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## Relaxation time spectra of star polymers

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**Abstract** The linear viscoelastic data for model star polymer melts with varying functionality and arm molecular weight were represented by means of a modified Baumgaertel-Schausberger-Winter (BSW) relaxation time spectrum, based on data analysis with the parsimonius model of Baumgaertel et al., reported in 1990. In the case of high arm functionality, the second slow terminal relaxation observed by Vlassopoulos et al. in 1997, was captured with a straightforward extension of the BSW model using broad cut-off functions. This study represents a potentially promising attempt to extend the applicability of this representation of viscoelastic data to more complex architectures, beyond simple linear chains which are characterized by self-similarity.

The casting of linear viscoelastic data into spectra allows the exploration of star polymer behavior. It is a necessary step in preparation for large scale complex flow calculations in conjunction with constitutive models and for material databases.

**Key words** Relaxation time spectra · Linear viscoelasticity · Star polymers · Parsimonius model · BSW spectrum

### Introduction

It is well known that polymer stars represent the simplest example of branched polymers, consisting of linear macromolecules attached by one end to a central core. Their physics is rather well understood, and the key feature is the exponential dependence of viscosity (or arm relaxation time) on arm molecular weight but not on functionality (Fetters et al. 1993; McLeish 1995, 1997). High functionality multiarm stars (Roovers et al. 1993) were found to order both in solution (Richter et al. 1994; Ishizu et al. 1997; Seghrouchni et al. 1998) and in the melt (Vlassopoulos et al. 1997). This was attributed to their topologically induced non-uniform monomer density distribution. These systems are anal-

ogous in behavior to the block copolymer micelles in selective solvents, studied extensively by several groups (Gast 1996; Buitenhuis and Förster 1997; Watanabe 1997). In a recent study of the linear viscoelastic response of a series of such polybutadiene star melts, Vlassopoulos et al. (1997) and Pakula et al. (1998) found that in addition to the arm relaxation, an additional slow relaxation process appeared. This relaxation process was attributed to the cooperative rearrangements of the liquid-like structure.

Obtaining viscoelastic relaxation time spectra,  $H(\lambda)$ , for such complex architectures, by capturing the main features of the measured  $G'$  and  $G''$  with an analytical function, has practical implications in extending the applicability of the Baumgaertel-Schausberger-Winter

(BSW) spectrum (Baumgaertel et al. 1990) which is already established for linear chains and is used here to analyze the linear viscoelastic response of the star systems. This is precisely the scope of this work, i.e., the determination of the relaxation time spectra  $H(\lambda)$  of star polymers with varying molecular characteristics. Knowledge of  $H(\lambda)$  allows engineering calculations of linear viscoelastic material functions, complex flows, as well as material databases for star polymers to be made. Based on the established physical understanding of the dynamics of star polymers, we attempt to obtain their viscoelastic relaxation spectra in a consistent way for practical applications.

## Experimental information

The seven model ( $M_w/M_n < 1.1$ ) 1,4-polybutadiene (PB) star polymers of various functionalities used are presented in Table 1 with their molecular characteristics, namely their functionality ( $f$ ), arm molecular weight ( $M_a$ ) and glass transition temperature ( $T_g$ ). A well-entangled linear 1,4-PB chain is included for comparison. Details about the synthesis and characterization of these materials can be found in the work of Roovers et al. (1993). Vlassopoulos et al. (1997) and Pakula et al. (1998) have investigated the structure and linear viscoelasticity of the above PB melts. They obtained master curves of  $G'$  and  $G''$  for the various stars over a wide temperature range ( $-103$  to  $60$  °C, with a reference temperature of  $-83$  °C). After applying time-temperature superposition, the dynamic moduli data cover a wide frequency range ( $10^{-8}$ – $10^6$  rad/s). The data are utilized in this work for the determination and evaluation of the respective linear viscoelastic spectra.

