainly into account that in this process, the inversion of  $\lambda = \lambda(M, f_w(M))$  is rather complex for polydisperse polymers.

In fact, since the relaxation law for the region of intermediate  $M$  does not follows neither  $\lambda \propto M^b$  nor  $\lambda \propto M^\alpha$ , below it is shown that moments  $\mu_n$  of the DDF can be calculated numerically with some degree of invariance, which in turn depends on intrinsic errors associated to the method used to obtain  $f_w(M)$  from the ill-posed problem.

Thus, we found, for instance, five solutions of Eqn. (1), which were obtained with different numbers of initialization modes  $N = 14, 17, 28, 29$  and  $30$  giving effective modes  $W = 8, 10, 13, 12$  and  $11$ , respectively. The fitting error  $E_2$  of the five solutions obtained for the values of  $N$  used was not allowed to be greater than 1%. The relevant result found was that the prediction of moments  $\mu_n$  with any of these solutions were close one another as far as  $E_2$  was kept small, despite they were effectively different solutions. This result was also consistent with a simple analysis showing that the moments  $\mu_n$  were functions of the moments  $\mu_n^*$ . This last consideration has been also validated numerically in this work.

We conclude here that although Eqn. (1) generates an ill-posed problem in the evaluation of the DDF, in the sense that many solutions can be found satisfying the integral of first kind, the moments  $\mu_n$  and  $\mu_n^*$ , are rather unique numerically and are determined from the knowledge of numerical values of the relaxation modulus as indicated in Eqns (11) and (12). Therefore, it is clear that we can use the set of moments thus determined, to look for a numerical method in the determination of  $f_w(M)$ , which is the purpose of the section below.

#### IV. ESTIMATION OF THE DDF FROM SERIES EXPANTIONS

##### Hermite Polynomials

From the fundamentals of statistics (Kendall, 1977) it is shown that, in principle, a DDF can be fully determined from the knowledge of its moments. Having this result in mind, in this work the moments of the basic DDF are calculated from Eqns (6), (7) and (8) as follows:

$$\mu_n = \sum_{i=1}^N \frac{a_i}{M_i} (\ln M_i - \langle \ln M \rangle)^n \quad (13)$$

$$\langle \ln M \rangle = \sum_{i=1}^N \frac{a_i}{M_i} \ln M_i \quad (14)$$

From the previous sections, it is clear that the basic DDF has not necessarily the shape of the physical DDF. This last one is associated to that obtained with SEC as a first approximation (see also, Steeman, 1998). In this sense, we will find here an approximate  $f_w(M)$  obtained from the moments evaluated with Eqns (13) and (14). Therefore, to proceed in this way, it is recommended to convert the DDF to the standard mode by defining a new statistical variable  $\xi = (\ln M - \langle \ln M \rangle) / \sigma$  where  $\sigma = \sqrt{\mu_2}$  is the standard deviation. Thus the moments of the standard DDF  $f_w^s(\xi)$  are readily found to be  $\theta_n = \mu_n / \sigma^n$  satisfying  $\theta_1 = 0$  and  $\theta_2 = 1$ . The standard DDF can be expanded in series of Hermite polynomials  $H_n(\xi)$  for  $n = 1 \dots \infty$ , together with the standard normal-DDF,

$$\alpha(\xi) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2}\right) \quad (15)$$

Therefore the following expression is obtained (Kendall, 1977),

$$f_w^s(\xi) = \sum_{j=0}^{\infty} c_j H_j(\xi) \alpha(\xi) \quad (16)$$

where,

$$H_n(\xi) = \xi^n + \sum_{k=1}^K (-1)^k \frac{n^{[2k]}}{2^k k!} \xi^{n-2k} \quad (17)$$

and

$$c_n = \frac{1}{n!} \int_{-\infty}^{\infty} f_w^s(\xi) H_n(\xi) d\xi \quad (18)$$

with  $n \geq 2K$ . From Eqn. (18), coefficients  $c_n$  for  $n=1.. \infty$ , can be written in terms of moments  $\theta_n$ . Kendall (1977) presents detailed expressions to calculate these coefficients until  $n=8$ . For the present work, a numerical code was prepared with the condition that Eqn. (16) could be calculated to any arbitrary number of modes (usually  $n$  can be as large as 16 in the cases analyzed in this work) with,

$$c_n = \frac{1}{n!} \left\{ \theta_n + \sum_{k=1}^K (-1)^k \frac{n^{[2k]}}{2^k k!} \theta_{n-2k} \right\} \quad (19)$$

