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Linear viscoelastic relaxation modulus of polydisperse poly(dimethylsiloxane) melts containing unentangled chains

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Abstract

This work analyzes the relationship between the shear relaxation modulus of entangled, linear and flexible homopolymer blends and its molecular weight distribution (MWD) when a fraction of the sample contains chains with molecular weight M lower than the effective critical molecular weight between entanglements Mc_{eff}. This effective critical parameter is defined in terms of the critical molecular weight between entanglements M_c of the bulk polymer that forms the physical network and the effective mass fraction Wc_{eff} of the unentangled chains. In the terminal zone of the linear viscoelastic response, the double reptation mixing rule for blended entangled chains and a modified law for the relaxation time of chains in a polydisperse matrix are considered, where the effect of chains with $M < Mc_{\mathrm{eff}}$ is included. Although chain reptation with contour length fluctuations and tube constraint release are still the relevant mechanisms of chain relaxation in the terminal zone when the polydispersity is high, it is found that the presence of a fraction of molecules with $M < Mc_{\mathrm{eff}}$ modifies substantially the tube constrain release mode of chain relaxation. In this sense, a modified relaxation law for polymer chains in a polydisperse entangled melt that includes the effect of the MWD of unentangled chains is proposed. This law is validated with rheometric data of linear viscoelasticity for well-characterized polydimethylsiloxane (PDMS) blends and their MWD obtained from size exclusion chromatography. The short time response of PDMS, which involves the glassy modes of relaxation, is modeled by considering Rouse diffusion between entanglement points of chains with $M > Mc_{\mathrm{eff}}$. This mechanism is independent from the MWD. The unentangled chains with $M < Mc_{\mathrm{eff}}$ occluded in the polymer network also follow Rouse modes of relaxation although they exhibit dependence on the MWD. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Diluted entangled polymer melts; Unentangled molecular weight distribution; Polymer relaxation mechanisms

1. Introduction

Polymer melts are characterized, basically, through the macromolecular statistics of the polymer matrix. These statistics depend on the specific formulations of polymer blends, and involves typically the mass average molecular weight, M_w, the number average molecular weight, M_n, giving a polydispersity $P_o = M_w/M_n \geq 1$, and the molecular weight distribution (MWD) expressed through the density distribution function (DDF) $f_w(M)$. In this work this DDF is based on mass fractions.

In the last decade, several studies have been carried out to find a relationship between the relaxation modulus $G(t)$ of linear viscoelasticity with $f_w(M)$, when all the chains are long enough to conform an entangled polymer melt [1–4]. All these works consider the particular case in which $M > M_c$, where the critical molecular weight required to form a physical network is $M_c \cong 2M_e$. Here $M_e \cong \rho RT/G_N^0$ is the average molecular weight between two consecutive entanglements, ρ the polymer density, T the absolute temperature, R the universal gas constant and G_N^0 is the plateau modulus of the undiluted entangled polymer melt.

The interplay between the MWD and the retardation spectra for the case of homopolymer blends containing a significant fraction of unentangled chains of low molecular weight ($M < M_c$) was considered by Orbon and Plazek for different bimodal blends [5]. In this study different mechanisms of chain relaxation were analyzed. More recently, several works have presented theoretical developments for the same type of blends where a relation between $G(t)$ and $f_w(M)$ was considered in a wide range of molecular weights, from the terminal to the glassy zones of the viscoelastic material [6–8].

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At present, the aim of this subject is to find a complete theory able to predict the relaxation of shear stress within the linear viscoelastic response when the polymer blend contains a fraction of homopolymer chains with molecular weight lower than the critical molecular weight between entanglements. This is due, in part, to the lack of a complete knowledge of the relaxation law $\lambda(M)$ that relates the relaxation time λ of a polymer chain with its molecular weight M, when the surrounding polymeric matrix is rather complex (polydisperse and diluted with short chains). For monodisperse polymers and $M > M_c$, it is known that $\lambda_r = K_r M^b$ with $b \sim 3.4$, and the chain relaxation is controlled mainly by reptation with contour length fluctuations [9,10]. For high values of P_o, several studies showed that an effective relaxation time of chains is required. When this effective relaxation time is taken into account, a good agreement between theory and experimental data is obtained [1,3]. The effect of unentangled chains occluded in the melt has been much less analyzed [5]. It is known, however, that small chains should affect significantly the relaxation time of long chains apart from the dilution effect yielded on the plateau modulus. In the asymptotic case for concentrated entangled solutions, the effective plateau modulus G_N^{eff} and the effective critical molecular weight between entanglement Mc_{eff} follow power law dependencies as functions of the polymer volume fraction φ. This particular case has two aspects that make less difficult and more tractable the search for correlations of G_N^{eff} and Mc_{eff} with φ: (a) the presence of a low molecular weight solvent, the value of which is much smaller than M_c of the entangled polymer, (b) the polymer volume fraction φ is composed of chains with molecular weights substantially higher than M_c. Therefore, the evaluation of an effective volume fraction of the entangled polymer chains φ_{eff} corresponding to chains with $M > Mc_{\mathrm{eff}}$ is not required. In this sense, Raju et al. [11] and Marin et al. [12] found that $G_N^{\mathrm{eff}} \cong G_N^0 \varphi^{2.25}$ and $Mc_{\mathrm{eff}} \cong M_c \varphi^{-1.25}$ for narrow MWDs of different linear and star polybutadienes, polystyrenes and polyisoprenes in several low molecular weight solvents (diluters). For the case proposed here, the dilution of the entangled polymer chains is formulated in such a way that the whole MWD covers the right and left ranges of M around M_c (also around Mc_{eff}). Consequently, the short chains of the homopolymer added have a significant effect on the melt elasticity as well as on the MWD, apart from modifying the chain segmental mobility (solvents modify this last property only). This implies that in addition to the evaluation of the effective Mc_{eff}, the corresponding effective volume fraction φ_{eff} of polymer must be also found due to the shift $M_c \rightarrow Mc_{\mathrm{eff}}$ of the critical molecular weight between entanglements, which is a direct consequence of the interplay between unentangled and entangled chains. Thus, due to the addition of unentangled homopolymer chains to the entangled chains covering the range around M_c, a fraction of entangled chains becomes a part of the unentangled polymer fraction. The extension of these concepts to homopolymer blends (valid for concentrated entangled solutions) is considered a first approximation at this stage. This aspect will be discussed with more detail in the Section 4.