For the data analysis in terms of discrete relaxation time spectra, we use the so-called parsimonious (PM) model (Baumgaertel and Winter 1989) in which the relaxation time spectrum of a polymer is expressed in a discrete set of Maxwell modes ( $\lambda_i, g_i$ ),  $i = 1, \dots, N$  where  $\lambda_i$  is the  $i$ -th relaxation time,  $g_i$  is the  $i$ -th relaxation strength, and  $N$  is the number of Maxwell modes. The dynamic moduli can be rewritten as:

$$G'(\omega) = \sum_{i=1}^N g_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \quad (1)$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2} \quad (2)$$

The parameters of a discrete relaxation spectrum are found by fitting Eqs. (1) and (2) to the experimental data by means of a suitable minimization technique. As the criterion for minimization,

the average square deviation between model-based and measured values of  $G', G''$  was chosen:

$$\frac{1}{M} \sum_{i=1}^M \left[ \left( \frac{G'(\omega_i)}{\hat{G}'_i} - 1 \right)^2 + \left( \frac{G''(\omega_i)}{\hat{G}''_i} - 1 \right)^2 \right] = \min \quad (3)$$

where  $\hat{G}'_i, \hat{G}''_i$  are the measured data at  $M$  frequencies  $\omega_i$  and  $G', G''$  are the calculated values from Eqs. (1) and (2). The values of  $\lambda_i, g_i$ , and  $N$  were freely adjusted during minimization. The mode density  $[N/\log(\omega_{\max}/\omega_{\min})]$  is limited by the noise in the data; this is accounted for in the PM model (Winter 1997).

## Results and discussion

### Linear monodisperse PBs

The spectrum of the linear flexible molecules serves as a reference for the analysis of star-shaped molecules. Baumgaertel et al. (1990) found that the relaxation spectrum of linear flexible polymers with molecules of (nearly) uniform length can be very well represented as:

$$H(\lambda) = \begin{cases} n_e G_N^0 \left[ \left( \frac{\lambda}{\lambda_c} \right)^{-n_g} + \left( \frac{\lambda}{\lambda_{\max}} \right)^{n_c} \right], & \text{for } \lambda \leq \lambda_{\max} \\ 0, & \text{for } \lambda > \lambda_{\max} \end{cases} \quad (4)$$

for  $M_w \gg M_c$

where  $\lambda_{\max}$  is the longest relaxation time,  $n_e$  and  $n_g$  are the slopes of the spectrum in the entanglement and short-time scale zones, respectively, and  $\lambda_c$  is the crossover time to the short-time scale region (which relates to segmental short-time scale dynamics). The first term in the brackets represents the high frequency region, whereas the second term describes the entanglement and flow regions. Equation (4) was tested using data for narrowly distributed PBs and polystyrenes and gave excellent results. This spectrum was then modified (Baumgaertel and Winter 1992) to account for broadly distributed polymers by replacing the abrupt cut-off at the longest relaxation time with a stretched exponential cut-off, as follows:

$$H(\lambda) = \left[ H_g \left( \frac{\lambda}{\lambda_c} \right)^{-n_g} + n_e G_N^0 \left( \frac{\lambda}{\lambda_{\max}} \right)^{n_c} \right] \exp[-(\lambda/\lambda_{\max})^\beta] \quad (5)$$

for  $M_w \gg M_c$

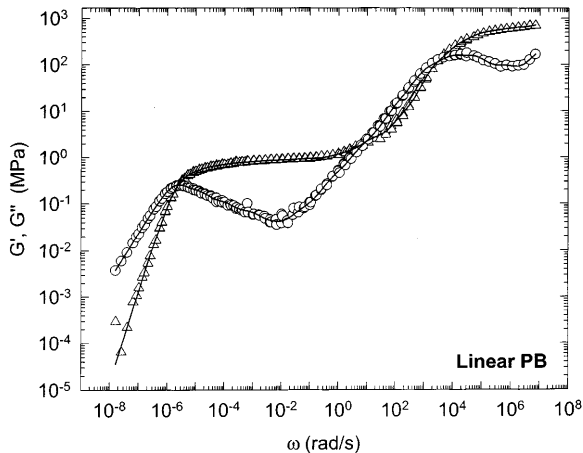
In this expression  $M_c$  is the critical molecular weight, and  $H_g = n_e G_N^0 \left( \frac{\lambda_1}{\lambda_c} \right)^{n_g} \left( \frac{\lambda_1}{\lambda_{\max}} \right)^{n_c}$ , with  $\lambda_1$  being the time where the contributions from the short-time scale and entanglement zones are the same (see also Fig. 2 below). Due to the exponential term, this equation provides an improved representation of the relaxation spectrum compared to Eq. (4), in particular in the terminal region. Equation (5) essentially tends closer to Eq. (4) with increasing  $\beta$ . In addition, using Eq. (5) to fit the spectrum of polymers yields directly the maximum relaxation time,  $\lambda_{\max}$ .