The number of modes of this series shall be determined with the following constraints, which allow one to cut the series at a specific and optimum value of  $n$ :

$$\left\{ \int_{-\infty}^{\infty} f_w^s(\xi) d\xi \right\} - 1 \leq 10^{-5} \quad (20)$$

$$f_w^s(\xi) + \varepsilon \geq 0 \quad (21)$$

Equation (20) is the normalization of the standard DDF, while Eqn. (21) does not allow the DDF to take negative values outside a small negative range  $-\varepsilon$  associated to typical numerical errors. In our algorithm  $\varepsilon \approx 10^{-3}$ . These equations are crucial to define the number of moments  $\mu_n$  required to evaluate the DDF. Therefore, one must calculate the series for high  $n$  to find the solution that satisfies the proposed constraints.

Then the standard DDF,  $f_w^s(\xi)$ , can be readily converted back to  $f_w(M)$  through the following expression,

$$f_w(M) = \sum_{j=1}^N \frac{c_j(\theta_n)}{\sqrt{2\pi\sigma^2}} H_j\left(\frac{[\ln M - \langle \ln M \rangle]}{\sigma}\right) \exp\left(-\frac{[\ln M - \langle \ln M \rangle]^2}{2\sigma^2}\right) \quad (22)$$

In the discussion section, we present and analyze results obtained with Eqn. (22) for the samples studied in this work, according to Table 1.

### Laguerre Polynomials

With a procedure similar to that presented above, the DDF can be expanded through Laguerre polynomials. For this purpose the moments required are,

$$\mu'_n = \int_{\ln M_c}^{\infty} (\ln M)^n f_w(M) d \ln M \quad (23)$$

which can be also expressed,  $\mu'_n = \sum_{i=1}^N a_i / M_i (\ln M_i)^n$ .

In order to avoid calculations with high values of moments  $\mu'_n$  we define, in addition,  $\bar{\mu}_n = \mu'_n / (\ln M_w)^n$ . Therefore, with  $f(X) = f_w(M) \ln(M_w)$  one can express  $f(X)$  as follows:

$$f(X) = \sum_{n=0}^{\infty} k_n L_n^{(b)}(X) G(X) \quad (24)$$

where  $G(X) = (b/a) X^{b-1} \exp(-X) / \Gamma(b)$  is the gamma-DDF in terms of the new variable  $X = \frac{b \ln M}{a \ln M_w}$ . Also,

$a = \bar{\mu}_1 / \bar{\mu}_0$  and  $b = a^2 / [\bar{\mu}_2 / \bar{\mu}_0 - a^2]$ . Consequently, Laguerre polynomials are,

$$L_n^{(b)} = \sum_{j=0}^n (-1)^j \frac{n! (n+b-1)!}{j! (n-j)! (n+b-1-j)!} \left( \frac{b \ln M}{a \ln M_w} \right)^{n-j} \quad (25)$$

From the orthogonal properties of Laguerre polynomials, one readily obtains (Cramér, 1974),

$$k_n = \frac{(b-1)!}{(n+b-1)! n!} \int_0^{\infty} f(X) L_n^{(b)}(X) dX \quad (26)$$

giving thus,

$$k_n = \sum_{j=0}^n (-1)^j \frac{(b-1)! (b/a)^{n-j}}{j! (n-j)! (n+b-1-j)!} \bar{\mu}_{n-j} \quad (27)$$

The DDF obtained in terms of moments  $\bar{\mu}_n$  is for this case,

$$f_w(M) = \frac{b}{a(b-1)!} \left( \frac{b \ln M}{a \ln M_w} \right)^{b-1} \exp\left(-\frac{b \ln M}{a \ln M_w}\right) \left[ \bar{\mu}_0 + \sum_{j=3}^N k_n L_n^{(b)} \left( \frac{b \ln M}{a \ln M_w} \right) \right] \ln M_w \quad (28)$$

Once more, the number of modes of this series shall be determined with the constraints imposed by Eqns (20) and (21) to cut the series at a specific and optimum value of  $n$ .

