

## Determining Rouse relaxation times from the dynamic modulus of entangled polymers

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### Synopsis

Different methods of finding the Rouse relaxation times  $\tau_e$ , demarcating the onset of entanglement effects, were evaluated for entangled solutions of high molecular weight polystyrene in diethyl phthalate. Five expressions were utilized, involving variously the zero shear viscosity, the storage modulus at frequencies just beyond the rubbery plateau, the terminal Andrade creep region in the retardation spectrum, and the recoverable creep compliance. Values of  $\tau_e$  determined by a procedure which assumes that the deformation modes are additive in the strain were substantially larger than the Rouse times extracted from the storage modulus by assuming stress additivity. © 2004 The Society of Rheology. [DOI: 10.1122/1.1645516]

This note evaluates different methods for determining the Rouse relaxation time  $\tau_e$  beyond which entanglements constrain the dynamics, for an entangled polymer solution. It is motivated by the importance of Rouse contributions to the nonlinear relaxation dynamics of entangled polymer liquids, as well as the general significance of the Rouse model to theories of polymer relaxation. Our main objective is to compare predictions of  $\tau_e$  obtained using deconvolution schemes based on additivity of the compliance (or strain) to results based on additivity of the modulus (or stress). For a relaxation spectrum comprised of weakly overlapping modes, the two approaches are expected to yield comparable results. However, as is often the case, the modes overlap whereby the method of deconvolution can influence the results. There is literature strongly advocating additivity

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**TABLE I.** Comparison of different determination of the longest Rouse relaxation  $\tau_R$  and retardation  $\lambda_R$  times for entangled solutions of polystyrene in diethylphthalate.

Solution (%)	$M_w \times 10^{-6}$ (Daltons)	$M_w/M_n$	$\phi$	$\tau_e$ (s)			$\lambda_e$ (s)	
				Eqs. (1) and (2)	Eqs. (2) and (3)	Eq. (4)	Eq. (5)	Eq. (6)
PS3.8M6	3.84	1.04	0.06	$3 \times 10^{-3}$	$1 \times 10^{-3}$	$9 \times 10^{-4}$	$0.016 \pm 0.01$	—
PS5.48M6	5.48	1.15	0.058	$4 \times 10^{-3}$	$9 \times 10^{-4}$	$9 \times 10^{-4}$	$0.027 \pm 0.01$	—
PS8.4M6	8.42	1.2	0.067	$3 \times 10^{-3}$	$7 \times 10^{-4}$ <sup>a</sup>	$7 \times 10^{-4}$ <sup>b</sup>	$0.026 \pm 0.03$	$0.02 \pm 0.002$
PS20M8	20.07	1.2	0.079	$9 \times 10^{-4}$	$1 \times 10^{-3}$	$1 \times 10^{-3}$	$0.50 \pm 0.05$	$0.56 \pm 0.02$

<sup>a</sup>The value of  $\tau_R$  was incorrectly reported as 0.5 s in the publication of Sanchez-Reyes and Archer (2003).

<sup>b</sup>The original estimate was  $\tau_e \sim 3.6 \times 10^{-4}$  s [Sanchez-Reyes and Archer (2003)].