Figure 1 depicts the viscoelastic moduli of the linear PB at the reference temperature. This polymer, as well as

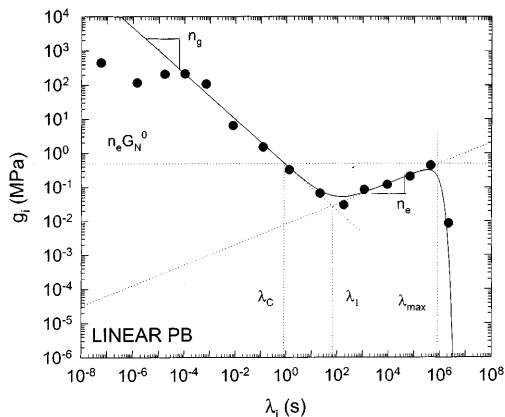
**Table 1** Molecular characteristics of the model star polybutadienes used

Code	$f$	$M_a$	$T_g$ (°C)
PB	Linear	155,000	-96
4S	4	11,250	-96
6407	62	6,300	-92
6430	64	23,900	-92
12807	124	6,800	-92
12814	125	13,000	-92
12828	114	26,100	-92
12856	127	47,000	-92

all the polymers tested in this work, was found to be a thermorheologically simple fluid. The continuous lines represent the fitting results of the parsimonius spectrum, determined by the non-linear optimization procedure discussed above. It can be seen that the overall fitting



**Fig. 1** The dynamic moduli of the linear polybutadiene (PB) at  $-83\text{ }^{\circ}\text{C}$  along with the fitting results of the parsimonius (PM) spectrum



**Fig. 2** The PM relaxation spectrum of the linear PB along with its fit with the modified Baumgaertel-Schausberger-Winter (mBSW) spectrum

(employing 15 relaxation times) is very good. Figure 2 plots the PM spectrum along with its fit, representing the modified BSW (hereafter called mBSW) continuous spectrum of Eq. (5). The value of the shape parameter is  $\beta = 2$ , indicating an abrupt cut-off (Baumgaertel and Winter 1992). It can be seen that Eq. (5) represents well the basic structure of the PM spectrum (terminal flow and segmental regimes). In this respect, calculations of discrete spectra (PM spectra) showed a very good agreement with the continuous representation (mBSW) of the relaxation spectrum: this result confirms the interchangeability in the form of relaxation spectra, i.e., continuous versus discrete, as originally established by Baumgaertel and Winter (1992). This allows the accurate representation of the linear viscoelastic relaxation with the smallest possible number of modes; the high accuracy is verified by essentially backing-up the experimental  $G'(\omega)$  and  $G''(\omega)$  from the calculated linear viscoelastic spectra. The values of the parameters calculated from the fitting procedure (Eq. 5) are listed in Table 2. The plateau modulus is 1.65 MPa (in agreement with the value determined by conventional means, e.g., Ferry 1980), and the slopes of the two regimes are 0.30 and  $-0.67$  (entanglement and short-time scale regimes, respectively). These values agree reasonably well with those reported by Jackson et al. (1994), namely 1.65 MPa for the plateau modulus, and 0.23 and  $-0.73$  for the slopes of the entanglement and short-time scale regimes, respectively. An approximation of  $G_N^0$  can be obtained from the experimental observation that  $G_N^0/G_{\max}'' = 3.56$  (Raju et al. 1981; Graessley 1993) or 4.8 (Carri and Winter 1997). A value of 0.26 MPa can be obtained from Fig. 1 for  $G_{\max}''$ , which results in a value for  $G_N^0$  of 0.93 MPa or 1.25 MPa depending on the approximation used. The parameters resulting from the fitting procedure are also indicated geometrically in Fig. 2. Thus, the above ideas work quite well for linear nearly monodisperse and slightly polydisperse polymers (Rosenbaum et al. 1998).