## V. ESTIMATION OF THE DDF FROM THE MEAN VALUE THEOREM OF CONTINUOUS FUNCTIONS

In this section, we show that the integral of first kind (Eqn. (1)) can be reduced rigorously to the differential form. Although this form is still ill-posed mathematically in the sense that its solution is not free from the experimental noises present also in the basic solution described in Section II, it is useful for guessing the approximate shape of the DDF in practical situations, in a rather easy procedure. This procedure also allows one to visualize the conceptual structure of the basic theory, which involves a neat relationship

between time  $t$ , relaxation time  $\lambda$  and molecular weight  $M$ .

Therefore, by using the mean value theorem of continuous functions (Korn and Korn, 1968), Eqn. (1) can be expressed as follows,

$$\sqrt{\frac{G(t)}{G_N^o}} = \exp\left(-\frac{t}{2\lambda(M_c)}\right) \int_{M_c}^M \frac{f_w(M')}{M'} dM' + \exp\left(-\frac{t}{2\lambda(M_{max})}\right) \int_M^{M_{max}} \frac{f_w(M')}{M'} dM' \quad (29)$$

where  $M_{max}$  is defined here as the maximum molecular weight at the value of which  $f_w(M) \rightarrow 0$ . Although  $M_{max}$  has been defined for the purposes of applying properly the theorem in the closed domain  $[M_c, M_{max}]$ , we found that indeed the numerical values obtained for  $f_w(M)$  are invariant enough when the domain  $[M_c, \infty)$

is used with  $\exp\left(-\frac{t}{2\lambda(M_{max})}\right) \rightarrow 1$ , thus making the value  $M_{max}$  arbitrary for  $M_{max} \gg M_w$ . In fact, the DDF tends rapidly to zero for  $M \gg M_w$ . In addition, Eqn. (29) has been obtained by realizing that  $\exp\left(-\frac{t}{2\lambda(M)}\right)$  is continuous and increasing in  $[M_c, \infty)$ . Of course,  $f_w(M)$  shall be continuous in the same interval and hence Eqn. (8) is not any more applicable to this particular procedure.

Since the DDF must be normalized, as required in Eqn. (10), one readily finds,

$$\int_M^{M_{max}} \frac{f_w(M')}{M'} dM' = 1 - \int_{M_c}^M \frac{f_w(M')}{M'} dM' \quad (30)$$

Then combining Eqns (29) and (30), the following cumulative distribution function  $F_w(M)$  is yielded,

$$F_w(M) = \frac{\int_{M_c}^M f_w(M') dM'}{\int_{M_c}^M f_w(M') dM'} = \frac{\sqrt{\frac{G(t)}{G_N^o}} - \exp\left(-\frac{t}{2\lambda(M_{max})}\right)}{\exp\left(-\frac{t}{2\lambda(M_c)}\right) - \exp\left(-\frac{t}{2\lambda(M_{max})}\right)} \quad (31)$$

Equation (31) establishes that from each value of  $t$  there exists a value of  $M$ . Thus a relationship  $t \leftrightarrow M$  can be found if the DDF is known in this equation. Nevertheless, since  $f_w(M)$  is not known in the context of this mathematical analysis because the basic solution of  $f_w(M)$  described in Section II is not unique, one may establish the relationship  $t \leftrightarrow M$  on physical terms only. In this sense, it is well known that  $t = \lambda(M, f_w(M))$  indicates that chains with molecular weights greater than  $M'$  giving  $\lambda' > t$  have not fully erased the molecular tube of confinement at time  $t$ , in

the evolution of a sudden shear relaxation rheometry, i.e., for the value of the relaxation modulus  $G(t)$  (see Doi and Edwards, 1986). Therefore, this relationship allows one to differentiate Eqn. (31) with respect to  $\ln M$  to obtain the DDF explicitly as follows:

$$f_w(M) = \frac{d}{d \ln M} \left[ \frac{\sqrt{\frac{G(t)}{G_N^o}} - \exp\left(-\frac{t}{2\lambda(M_{max})}\right)}{\exp\left(-\frac{t}{2\lambda(M_c)}\right) - \exp\left(-\frac{t}{2\lambda(M_{max})}\right)} \right]_{t=\lambda(M)} \quad (32)$$

where  $\lambda(M, f_w(M)) \equiv \lambda(M)$  is given by Eqn. (3) as obtained in Section II. One should observe that the integral  $\int_{-\infty}^{\infty} \frac{f_w(S) d \ln S}{S^{b-b_k}}$  in Eqn. (3) is a particular moment of  $f_w(M)$  and it may be calculated with the basic solution as described in Section II. We conclude here that the following differential expression analyzed previously (see, for example, Wasserman and Graessley, 1992; Mead, 1994; Deiber *et al.*, 1997),