The problem placed in this work has both theoretical and practical importance. One involves the relationship between the MWD and rheological responses of plasticized blends of high P_o, in order to understand better the complex dependence of rheological parameters and rheometric functions on the MWD represented either through $f_w(M)$ or its moments. In fact, simple relationships involving the first moments like M_w and M_n (alternatively P_o) may be found only under very special physical conditions and rather ideal topological constraints in the network microstructure. The other consideration consists, for instance, of understanding the formulation of hot-melt adhesives by adding to the basic polymer a tackifying resin to soften and improve the tack of the compound [8].

Therefore, the purpose of this work is to study polydisperse polydimethylsiloxane (PDMS) homopolymer blends containing a significant fraction of unentangled chains of low molecular weight ($M < Mc_{\mathrm{eff}}$), either theoretically and experimentally, as an extension to previous works [5,6–8,11,12]. Since the effect of polydispersity and unentangled chains on the relaxation modulus is still an important problem of practical interest that must be solved from fundamental principles [6], we briefly reconsider first the theoretical framework by analyzing the sequence of relaxation mechanisms associated with both the physical network and the unentangled fraction. Then, a description of the experimental program characterizing these samples via rheology and size exclusion chromatography (SEC) is presented in detail. Finally, a comparison between numerical predictions from theory and experimental data concerning $G(t)$ is carried out to find out the relevant mechanisms of chain relaxation and to discuss some aspects for further research on the subject. Results related to the prediction of MWD and P_o are also presented for the samples studied in this work.

2. Theoretical background

Since the PDMS blends analyzed in this work contain a significant fraction of molecules of low molecular weight ($M < M_c$) it is convenient to split the DDF into two parts. For this purpose it is required to introduce an effective critical molecular weight Mc_{eff} which accounts the presence of the fraction of unentangled chains [8,13]. Thus, one can define $Mc_{\mathrm{eff}} = M_c(1 - Wc_{\mathrm{eff}})^{-\delta}$ ($\delta \approx 1.25$ for concentrated solutions) where Wc_{eff} is associated with the effective mass fraction of chains with $M < Mc_{\mathrm{eff}}$, and it can be estimated as indicated in Section 3. Here, Wc_{eff} has the same value as the volume fraction $(1 - \varphi_{\mathrm{eff}})$ because a homopolymer blend is considered. In this context of analysis, the DDF of chains composing the entangled polymer chains (physical network) is designated $f_w^E(M)$. The other is $f_w^U(M)$ and gives the statistics of the unentangled chains with $M < Mc_{\mathrm{eff}}$. Therefore, both DDFs must be normalized individually as follows:

$$\int_{-\infty}^{\ln Mc_{\mathrm{eff}}} f_{\mathrm{w}}^{\mathrm{U}}(M)\mathrm{d}\ln M = 1 \tag{1}$$

$$\int_{\ln Mc_{\mathrm{eff}}}^{\infty} f_{\mathrm{w}}^{\mathrm{E}}(M)\mathrm{d}\ln M = 1. \tag{2}$$

These DDFs can be readily converted to the global DDF $f_{\mathrm{w}}(M)$ obtained from the classical SEC technique, as it is described in Section 3. Eqs. (1) and (2) indicate that two sets of relevant statistical parameters are obtained for the two polymer fractions. Thus, $M_{\mathrm{w}}^{\mathrm{E}}$ and $M_{\mathrm{w}}^{\mathrm{U}}$ are the mass average molecular weights of the entangled and unentangled chain fractions, respectively. Similarly, we also define and evaluate the polydispersities $P_{\mathrm{o}}^{\mathrm{E}}$ and $P_{\mathrm{o}}^{\mathrm{U}}$ and the number average molecular weights $M_{\mathrm{n}}^{\mathrm{E}}$ and $M_{\mathrm{n}}^{\mathrm{U}}$ for later use, where throughout this work the super indexes E and U refer to entangled and unentangled chain fractions, respectively. Consequently, we can define different contributions to the relaxation modulus $G(t)$ from each monodisperse fraction of the blend, as they are described later [8].

2.1. Contribution of entangled chains to the relaxation modulus

The relaxation modulus of flexible, linear and monodisperse polymer chains with $M > Mc_{\mathrm{eff}}$ is described through the double reptation mixing rule [14,15]

$$\sqrt{\frac{G_{\mathrm{N}}(t)}{G_{\mathrm{N}}^{\mathrm{eff}}}} = \int_{\ln Mc_{\mathrm{eff}}}^{\infty} \left[\exp\left(-\frac{t}{2\lambda_{\mathrm{N}}(M)}\right)\right] f_{\mathrm{w}}^{\mathrm{E}}(M)\mathrm{d}\ln M \tag{3}$$

where $G_{\mathrm{N}}^{\mathrm{eff}} \cong G_{\mathrm{N}}^{0}\ (1 - Wc_{\mathrm{eff}})^{\nu}$ is the effective rubbery plateau of the diluted or plasticized physical network. In Eq. (3), the dilution effect of the unentangled chains has been accounted through the term $(1 - Wc_{\mathrm{eff}})^{\nu}$. The exponent ν takes values between 2 and 2.25 for concentrated solutions [8]. In Eq. (3), $\lambda_{\mathrm{N}}(M)$ is the maximum relaxation time of a monodisperse fraction expressed as function of M. This function, designated relaxation law in this work, must be found taking into account both effects: high polydispersity values of the polymer and the presence of a fraction of molecules with $M < Mc_{\mathrm{eff}}$, the mass fraction of which is Wc_{eff}. The relaxation of any monodisperse polymer fraction of the blend is approximated, in Eq. (3), to a single exponential function of time t as in previous works [1,3].

Eq. (3) is valid for the long time response (terminal zone) and can be used to fit experimental data of $G(t)$ for $t > t_{\mathrm{c}}$ where $t_{\mathrm{c}} \cong 1/\omega_{\mathrm{c}}$ and ω_{c} is the frequency at which the relaxation moduli of dynamic rheometry satisfy $G'(\omega_{\mathrm{c}}) \cong G''(\omega_{\mathrm{c}})$. Thus, up to frequencies in the vicinity of ω_{c}, Eq. (3) is the most relevant contribution to the relaxation modulus in the frequency domain.

In general, $G_{\mathrm{N}}^{\mathrm{eff}}$ is masked by the glassy modes that become evident after the cross over frequency. These modes may appear in the rubbery plateau when the dynamic test is carried out on a polymeric sample of high P_{o} containing an unentangled chain fraction. In this work, $G_{\mathrm{N}}^{\mathrm{eff}}$ is obtained from the cross over of dynamic moduli $G'(\omega)$ and $G''(\omega)$ which are measured experimentally as described later [16]. For this purpose it is known that $G_{\mathrm{N}}^{0} \cong 2.0 \times 10^{5}$ Pa at 20 °C for PDMS chains forming the undiluted physical network [17].