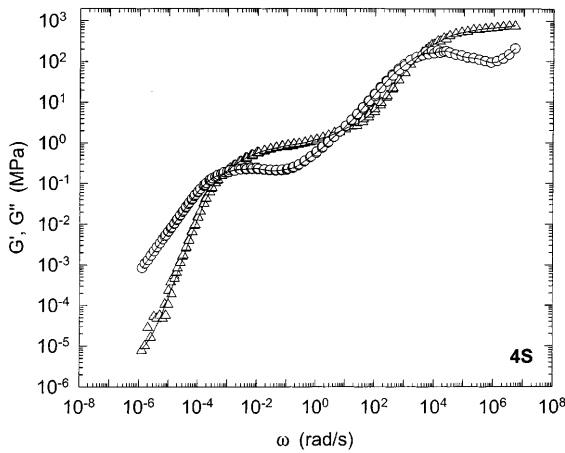
### Regular star polymers

Next, we investigate the relaxation spectrum of a regular star polymer with four arms (4S in Table 1). Its main

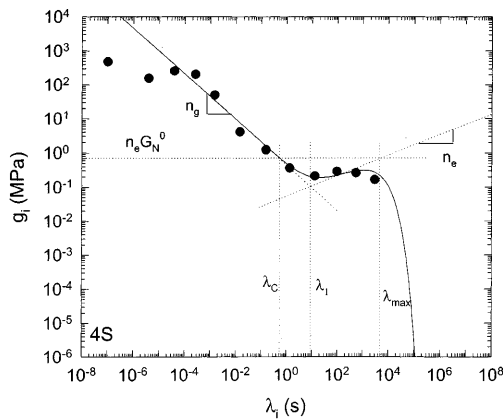
**Table 2** Parameters of the mBSW spectrum resulting from fitting of the parsimonius spectrum

Polymer	$G_N^0$ (MPa)	$n_e$	$n_g$	$\lambda_c$ (s)	$\lambda_{\max}$ (s)	$\lambda_1$ (s)	$H_g$ (MPa)	$G_0$ (MPa)	$n_0$	$\lambda_0$ (s)
PB-linear	1.65	0.30	0.67	0.86	$9.0 \times 10^5$	40.5	0.49	—	—	—
4S	2.19	0.30	0.67	0.55	$4.0 \times 10^3$	8.61	0.66	—	—	—
6407	2.51	0.30	0.67	0.37	$1.5 \times 10^2$	2.38	0.75	$6.08 \times 10^{-3}$	0.30	$6.50 \times 10^3$
6430	2.00	0.30	0.67	0.53	$7.5 \times 10^3$	10.2	0.59	$1.78 \times 10^{-2}$	0.30	$5.50 \times 10^5$
12807	2.51	0.30	0.67	0.37	$1.5 \times 10^2$	2.38	0.75	$6.08 \times 10^{-3}$	0.30	$3.05 \times 10^4$
12814	2.72	0.30	0.67	0.54	$3.0 \times 10^3$	7.75	0.82	$1.48 \times 10^{-3}$	0.30	$6.00 \times 10^5$
12828	2.05	0.30	0.67	0.66	$2.5 \times 10^4$	17.40	0.62	$0.89 \times 10^{-3}$	0.30	$4.92 \times 10^6$
12856	1.66	0.30	0.67	1.00	$5.4 \times 10^4$	25.50	0.49	$1.12 \times 10^{-2}$	0.30	$1.32 \times 10^7$

qualitative features in terms of contributing relaxation processes were found to be similar to those of the linear polymer. Figure 3 depicts the  $G'$  and  $G''$  of 4S at the reference temperature. It is noted that in the star case the molecular weight (for instance in Eq. 5) is actually the arm molecular weight; this is due to the fact that the arm relaxation determines the overall star relaxation, as already mentioned in the Introduction. In this respect, the time  $\lambda_{\max}$  should depend exponentially on the arm molecular weight (McLeish 1997). The continuous lines represent the fitting results of the PM spectrum that was determined by the nonlinear optimization procedure above. Figure 4 plots the PM spectrum along with its fit that represents the mBSW continuous spectrum indicated by Eq. (5), with  $\beta = 0.8$ . Considering the rather short range of the self-similar regions in this set of data, and the associated ambiguity involved, the overall procedure (with 14 relaxation



**Fig. 3** The dynamic moduli of the 4S PB ( $f = 4$ ,  $M_a = 10,900$ ) at  $-83$  °C along with the fitting results of the PM spectrum