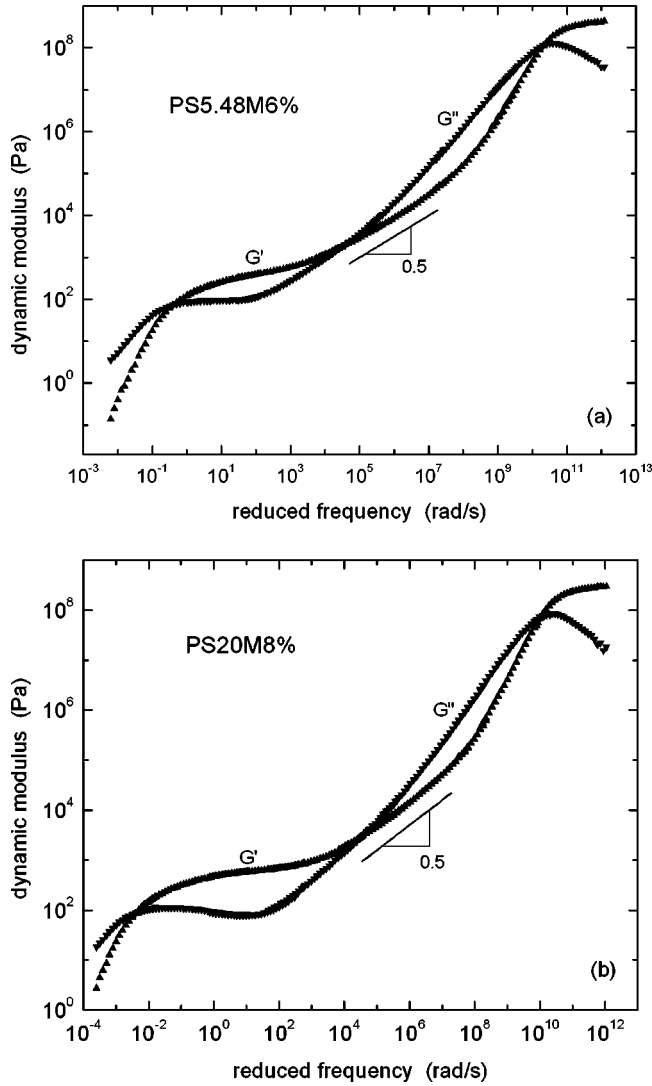
of the compliance functions [Dean *et al.* (1990); Plazek (1992); Mott and Roland (1998); Roland and Mott (1999); Plazek and Echeverria (2000)], although the alternate approach has been adopted by various workers [Read (1983); Okamoto *et al.* (1995); Sanchez-Reyes and Archer (2003)]. We find herein for entangled solutions of high-molar mass polystyrenes (PS) in diethyl phthalate (Table I) that the entanglement Rouse relaxation time obtained assuming stress additivity is at least an order of magnitude smaller than  $\tau_e$  obtained using strain additivity.

The Doi and Edwards (1986) constitutive theory for entangled polymer rheology contends that a polymeric liquid relaxes stress in two stages. At short times following deformation, entangled molecules equilibrate their contour length by Rouse dynamic processes, while at long times reptation randomizes any orientation of segments produced by the deformation. This clear separation between the time scales on which molecules relax orientation and length carries over to all constitutive theories for entangled linear polymers based on the tube model. In these theories, the average molecular orientation relaxation time is the reptation time, while the contour length relaxation time is taken to be the longest Rouse relaxation time  $\tau_R$ . In principle, this assumption can be evaluated from stress growth or stress relaxation experiments in steady shear or following step shear deformations [Einaga *et al.* (1971); Osaki *et al.* (1982); Archer (1999); Sanchez-Reyes and Archer (2002), (2003)]. Unfortunately, the longest Rouse relaxation time of entangled polymers is not easily obtained from such experiments, impeding rigorous comparisons. Indeed, the Rouse model *per se* breaks down upon the onset of entanglement effects at  $\tau_e$ .

In the absence of data for the viscoelastic spectrum other than the zero-shear viscosity  $\eta_0$ , an estimate of  $\tau_R$  can be found from the relationship between  $\eta_0$  and polymer molecular weight [Menezes and Graessley (1982)]:

$$\tau_R = \frac{6M_w^{2-\mu}}{\pi^2 \rho RT} \frac{M_c^{\mu-1}}{\phi^{4/3(\mu-1)+1}} \eta_0. \quad (1)$$