For the more general situation considered in this work, the relaxation law used in Eq. (3) must include the effect of short chains associated with the unentangled chain fraction. Therefore, the relaxation law described previously for high P_{o} samples [3] is modified in the present work in order to consider this new system. Thus, it is well-known that the relaxation law for reptation with contour length fluctuations does not apply to polydisperse samples (e.g. $P_{\mathrm{o}} > 2$). In fact, for binary blends of linear homopolymers, another relaxation mechanism exists, which is designated tube constraint release (also known as tube renewal in the literature). When $M > S$, this relaxation time $\lambda_{\mathrm{t}}(M, S)$ can be expressed as,

$$\lambda_{\mathrm{t}}(M,S) \approx \frac{\lambda_{\mathrm{r}}(S)}{S^{b_{\mathrm{k}}}}\left(\frac{M}{M_{\mathrm{e}}}\right)^{\alpha}. \tag{4}$$

Thus, the polymer matrix that forms the tube has a molecular weight S and relaxes proportionally to λ_{r} (reptation with contour length fluctuation) corrected by a factor b_{k} [18–21]. The exponent α in Eq. (4) indicates that the confined chain follows the tube constrain release through Rouse to Zimm modes of relaxation. Additionally, Green and Kramer [22] generalized this result to describe unentangled matrices ($S < Mc_{\mathrm{eff}}$) and found

$$\lambda_{\mathrm{t}} \propto SM^{2} \tag{5}$$

when Rouse modes were still important and

$$\lambda_{\mathrm{t}} \propto SM^{1.5} \tag{6}$$

for the case of high dilution effects, i.e. for Zimm modes. From Eqs. (5) and (6), it is clear that when an unentangled chain fraction is occluded in the entangled polymer melt, an additional relaxation mechanism for the M-chain associated with the tube constraint release can be expressed,

$$\lambda_{\mathrm{t}} \propto SM^{\alpha} \tag{7}$$

where $\mathrm{S} < \mathrm{Mc}_{\mathrm{eff}}$ and $\mathrm{M} > \mathrm{Mc}_{\mathrm{eff}}$.

In practice, the two fractions composing the sample are polydisperse in general, then $P_{\mathrm{o}}^{\mathrm{E}} > 1$ and $P_{\mathrm{o}}^{\mathrm{U}} > 1$. Thus, for polydisperse polymers, we cannot use directly Eqs. (4) and (7) to describe the tube release mechanism. In fact, the expression for the global relaxation time of an M-chain in a polydisperse matrix with an occluded fraction of unentangled chains may be expressed as $\lambda_{\mathrm{N}} = \lambda_{\mathrm{N}}\ (M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M))$ where the DDF of both polymer fractions are considered now. Following our previous work [4], the global relaxation time of a chain is accounted through two parts: one involves reptation with contour length fluctuations and the other is a consequence of the tube renewal effect, which is important when the polydispersity of the sample is substantially high and when unentangled chains are present in the network. Since it is possible to assume that the macromolecular diffusion in both processes (reptation and tube renewal) are additive and relaxation times scale inversely with diffusion coefficients [23], an approximation for the global relaxation time can be obtained [1]

$$\lambda_{\mathrm{N}}\left(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M)\right) = \frac{\lambda_{\mathrm{r}}(M)}{1 + \dfrac{\lambda_{\mathrm{r}}(M)}{\lambda_{\mathrm{t}}\left(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M)\right)}} \tag{8}$$

where λ_{r} and λ_{t} are the reptational and the tube renewal relaxation times, respectively. The tube renewal is now dependent on both $f_{\mathrm{w}}^{\mathrm{E}}(M)$ and $f_{\mathrm{w}}^{\mathrm{U}}(M)$ and it is also clear that the global relaxation time of a chain in a polydisperse matrix shall carry information on the MWDs of both the entangled and unentangled chain fractions.

Eq. (3) cannot be solved for $G(t)$ with Eq. (8) without an appropriate expression for $\lambda_{\mathrm{t}} = \lambda_{\mathrm{t}}$ $(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M))$. Therefore, since the average diffusion of the polymer matrix may be defined as the weight average of the diffusion coefficients of each monodisperse fractions, the expression for $\lambda_{\mathrm{t}} = \lambda_{\mathrm{t}}$ $(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M))$ is obtained from Eqs. (4) and (7) pairwise averaged with the DDFs, as follows [3]

$$\frac{1}{\lambda_{\mathrm{t}}\left(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M)\right)} = \int_{\ln Mc_{\mathrm{eff}}}^{\infty} \frac{f_{\mathrm{w}}^{\mathrm{E}}(S)\mathrm{d}\ln S}{K_{\mathrm{t}}' S^{b-b_{\mathrm{k}}} M^{\alpha}} + \int_{-\infty}^{\ln Mc_{\mathrm{eff}}} \frac{f_{\mathrm{w}}^{\mathrm{U}}(S)\mathrm{d}\ln S}{K_{\mathrm{t}}'' S M^{\alpha}} \tag{9}$$

to obtain from Eq. (8) the global relaxation time,

$$\lambda_{\mathrm{N}}\left(M, f_{\mathrm{w}}^{\mathrm{E}}(M), f_{\mathrm{w}}^{\mathrm{U}}(M)\right) = \frac{K_{\mathrm{r}} M^{b}}{1 + z Me_{\mathrm{eff}}^{\alpha} M^{b-\alpha}\left(\displaystyle\int_{\ln Mc_{\mathrm{eff}}}^{\infty} \frac{f_{\mathrm{w}}^{\mathrm{E}}(S)\mathrm{d}\ln S}{S^{b-b_{\mathrm{k}}}} + \int_{-\infty}^{\ln Mc_{\mathrm{eff}}} \frac{f_{\mathrm{w}}^{\mathrm{U}}(S)\mathrm{d}\ln S}{S}\right)} \tag{10}$$

where the constant values are approximated according to $K_{\mathrm{t}}' \cong K_{\mathrm{t}}'' \cong K_{\mathrm{r}}/zMe_{\mathrm{eff}}^{\alpha}$ with $Me_{\mathrm{eff}} \approx Me_{\mathrm{eff}}/2$.