$$f_w(M) = -\frac{d}{d \ln M} \left[ \sqrt{\frac{G(t)}{G_N^o}} \right]_{t=\lambda(M)} \quad (33)$$

for the particular reduced relaxation function  $\sqrt{f(t, \lambda)} = 1 - u(t - \lambda)$  (here,  $u(t - \lambda)$  is the Heaviside step function; i. e.,  $u = 0$  for  $t < \lambda$  and  $u = 1$  for  $t \geq \lambda$ ) is an asymptotic result of the differential solution corresponding to the double reptation-mixing rule given by Eqn. (32) above.

## VI. ESTIMATION OF THE DDF FROM THE RELAXATION SPECTRUM

A method that evaluates the DDF from data of the relaxation spectrum  $H(\lambda)$  (Thimm *et al.*, 2000) is available in the literature and we found that it can be applied to any relaxation law  $\lambda(M, f_w(M))$  apart from the case  $\lambda = K_r M^b$ . We generalized this solution, the version of which is reported below according to the nomenclature of our work as follows:

$$f_w(M) = \frac{M}{\beta \sqrt[\beta]{G_N^o}} \frac{H(\lambda(M))}{\lambda(M)} \exp\left(-\frac{t}{\beta \lambda(M)}\right) \frac{d\lambda(M)}{dM} \left\{ \int_M^{\infty} \frac{H(\lambda(M'))}{\lambda(M')} \frac{d\lambda(M')}{dM'} \exp\left(-\frac{t}{\lambda(M')}\right) dM' \right\}^{\left(\frac{1}{\beta}-1\right)} \quad (34)$$

where  $\lambda(M) \equiv \lambda(M, f_w(M))$ . Therefore, we find here that the physical situation implying  $t = \lambda(M) \equiv \lambda(M, f_w(M))$  in Section V is consistent with the fact that Eqn. (34) becomes independent from time  $t$ .

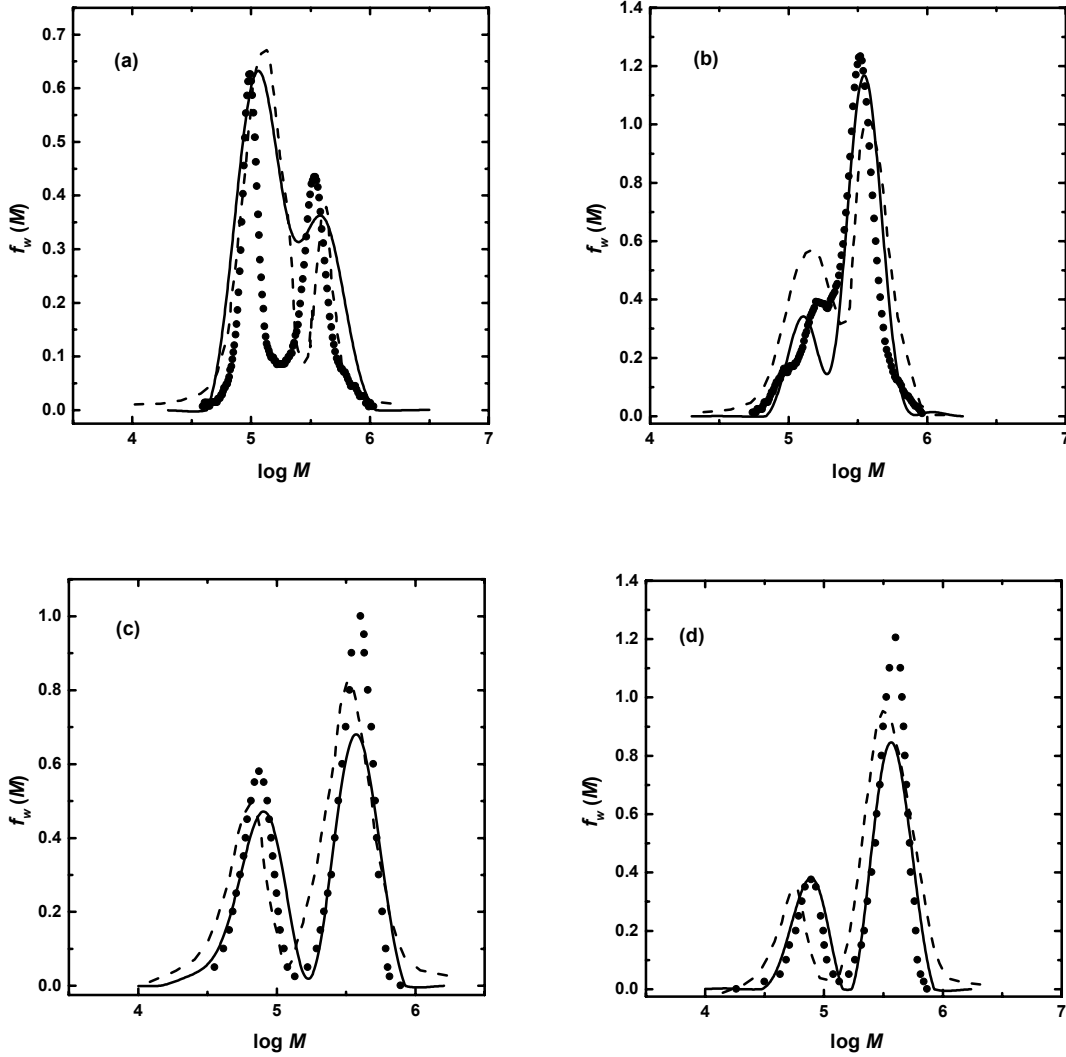
This equation can be also reduced to the same differential form as described in Section V because (Ferry, 1970),