Here  $\mu$  is the scaling exponent of  $\eta_0$  ( $= 3.4 \pm 0.3$ ) [Ferry (1980)],  $M_w$  is the weight average molecular weight,  $M_c$  the critical molecular weight at which entanglement effects become apparent ( $\approx 31\,000$  Daltons for PS [Fetters *et al.* (1999)]),  $\rho$  the solvent density,  $\phi$  the polymer volume fraction in solution, and RT have their usual significance. This method can be in error by as much as a factor of ten [Osaki *et al.* (2000), (2001)], which is unsurprising, given the uncertainties in  $M_c$  and the exponents. Using the usual Rouse scaling relation,  $\tau_R \sim M_w^2$ , values of  $\tau_e$  were calculated as



**FIG. 1.** Dynamic storage and loss modulus vs reduced frequency, for (a) 6% PS ( $5.48 \times 10^6$  Daltons) solution, and (b) 8% PS ( $20.07 \times 10^6$  Daltons) solution, in diethyl phthalate.

$$\tau_e = \tau_R (M_e / M_w)^{1/2}, \quad (2)$$

with the molecular weight between entanglements  $M_e$  taken to vary as the  $-4/3$  power of the polymer volume fraction. (Generally, this exponent is found to range from  $-1$  to  $-1.5$  [Tao *et al.* (1999)]). For neat PS,  $M_e = 18\,100$  D [Fetters *et al.* (1999)]. The results are listed in Table I for the four entangled solutions of high molecular weight polystyrene (PS) in diethyl phthalate (DEP) studied by Sanchez-Reyes and Archer (2003).

Osaki and coworkers (2001) recently presented a simple approach for determining  $\tau_R$  from high-frequency oscillatory shear rheology experiments. The storage modulus  $G'(\omega)$ , at frequencies  $\omega$  just beyond the rubbery plateau regime, is fitted to the Rouse modulus expression  $G'(\omega) = \alpha \omega^{1/2}$  [see Fig. 1(a)], and the longest Rouse relaxation time is found from

$$\tau_R = \left( \frac{\alpha M_w}{1.11cRT} \right)^2, \quad (3)$$

where  $c$  is the mass of polymer per unit volume of solution. The entanglement Rouse time is in turn calculated using Eq. (2). One problem with Osaki's procedure is that the classical Rouse scaling relationship,  $G'(\omega) = \alpha\omega^{1/2}$ , is only observed over a limited range of frequencies. The prefactor  $\alpha$  must then be determined from a relatively small amount of experimental data, reducing the accuracy of  $\tau_R$  or  $\tau_e$  estimates. This problem arises from overlap of the local segmental and solvent contributions to the relaxation modulus with the Rouse chain modes. A second potential limitation of the method of Osaki is that some portion of the spectrum will always have the correct "Rouse" slope ( $\sim \omega^{1/2}$ ), since the strong frequency-dependence of the modulus in the transition zone must segue into the flat plateau region. Since it is not possible to evaluate *a priori* the origin of the narrow ( $\sim \omega^{1/2}$ ) scaling regime, the possibility exists for large errors.

Sanchez-Reyes and Archer (2003) recently suggested a procedure for removing solvent and segmental contributions from the dynamic moduli of entangled polymer solutions. In their approach, the high-frequency storage and loss moduli are first fitted using a multimode Maxwell model. The resulting Maxwell model expressions are used to calculate the segmental and solvent contributions,  $G'_S(\omega)$  and  $G''_S(\omega)$ , for the entire range of frequencies. Local segmental and solvent contributions are then removed by subtracting  $G'_S(\omega)$  and  $G''_S(\omega)$  from the experimental  $G'(\omega)$  and  $G''(\omega)$  data. This method is illustrated in Figs. 1(a) and 1(b), showing master curves of the dynamic mechanical moduli measured using two PS/DEP solutions (PS5.48M6 and PS20M8%, see Table I) at a reference temperature of 28.5 °C. Figures 2(a) and 2(b) are the respective moduli obtained after subtracting the solvent and segmental contributions. It is clear from both the latter plots that the procedure yields dynamic moduli exhibiting Rouse scaling over a relatively broad frequency range. For the PS20M8% sample, the storage modulus shows more deviation from the  $\omega^{1/2}$  behavior. This may reflect some ambiguity in the shape of the curves due to the well-established breakdown of time-temperature superpositioning in the transition zone [Roland *et al.* (2001); Santangelo and Roland (1998); Plazek (1996); Plazek *et al.* (1995)]. The ratio  $G''/G'$  increases with decreasing temperature in this region of the spectrum, reflecting the overlap of the local segmental and the chain modes.