In addition, in the high frequency range, the sample experiences the re-equilibration of monomers between fixed entanglement points. This process does not depend on the overall chain length and it can be described as a Rouse relaxation of the monomeric fractions of the entangled chains. This physical aspect also indicates that for the short time response, i.e. for $t < t_{\mathrm{c}}$, there is an additional contribution of the physical network to the relaxation modulus involving chains with $M > Mc_{\mathrm{eff}}$. This contribution, designated here as $G_{\mathrm{E}}(t)$, does not depend on the MWD of chains and can be expressed as [8]

$$G_{\mathrm{E}}(t) = G^{0} \exp\left(-\frac{t}{\lambda_{\mathrm{E}}}\right) \tag{11}$$

where the constant $G^{0} \cong G_{\mathrm{R}}^{0}$ $(1 - Wc_{\mathrm{eff}})$ is the contribution of the effective glassy modulus and $\lambda_{\mathrm{E}} = K_{\mathrm{R}} Me_{\mathrm{eff}}^{2}$ is the Rouse relaxation time of the chain portions comprised between two consecutive entanglements. Here, G_{R}^{0} is the contribution to the Rouse glassy mode of the undiluted physical network [13]. Eq. (11) is generally neglected when homopolymer blends have the MWD in the range $M_{\mathrm{c}} < M < \infty$ (there is not an unentangled chain fraction) and the experimental range considered is $t > t_{\mathrm{c}}$, as it is the most frequent case reported in the literature when polymer melts are studied.

In addition, for relatively high frequencies, starting from around the cross over frequency, the polymer experiences the re-equilibration of segments along the overall chain. Thus, the chains recover its natural curvilinear monomer density through the slip-links, which keep the relative positions approximately fixed. This microstructural phenomenon has also associated a Rouse mode of relaxation, but now, the whole length of the chain is involved. Viovy reported an expression describing this relaxation process [24]. In the linear viscoelastic response (small shear strain) the re-equilibration of segments along the overall chain can be neglected as described by Doi and Edwards [10].

2.2. Contribution of the unentangled chain fraction to the relaxation modulus

The unentangled chain fraction can be considered occluded in the physical network acting as a solvent of relatively high molecular weight, which is still less than Mc_{eff}. Therefore, one expects a contribution of Rouse type to the relaxation modulus designated here $G_{\mathrm{R}}(t)$ and expressed as [6,7]

$$\frac{G_{\mathrm{R}}(t)}{G^{0}} = \int_{-\infty}^{\ln Mc_{\mathrm{eff}}} \exp\left(-\frac{t}{\lambda_{\mathrm{R}}(M)}\right) f_{\mathrm{w}}^{\mathrm{U}}(M)\mathrm{d}\ln M \tag{12}$$

where $\lambda_{\mathrm{R}} = K_{\mathrm{R}} M^{2}$ indicates that the occluded chain fraction ($M < Mc_{\mathrm{eff}}$) follows the Rouse mode of relaxation. Therefore, Eq. (12) applies only for short times, viz. for $t < t_{\mathrm{c}} \approx 1/\omega_{\mathrm{c}}$.

3. Experimental

Nine polydisperse homopolymer blends containing a significant unentangled chain fraction of low molecular weight ($M < M_{\mathrm{c}}$, and hence $M < Mc_{\mathrm{eff}}$) were prepared from 11 commercial PDMS samples (Table 1) by mixing the proportions indicated in Table 2. All the polymers and blends were characterized using SEC in a Waters model 440 Liquid Chromatograph at room temperature. Toluene was used as mobile phase at a flow rate of 1 ml/min. A set of four PL gel columns (500, 10^{3}, 10^{4} and 10^{6} Å) was employed. Number and weight average molecular weights (M_{n} and M_{w}) of the linear polymers were obtained by calibrating the SEC columns with narrow MWD polystyrene (PS) standards (Press Chem. Corp.). Benoit universal calibration [25] was used and the Mark–Houwink constants for PDMS and PS in

Table 1
Commercial PDMS samples used to prepare polydisperse homopolymer blends containing a diluent fraction of low molecular weigth ($M < M_c$) as reported in Table 2

Polymer	M_n (Da)	M_w (Da)	$P_o = M_w/M_n$
PDMS-A	5 000	11 900	2.38
PDMS-B	7 900	22 100	2.80
PDMS-C	22 500	35 900	1.60
PDMS-D	35 300	55 500	1.57
PDMS-E	41 500	64 400	1.55
PDMS-F	46 300	70 900	1.53
PDMS-G	51 800	83 700	1.62
PDMS-H	72 600	111 200	1.53
PDMS-I	101 100	144 700	1.43
PDMS-J	108 900	250 900	2.30
PDMS-K	331 800	505 700	1.52

toluene at 20 °C were obtained from the literature [26]. The adopted values for the Mark–Houwink constants were $K = 4.16 \times 10^{-3}$ dl/g and $a = 0.788$ for PS and $K = 2.43 \times 10^{-3}$ dl/g and $a = 0.84$ for PDMS. The resulting molecular weights are reported in Tables 1 and 3 [27].

Rheological measurements of the PDMS samples were carried out in a Rheometrics Dynamics Analyzer RDA-II at temperatures ranging from −40 to 150 °C. Shear flow was obtained by dynamic tests using 25 mm diameter parallel plates. Strain sweep tests were performed for the different samples at predetermined temperatures and frequencies in order to determine the operable strain range where linear viscoelasticity is achieved. The storage G' and the loss G'' moduli were measured for frequencies ranging from 0.05 to 500 s^{-1}. Master curves for G' and G'' were obtained using the time–temperature superposition principle at 20 °C as reference temperature [17]. With this procedure the range of measured frequencies was increased by almost two decades.

Numerical values of $G(t)$ versus t are obtained from the viscoelastic spectrum evaluated with experimental data of moduli $G'(\omega)$ and $G''(\omega)$ and the use of Fourier transform to convert frequency ω to time t in the interrelations between functions. For this purpose, the generalized Maxwell model in the asymptotic limit of small shear strains is used to process the experimental data obtained from the mechanical spectrometer. At this step, G_N^{eff} is determined and Wc_{eff} and Mc_{eff} are calculated.

4. Results and discussion

Numerical values of $G(t)$ obtained in Section 3 are fitted with the equations modeling the relaxation modulus (Eqs. (3), (11) and (12)). The numerical problem thus generated is nonlinear and it has to be solved iteratively through an algorithm described elsewhere [4,28] (also see Appendix A). In this sense, sets of values $\{M_i\}$ with dimension N for each one of the relaxation modulus $G_N(t)$ and $G_R(t)$ described before are defined, where the molecular weights are equally spaced in the decimal logarithmic scale. The resulting number of modes yielded by the numerical solutions minimizes the errors in the process of fitting Eqs. (3), (11) and (12) to numerical data of $G(t)$. In our calculations, these errors are less than around 0.5% when the model prediction of $G(t)$ and its value obtained from rheometry are compared. In this numerical algorithm, the predictions of polydispersities and mass average molecular weights shall approximate the values M_w^E, M_w^U, P_o^E, and P_o^U calculated from data provided by SEC (see Table 3). We point out here that with the solution of this numerical problem, the molecular parameters α, b_K, K_r, z, and K_R are determined together with an estimation of $f_w(M)$, and hence, the expressions for the relaxation times $\lambda_N = \lambda_N\ (M, f_w^E(M), f_w^U(M))$ and $\lambda_R = K_R M^2$ are available. It is also found that $\alpha \approx 2$ and $b_K \approx 0.5$ for the nine blends considered and these values were within the expected physical ranges described before [4]. Tables 4 and 5 present the numerical values of the molecular parameters for these samples. In these tables, the weight average molecular weights and polydispersities obtained from SEC are also reported for comparison with the theoretical predictions.