**Fig. 4** The PM relaxation spectrum of the 4S PB ( $f = 4$ ,  $M_a = 10,900$ ) along with its fit with the mBSW spectrum

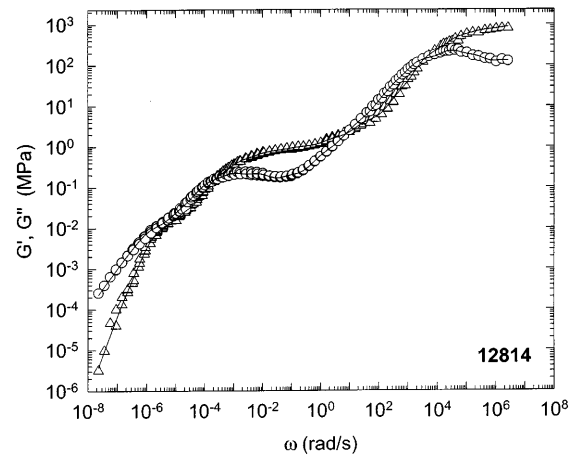
times) is considered to be satisfactory. It is evident that Eq. (5) represents reasonably well the basic pattern of the PM spectrum, with the parameters listed in Table 2. The plateau modulus is somewhat overestimated and this is probably due to the few data points that determine the flow regime; such an overestimation has been reported in the past as well for linear chains (Jackson et al. 1994).

### Multiarmed star polymers

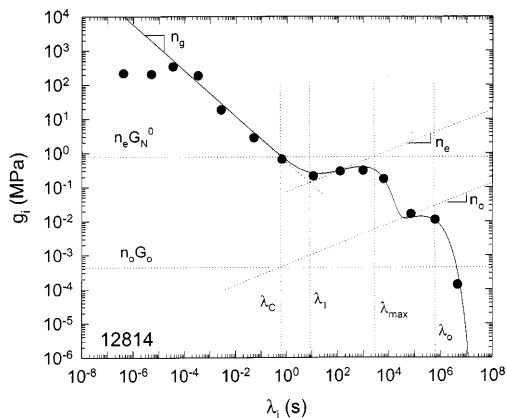
Figure 5 depicts the viscoelastic moduli of the 125-arm star polymer (12814) at the reference temperature, where the terminal regime is now characterized by the two-step decay already discussed. The continuous lines in Fig. 5 represent the fitting results of the PM spectrum; much as for the case of regular stars, and given the short separation between the two terminal processes, the overall fitting (with 16 relaxation time) is satisfactory. The continuous spectrum (Fig. 6) is based on the following simple extension to the BSW spectrum (given by Eq. 5), incorporating a similar empirical description of the slow relaxation

$$H(\lambda) = \left[ H_g \left( \frac{\lambda}{\lambda_c} \right)^{-n_g} + n_e G_N^0 \left( \frac{\lambda}{\lambda_{\max}} \right)^{n_e} \right] \exp[-(\lambda/\lambda_{\max})^\beta] + n_0 G_0 \left( \frac{\lambda}{\lambda_0} \right)^{n_0} \exp(-\lambda/\lambda_0) \quad \text{for } M_w \gg M_c . \quad (6)$$

An exponential cut-off to the spectrum is used, and  $n_0$  is the slope and  $G_0$  the modulus of the spectrum in the ordering regime.  $M_w$  stands for the arm molecular weight. The continuous spectrum, Eq. (6), closely represents the PM (see Fig. 6). The geometrical interpretation of the parameters of Eq. (6) resulting from this



**Fig. 5** The dynamic moduli of the 12814 PB ( $f = 125$ ,  $M_a = 13,000$ ) at  $-83$  °C along with the fitting results of the PM spectrum



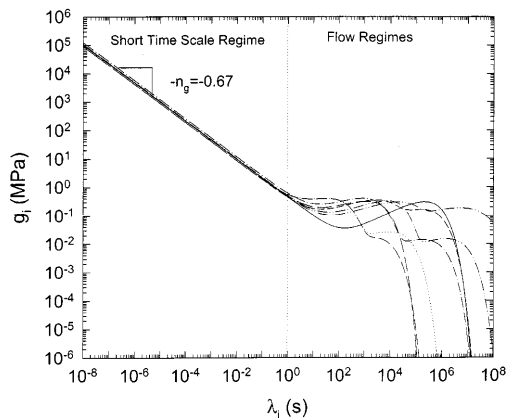
**Fig. 6** The PM relaxation spectrum of the 12814 PB ( $f = 125$ ,  $M_a = 13,000$ ) along with its fit with the extended mBSW spectrum (Eq. 6)

fitting procedure is also depicted in Fig. 6 and listed in Table 2. The same features were observed for the spectra of all other star polymers examined in this work. It is noted that in all cases  $\beta$  varied between 0.8 and 1.0.