$$H(\lambda) \equiv -\frac{d[G(t)]_{t=\lambda}}{d \ln \lambda} \quad (35)$$

In fact, Eqn. (35) inserted into Eqn. (34) yields a differential form that is exactly equal to Eqn. (33).

## VII. RESULTS AND DISCUSSION

The values obtained for the molecular parameters ( $K_r, \alpha, b_k, z$ ) are evaluated according to Section II with the smallest fitting error allowed by the numerical code. They vary consistently within the expected ranges of values that are predicted by molecular theories as described previously (Daoud and de Gennes, 1979;



**Figure 1:** Density distribution function as function of logarithm of molecular weight. (●) Refers to SEC data. Full line and dashed lines are the numerical predictions with the HP and LP, respectively. (a) Sample B50 ( $Po=1.56$ ). (b) Sample D75 ( $Po=1.27$ ). (c) Sample PB3 ( $Po=1.95$ ). (d) Sample PB4 ( $Po=1.65$ ).

Green *et al.*, 1984; Montfort *et al.*, 1984 and 1986; Green and Kramer, 1986; Klein, 1986; Marin *et al.*, 1987; Wasserman and Graessley, 1996). Unfortunately, samples are not available at the same temperature, and hence, the comparison of these parameters from one another shall be carried out carefully (see also Deiber *et al.*, 1997 and Peirotti *et al.*, 1998). In general, it is consistently found that  $\alpha$  decreases and  $b_k$  increases for