From the theory analyzed before and the proposed relaxation time of the physical network, it is clear that the total relaxation modulus $G(t)$ is the sum of different expressions: $G_N(t)$, $G_E(t)$, and $G_R(t)$. In this sense, Figs. 1 and 2 show that model predictions are in good agreement with numerical

Table 2
Composition of the polydisperse homopolymer blends containing a diluent fraction of low molecular weight ($M < M_c$)

Blend	Weight percentage of each commercial PDMS sample (w/w%) in the blends										
	PDMS-A	PDMS-B	PDMS-C	PDMS-D	PDMS-E	PDMS-F	PDMS-G	PDMS-H	PDMS-I	PDMS-J	PDMS-K
B1	12.7	12.7	7	7	7	7	7	7.2	7	12.7	12.7
B2	15	15	7	7	7	4	4	4	7	15	15
B3	20	16	8	8	2	2	2	8	8	10	16
B4	18	15	9.9	9.9	–	–	–	6.9	7.1	15	18.2
B5	50	–	–	–	–	–	–	–	–	–	50
B6	30	–	–	–	40	–	–	–	–	–	30
B7	20	–	–	–	30	–	–	–	–	30	20
B8	19.8	19.8	–	–	19.8	–	–	–	–	19.8	20.8
B9	39.3	–	–	–	–	–	30	–	–	–	30.7

Table 3
SEC characterization and deconvolution values of M_w and P_o for the homopolymer blends

Blend	M_w (Da)			$P_o = M_w/M_n$		
	SEC	Deconvolution		SEC	Deconvolution	
		M_w^U	M_w^E		P_o^U	P_o^E
B1	136 900	20 300	244 300	7.96	2.26	2.01
B2	150 600	22 600	306 400	9.02	2.33	1.98
B3	143 400	21 200	303 200	8.44	2.09	1.95
B4	169 200	22 600	368 600	12.53	2.80	1.91
B5	253 400	14 800	532 800	20.27	2.13	1.84
B6	198 700	21 700	374 700	10.63	2.19	2.27
B7	209 700	17 600	313 200	10.81	2.33	2.13
B8	175 000	22 500	394 700	12.32	2.58	1.81
B9	161 400	21 900	372 400	12.42	2.72	1.80

data obtained from dynamic measurements. In these figures the cross over time $t_c \approx 1/\omega_c$ indicates the expected onset of glassy modes.

Fig. 3 shows the estimation of $f_w(M)$ that results from the fitting procedure used to obtain the numerical curves depicted in Fig. 1 for sample B5 and Fig. 2 for sample B7. The predictions of the theory (full lines) are promising in the sense that approximations to the expected shapes of the DDF are effectively obtained. Here, it must be taken into account that the inverse problem relating $G(t)$ and $f_w(M)$ is ill-posed [6]. Also, the shifts $M_c \rightarrow Mc_{\mathrm{eff}}$ and $W_c \rightarrow Wc_{\mathrm{eff}}$ belong to a phenomenon only described and correlated empirically at the present time. Additional theoretical analysis is required to consider the transition zone around Mc_{eff} where the mechanisms of chain relaxation are divided by a sharp cut involving different chain dynamics for $M < Mc_{\mathrm{eff}}$ and $M > Mc_{\mathrm{eff}}$, as a first approximation. Although this cut of the MWD facilitates the numerical analysis of the theory evaluated in the present work, one should expect a transition zone around Mc_{eff} concerning the dynamic of chains.

We also found that the logarithmic plot of $\lambda_N = \lambda_N$ (M, $f_w^E(M)$, $f_w^U(M)$) as function of molecular weight M shows straight lines with a slope approximately equal to α. Thus, the effective relaxation time of chains with $M > Mc_{\mathrm{eff}}$ does not present the transition from the predominant response involving reptation with contour length fluctuations (slope equal to 3.4) to a relaxation controlled by the tube constraint release when this slope approximates α. This transition is typically found in polydisperse entangled polymers that do not contain an unentangled chain fraction [3]. Therefore, it is clear that the relaxation law described by Eq. (10) can be approximated as follows for the nine blends studied in this work:

$$\lambda_N\Big(M, f_w^E(M), f_w^U(M)\Big) \cong \frac{K_r M^\alpha}{z Me_{\mathrm{eff}}^{\alpha}\left(\displaystyle\int_{\ln Mc_{\mathrm{eff}}}^{\infty} \frac{f_w^E(S)\,\mathrm{d}\ln S}{S^{b-b_k}} + \int_{-\infty}^{\ln Mc_{\mathrm{eff}}} \frac{f_w^U(S)\,\mathrm{d}\ln S}{S}\right)} \cong K_{\mathrm{eff}} M^\alpha \tag{13}$$

indicating that the presence of the unentangled chain fraction modifies substantially the relaxation law of entangled chains in polydisperse matrices. Thus, there are not chains with $M > Mc_{\mathrm{eff}}$ in the entangled system (physical network) that can follow Eq. (10) involving the asymptotic expression $\lambda_N(M, f_w^E(M), f_w^U(M)) \cong K_r M^b$ at low values of M, i.e. a fully reptation with contour length fluctuations response is not found for the nine blends studied.