It is apparent from the analysis of all star data that the separation between the two flow regimes is enhanced when  $f$  increases and  $M_a$  decreases, because of their different dependencies on these molecular parameters (Pakula et al. 1998; Kapnistos et al. 1999); however, the range of  $f$  and  $M_a$  available is insufficient, rendering the BSW analysis inappropriate for further quantitative elucidation of these effects.

A few additional remarks are in order. First of all, it is known that the short-time scale regime is independent of functionality and arm molecular weight (Pakula et al. 1998), and the comparison of the PM fits of the relaxation spectra of all polymers complies with this result (Fig. 7). The contribution of the short-time scale regime is  $g_e = H_g(\lambda/\lambda_c)^{-0.67}$ , and the scaling exponent is in agreement with the one reported by Jackson et al. (1994) for various linear chains. The variation of parameter  $H_g$  and that of the crossover relaxation time,  $\lambda_c$ , is not very significant (see Table 2);  $H_g$  varies from 0.49 to 0.82 MPa, the parameter  $\lambda_c$  from 0.37 to 0.86 s, and  $H_g(\lambda_c)^{0.67}$  from 0.39 to 0.54. While an average value for  $H_g$  and  $\lambda_c$  would represent this regime for all polymers equally well, a constant value for  $\lambda_c$  would influence the representation of the other flow regimes. The value of  $\lambda_c$  was found to be independent of molecular weight (Jackson et al. 1994) and this seems to be supported by the present results, given of course the relative error involved in such a multi-parameter fitting procedure. Therefore, within some error the values of  $H_g$  and  $\lambda_c$  can be considered as independent of  $M_a$  and  $f$ .

The values of the plateau modulus  $G_N^0$  resulting from the PM analysis were found to be in the range 2.00–



**Fig. 7** The mBSW spectra of all polymers studied. Note that the short-time scale regime is about the same for all polymers used independent of the functionality and arm molecular weight

2.51 MPa (Table 2). These values are higher than for linear PB, by 20–50%, and also higher than those obtained by conventional methods (Ferry 1980) by about 40%. Besides the uncertainty involved, a higher  $G_N^0$  for multiarm stars can be expected (Pakula et al. 1998) as the expression  $M_e = \rho RT/G_N^0$  suggests that  $M_e$  is lower compared to linear PB, because of the strong stretching of the arms near the core (Seghrouchi et al. 1998, and references therein). Therefore, the viscoelastic spectra obtained conform to the main qualitative features of the star polymers. However, it is premature at this point to use these results for quantitative physical interpretation. One problem is the short range of self-similar regions, which with the present systems can be overcome only with stars of the same chemistry but a much higher range of molecular weights; these are not currently available but such data would definitely lead to quantitatively improved parameters.

## Conclusions

The linear viscoelastic data of model star polymer melts of varying functionality and arm molecular weight are equally well expressed in terms of their discrete and their continuous relaxation time spectra. Discrete representation was achieved by means of a nonlinear optimization algorithm, i.e., the PM model of Baumgaertel and Winter (1989). The parsimonious relaxation time spectrum was then replaced by a suitably modified, semi-empirical, continuous BSW spectrum with an exponential cut-off function. In this way, the two relaxation times characterizing the complex terminal relaxation of multiarm stars were recovered together with the plateau modulus of the star polymers. Given the short range of self-similar regions in the polymers tested and the corresponding ambiguities, the results

can be considered as encouraging for further investigations in this direction with wider ranges of molecular weights and functionalities, and eventual calculation of linear viscoelastic material functions in a wide range of viscoelasticities. Although this type of analysis does not provide any new molecular insight, it could be of potential practical value for large-scale engineering calculations of complex flows and for material databases, as the resulting discrete spectra are consistent

with the main physics governing the dynamics of these macromolecules.

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