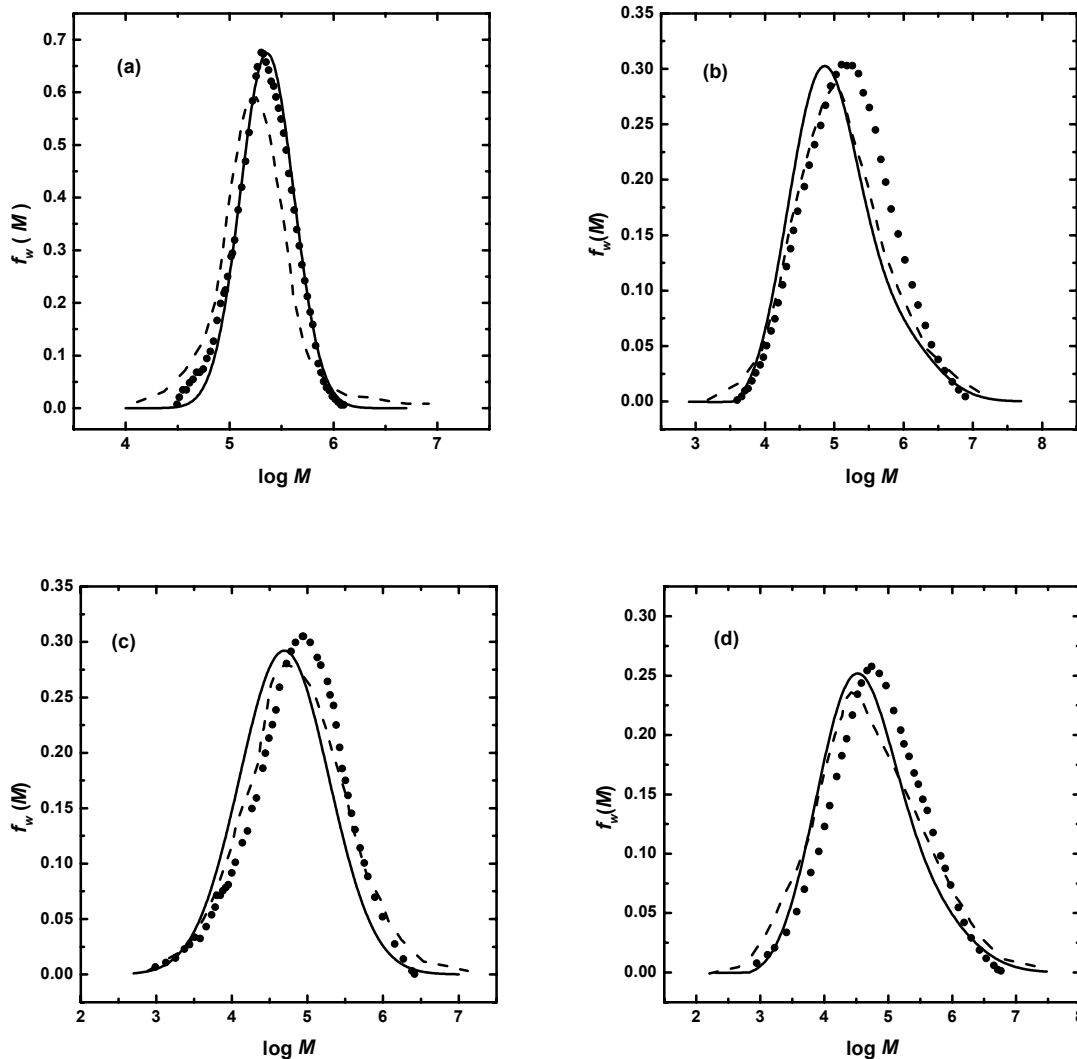
increasing  $Po$  and decreasing  $M_w$  at constant temperature. We found that the numerical predictions of  $M_w$  and  $Po$  compared well with those values obtained through the SEC technique, indicating a good convergence of the numerical code used to evaluate Eqn. (10). These results yield a set of basic solutions as described in Section II, which allow us to analyze and discuss the numerical prediction of the DDF through the

Hermite (HP), Laguerre (LP) and mean value theorem (MVTP) procedures presented in Sections IV and V, respectively. With this purpose, Fig. 1 compares the numerical and experimental values of the DDF for binary blends (samples B50, D75, PB3 and PB4). At most 16 moments are required to satisfy constrains imposed to the HP (Eqns (20) and (21)) for sample PB3. When the same case is solved with the LP, at least 40 moments are needed.

Although the estimation of bimodal DDFs of binary blends is a severe test of the procedures presented in

Sections III and IV, it is also required to verify if they are still appropriate for samples with at least  $Po > 5$ . In this sense, the prediction of the DDF with the HP and LP for polydisperse samples PP1, C1 and D1 compare well with SEC data as it is illustrated in Fig. 2.

A remarkable good prediction of the DDF is obtained for the near monodisperse sample L4 (Fig. 2-a) with the HP (three moments are required by Eqns (20)



**Figure 2:** Density distribution function as function of logarithm of molecular weight. (●) Refers to SEC data. Full line and dashed lines are the numerical predictions with the HP and LP, respectively. (a) Sample L4 ( $Po=1.47$ ). (b) Sample PP1 ( $Po=6.1$ ). (c) Sample C1 ( $Po=6.6$ ). (d) Sample D1 ( $Po=10.6$ ).

and (21)). For this sample a simpler relaxation law applies. Thus, Eqn. (3) is numerically close to  $K_r M^b$  because  $\alpha \approx 2$  and  $b_k \rightarrow 0$ . This result indicates that Eqn. (3) is relevant in the context of the theory under analysis mainly for binary and polydisperse blends. Since the relaxation law is less known for these cases, in

future works special emphasis shall be placed in accompanying the search for robust algorithms determining a unique DDF with the appropriate relaxation law of complex macromolecular networks.