From numerical results carried out with Eq. (10), we also conclude that the diluted entangled chains of the polydisperse blends studied here present higher values of the relaxation time λ_N than those obtained for the entangled chains containing only molecules with $M > M_c$. In fact, the analysis of the values of K_r (Table 4) indicates that λ_N increases substantially when a fraction of unentangled chains is present. To visualize this result, one should also observe two numerical aspects: (a) although λ_N is proportional to M^α with $\alpha < b$ for the microstructure of the blends studied here, K_r takes relatively high values, of the order of 10^{-8} (undiluted entangled PDMSs have $K_r \approx 10^{-21}$, as reported by Peirotti et al. [4]), (b) the denominator of Eq. (13) also increases for the case of diluted entangled polymers (contribution of tube constrain release associated to the fraction with $M < Mc_{\mathrm{eff}}$) but its value is not greater

Table 4
Numerical values of molecular parameters related to $G_N(t)$ for the blends studied in this work

Blend	Numerical predictions				Experimental data from SEC	
	K_r	G_N^{eff} (Pa)	M_w^E (Da)	P_o^E	M_w^E (Da)	P_o^E
B1	2.72×10^{-8}	2.73×10^4	244 200	2.08	244 300	2.01
B2	2.22×10^{-8}	1.76×10^4	306 400	1.99	306 400	1.98
B3	2.67×10^{-8}	1.89×10^4	299 300	2.03	303 200	1.95
B4	9.81×10^{-7}	1.46×10^4	369 600	1.92	368 600	1.91
B5	9.29×10^{-7}	1.68×10^4	538 600	1.70	532 800	1.84
B6	9.78×10^{-7}	1.01×10^4	368 300	2.39	374 700	2.27
B7	9.86×10^{-7}	2.85×10^4	316 900	2.16	313 200	2.13
B8	9.33×10^{-7}	1.18×10^4	382 100	1.69	394 700	1.81
B9	2.40×10^{-8}	1.01×10^4	369 500	1.69	372 400	1.80

Table 5
Numerical values of molecular parameters related to $G_R(t)$ for the blends studied in this work

Blend	Numerical predictions				Experimental data from SEC	
	K_R	G^0 (Pa)	M_w^U (Da)	P_o^U	M_w^U (Da)	P_o^U
B1	2.88×10^{-12}	4.03×10^{4}	19 700	2.20	20 300	2.36
B2	1.74×10^{-12}	7.26×10^{4}	22 600	2.32	22 600	2.33
B3	3.73×10^{-12}	3.67×10^{4}	20 100	1.93	21 200	2.09
B4	3.25×10^{-12}	4.22×10^{4}	22 200	2.82	22 600	2.80
B5	1.84×10^{-12}	2.60×10^{4}	14 600	2.33	14 800	2.13
B6	2.32×10^{-12}	3.43×10^{4}	22 100	2.32	21 700	2.19
B7	2.39×10^{-12}	8.36×10^{4}	17 700	2.44	17 600	2.33
B8	3.20×10^{-12}	7.22×10^{4}	22 800	2.60	22 500	2.58
B9	2.01×10^{-12}	2.86×10^{4}	22 000	2.61	21 900	2.72

enough to compensate the increment of K_r. These results are consistent with experimental data showing that diluted entangled PDMSs yield values for $t_c \cong 1/\omega_c$ relatively higher than those corresponding to the undiluted entangled PDMSs analyzed previously [4].

We also found numerically that the power δ becomes sensitive to the formulation of blends. Thus, our results show that $\delta \approx 1.6$–1.7 for samples like B1 to B4, which present two closed peaks in the DDF. For samples B6 to B9, which have three peaks in the DDF, $\delta \approx 1.8$–2. On the other hand, sample B5, having two separated peaks in the DDF, yields a rather high value of this parameter, viz.

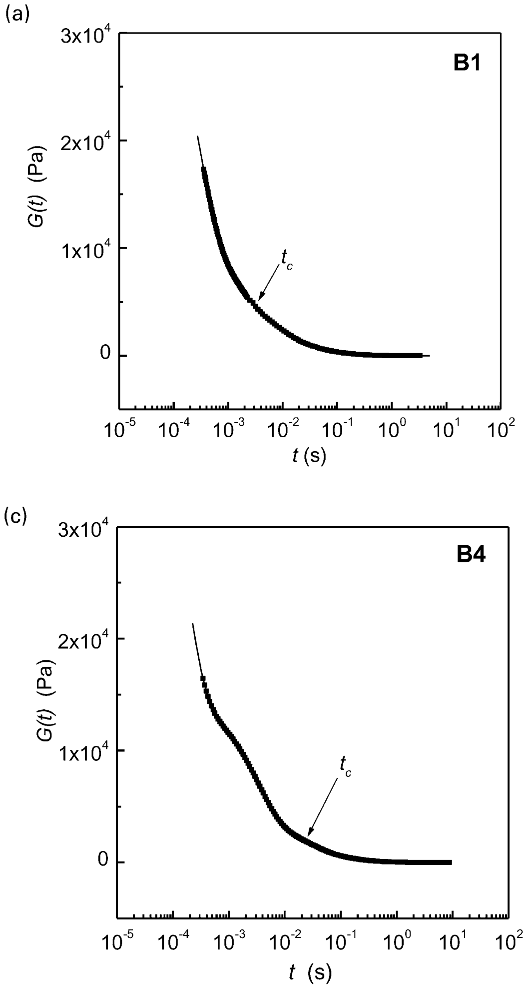

Fig. 1. Comparison between theoretical predictions of the relaxation modulus $G(t)$ (full lines) and rheometric data generated by the Fourier transform (symbols) for samples: (a) B1, (b) B3, (c) B4, and (d) B5. The cross over time $t_c \cong 1/\omega_c$ is indicated.