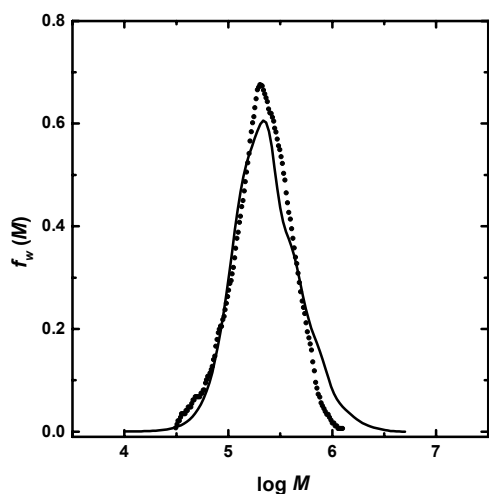
It is also found that for both binary and polydisperse samples, the number of moments required in the HP and LP are greater as  $Po$  increases. In addition, in these



procedures, binary blends require more moments than polydisperse samples despite these last ones have higher  $Po$ .

Although the comparisons between GPC data and the DDFs provided by the HP and LP do not show a complete agreement, the predictions of these procedures are satisfactory according to the experience obtained from previous works analyzing this ill-posed problem. One should also observe that dynamic rheometric data may present, in general, an uncertainty of  $\pm 5$  to 10% mainly in the low frequency zone, which may affect the evaluation of the high molecular weight tail of the MWD. The same uncertainty can be found in GPC techniques as discussed critically by Steeman (1998) and Thimm *et al.* (1999).

The solution obtained with the MVTP (full lines in Fig. 3) is a good approximation to the SEC data. Thus, we conclude that the MVTP can be a practical tool for cross checking the prediction of the DDF from dynamic rheometry when one has the complete expression for the relaxation time of chains in polydisperse matrixes (Eqn. (3)) obtained from the basic solution. In general the MVTP gives a good approximation to the DDF although wiggles are expected due to experimental noises that are typically found in converting the integral problem into the differential one, which is also ill-posed in this sense.



**Figure 3:** Density distribution function as function of logarithm of molecular weight for Sample L4. (●) Refers to SEC data. Full line is the numerical prediction with the MVTP and also the result obtained with Eqns (34) and (35).

Finally, it is appropriate to mention here that synthetic numerical data for both the relaxation modulus and the DDF with different degrees of random noises were also generated numerically to test the validity of the HP and LP (see, for instance, Honerkamp, 1989). Since the calculation of the DDF-moments involved numerical integration with the expected smoothing effect, results were not affected significantly by the

imposed pseudo-experimental noises, validating thus the procedures proposed here through the numerical strategy usually reported in the literature.

## VIII. CONCLUSIONS

The relation between the shear relaxation modulus of entangled, linear and flexible homopolymer blends and the molecular weight distribution is used to find the DDF  $f_w(M)$ . The procedures proposed here to estimate the DDF could be applied to binary and high polydisperse blends.

The results presented in Section VII are placing the prediction of the DDF from dynamic rheometry as a promissory technique to be used for practical situations and applications, including polymers that are candidates to be analyzed via SEC; this last technique being more complicated experimentally in the sense that a calibration curve shall be obtained with several standard polymers. This work shows that we have at hand a tool to predict the DDF through the mechanical spectrometer combined with the two basic data ( $M_n$  and  $M_w$ ) provided directly by osmometry and LALLS.

## IX. A CONSIDERATION FOR FURTHER RESEARCH

At the present time, most of the works published in the literature consider the simple relaxation law  $\lambda = K_r M^b$  that is valid for near monodisperse samples only. This work presents, however, approximate procedures to deal with rather complex relaxation laws like that described by Eqn. (3). It is then clear that further research is required to find both a robust algorithm and a complete relaxation law so that an improved evaluation of the DDF from the ill-posed problem is possible. Based on our results, it is also clear that researches must place emphasis on improving numerical algorithms that can consider multimodal and high polydisperse samples, where the relaxation law must include complex relaxations mechanisms of chains. For instance, tube constraint release coupled to plastization effects of the polymer matrix due to the presence of molecular fractions with MWD within the range  $M \leq M_c$  is a challenging problem at present (Deiber *et al.*, 2002).

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