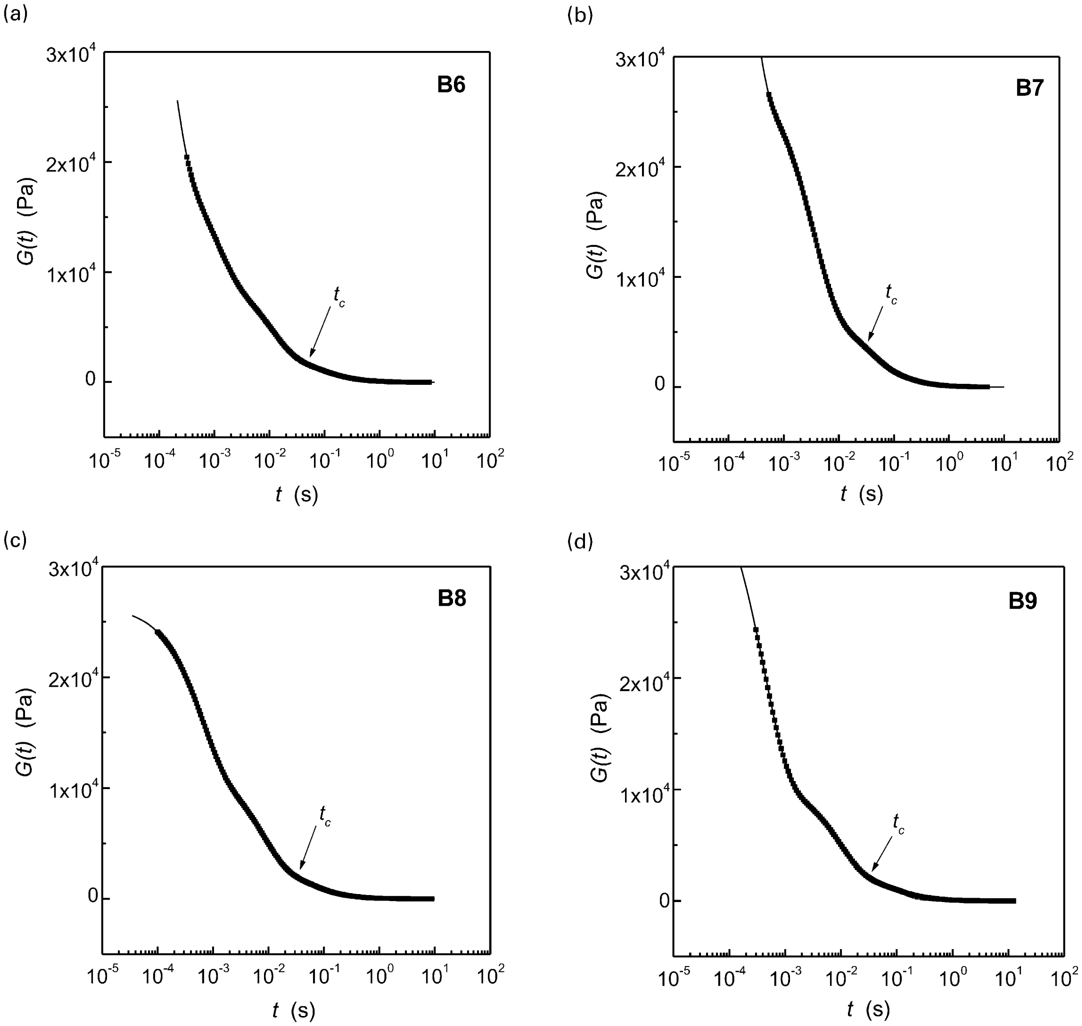

Fig. 2. Comparison between theoretical predictions of the relaxation modulus $G(t)$ (full lines) and rheometric data generated by the Fourier transform (symbols) for samples: (a) B6, (b) B7, (c) B8, and (d) B9. The cross over time $t_c \cong 1/\omega_c$ is indicated.

$\delta \approx 2.3$. In this sense, further research concerning other formulations of blends will be necessarily to elucidate the relationship between δ and the mass fraction of chains composing the samples studied.

Finally, it is important to discuss our experimental results in relation to the spectrum of relaxation time $H(\lambda)$, which can be obtained from data involving $G(t)$ (Figs. 1 and 2). In this context of analysis we show in Fig. 4 the relaxation spectrum of samples B4, B5, and B7. In this figure, sample B5 is an important reference point, since it is a bimodal blend with 50 wt% of the lower molecular weight component (acting as solvent) and the other 50 wt% of the higher molecular weight component (see Table 1). Since the relaxation spectrum can be inter-converted with the retardation spectrum, the three peaks observed for this sample in Fig. 4 can be associated directly to peaks A, B and C discussed previously by Orbon and Plazek [5]. Thus, we find a complete agreement with the results found by these authors in the sense that peak A corresponds to the relaxation of the unentangled chains with $M < Mc_{\rm eff}$ occluded in the physical network (see Eq. (12)), peak B is associated with glassy modes of relaxation involving only the parts of long chains comprised between entanglement points ($M > Mc_{\rm eff}$) (see Eq. (11)). In addition, as one should expect, peak C is related to the relaxation of the entangled chains in the network (see Eq. (3)). It is also interesting to point out here that the manifestation of peak A not only depends on the MWD and the amount of the low molecular weight fractions in the blend but also on the type of polymer under consideration. For instance, Orbon and Plazek resolved peak A in a shoulder type due to the low value of the orientational coupling constant, which is around 0.26 for the polystyrene oligomers they have used (see also Ylitalo et al. [29] for precise definitions and reported values of this parameter). In the case of the PDMS blends of our work, the orientational coupling parameter is around unity and hence the peak A reported in Fig. 4 is neatly observed. Samples B4 and B7 reported in Fig. 4 also presents a significant peak A because the low molecular weight fraction of the blends are poly-modal and it is

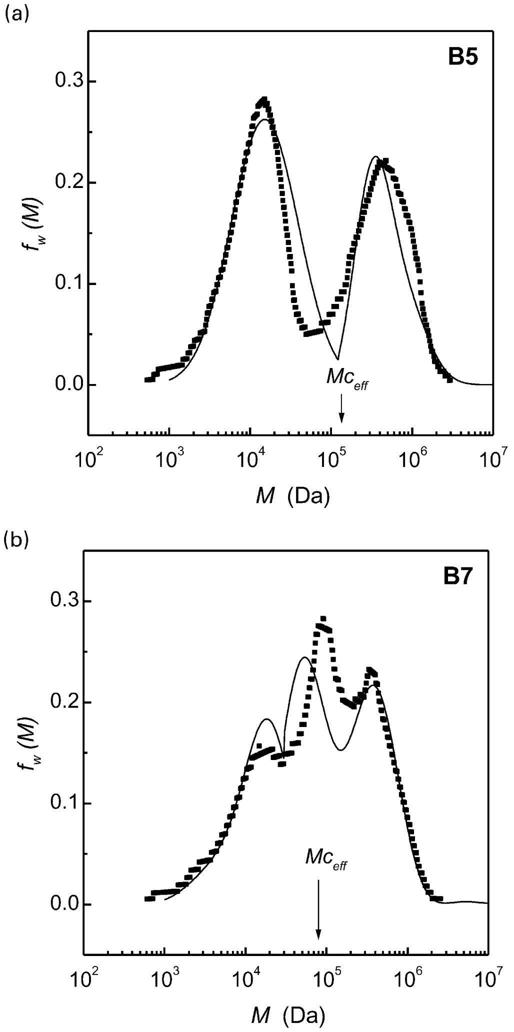

Fig. 3. Model prediction of the DDF $f_w(M)$ as a function of molecular weight M (full lines) for: (a) sample B5 (two peaks); (b) sample B7 (three peaks). Symbols refer to experimental data obtained from SEC.

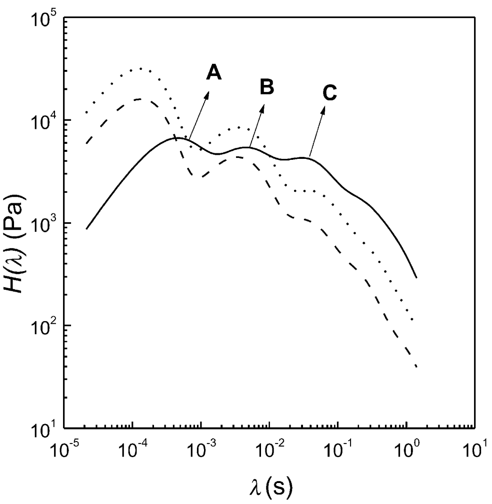

Fig. 4. Spectrum of relaxation times $H(\lambda)$ as a function of relaxation time λ for samples B4 (dashed line), B5 (full line), and B7 (dotted line). Peaks A, B, and C discussed in the text are indicated for sample B5.

present in a relative high volume fraction. All the samples studied in our work present systematically the three relaxation peaks described before indicating that the relaxation mechanisms proposed here and discussed previously by Orbon and Plazek [5] are representative of polymer networks having a low molecular fraction with a given MWD.

5. Conclusions

The shear relaxation modulus of entangled, linear and flexible blends containing homopolymer unentangled chains presents different relaxation modes from those found in the corresponding undiluted entangled homopolymer. In this sense, in the terminal zone of linear viscoelastic response, the double reptation mixing rule for blended entangled chains applies with a modified law for the relaxation time of chains in a polydisperse matrix which includes the effect of chains with $M < Mc_{\text{eff}}$. The presence of the unentangled chain fraction modifies substantially the tube constrain release mode of chain relaxation and the constant of proportionality K_r associated with the reptation of chains. The modified law of relaxation proposed validates rheometric data of linear viscoelasticity for well-characterized polydimethylsiloxane (PDMS) samples and their molecular parameters obtained from SEC. Two short time responses of PDMS (glassy modes) were considered both following the Rouse chain diffusion. One describes the relaxation of chains with $M > Mc_{\text{eff}}$. This mechanism is independent of MWD. Unentangled chains with $M < Mc_{\text{eff}}$ occluded in the entangled polymer melt also follow Rouse modes of relaxation although they present a dependence on the MWD. These results are consistent with previous analysis reported in the literature for other polymer systems [6–8,11,12].

The effect of the unentangled chain fraction on the effective relaxation time of chains in the polydisperse physical network is to eliminate the transition involving the values of the universal constant b from 3.4 to α for increasing values of M, typically found in high polydisperse entangled polymer melts with a mass distribution greater than Mc_{eff}.

Theoretical correlations involving the effective plateau relaxation modulus G_N^{eff} and the effective critical molecular weight between entanglements Mc_{eff} with the effective polymer mass fraction $(1 - Wc_{\text{eff}})$ (or volume fraction φ_{eff}) presented previously for solvent diluted entangled polymers were validated and extended to physical networks containing homopolymer unentangled chains.

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Appendix A

This appendix briefly presents the main steps followed in this work to find the approximate solution of the problem generated by the integrals of first kind (Eqs. (3) and (12)) relating the relaxation moduli of blends and MWDs. These steps are the following [28].

(a) The basic problem found in the determination of a DDF from dynamic rheometry is,

$$g(t) = \int_{\ln a}^{\ln b} [K(t,\lambda)]_{\lambda=\lambda(M)} f_{\mathrm{w}}(M)\,\mathrm{d}\ln M \tag{A1}$$

where the relaxation law $\lambda = \lambda(M)$ and the kernel $K(t,\lambda)$ are functions specified together with the integral limits a and b. In the inverse problem, one uses rheometric data $g(t)$ in Eq. (A1) to evaluate $f_{\mathrm{w}}(M)$. We first find a basic solution of the problem placed by Eq. (A1) according to Peirotti et al. [4]. The method uses

$$f_{\mathrm{w}}(M) = \sum_{i=1}^{N} a_i \delta_i(M - M_i)$$

where $\delta_i(M - M_i)$ are Dirac delta functions and a_i are constant coefficients to be determined in the inversion process. With the above formulation, numerical values for the spectrum $\{a_i\} - \{M_i\}$ with $i = 1\ldots W$ are found. In this numerical algorithm, the prediction of polydispersity and mass average molecular weight shall approximate the values $P_{\mathrm{o}} = M_{\mathrm{w}}/M_{\mathrm{n}}$ and M_{w} obtained from SEC. With the basic solution, the molecular parameters of the relaxations laws for λ_{N} and λ_{R} used in each integral are determined iteratively.

(b) The moments μ_n of $f_{\mathrm{w}}(M)$ are independent of the solution of the ill-posed problem because they are determined by the numerical data $g(t)$ [30]. Therefore, these moments can be numerically calculated, through a DDF obtained as a basic solution of Eq. (A1) within a small numerical error. The moments of the distribution function are

$$\mu_n = \int_{\ln a}^{\ln b} (\ln M - \langle \ln M \rangle)^n f_{\mathrm{w}}(M)\,\mathrm{d}\ln M$$

with

$$\langle \ln M \rangle = \int_{\ln a}^{\ln b} \ln M f_{\mathrm{w}}(M)\,\mathrm{d}\ln M.$$

The set of moments thus determined allows one to look for the evaluation of $f_{\mathrm{w}}(M)$ according to the next step.

(c) In principle, a DDF can be fully determined from the knowledge of its moments [31]. Having the moments from the previous step, 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 $f_{\mathrm{w}}^{\mathrm{s}}(\xi)$ 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 $n = 1\ldots\infty$, together with the standard normal-DDF, $\alpha(\xi) = \exp(-\xi^2/2)/\sqrt{2\pi}$. Therefore the following expression is obtained [31],

$$f_{\mathrm{w}}^{\mathrm{s}}(\xi) = \sum_{j=0}^{\infty} c_j H_j(\xi)\alpha(\xi)$$

where

$$c_n = \frac{1}{n!}\int_{-\infty}^{\infty} f_{\mathrm{w}}^{\mathrm{s}}(\xi) H_n(\xi)\,\mathrm{d}\xi$$

with $n \geq 2K$. Coefficients c_n for $n = 1\ldots\infty$, can be written in terms of moments θ_n through

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

The number of modes of this series shall be determined with the constraints,

$$\left\{\left(\int_{-\infty}^{\infty} f_{\mathrm{w}}^{\mathrm{s}}(\xi)\,\mathrm{d}\xi\right) - 1\right\} \leq 10^{-5}$$

and $f_{\mathrm{w}}^{\mathrm{s}}(\xi) + \varepsilon \geq 0$, which allows one to cut the series at a specific and optimum value of n. The first constraint is the normalization of the standard DDF, while the second does not allow the DDF to take negative values outside a small negative range $-\varepsilon$ associated with typical numerical errors. Therefore, one must calculate the series for high n to find the solution that satisfies the proposed constraints.

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