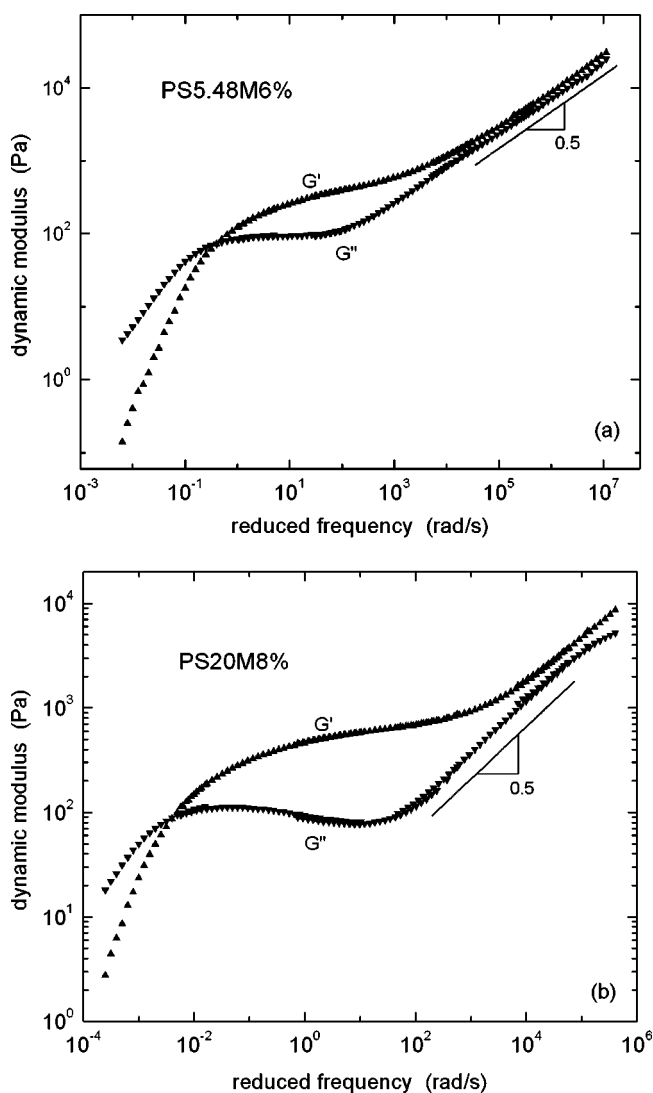
The longest Rouse relaxation time is determined by fitting the storage moduli in Figs. 2(a) and 2(b) to the expression  $G'(\omega) = \alpha\omega^{1/2}$ , and using Eq. (3) to compute  $\tau_R$ , with values of  $\tau_e$  then obtained from Eq. (2). Results for the four solutions are provided in Table I. These estimates are generally close to the values obtained by fitting the raw storage modulus data [Fig. 1(a)], in the manner of Osaki and coworkers (2001).

Finally, there is a direct method to deduce  $\tau_e$  from the modulus, as the intersection of the extrapolated rubber plateau  $G_N$  with the extrapolation of the  $\omega^{1/2}$  portion of the Rouse transition zone; thus,

$$\tau_e = (\alpha/G_N)^2. \quad (4)$$

These estimates of  $\tau_e$  are also given in the table.

The methods used by Osaki and coworkers (2001) and by Sanchez-Reyes and Archer (2003) for determining  $\tau_R$  assume that (i) a pure Rouse contribution can be isolated in at least a portion of the experimental  $G'(\omega)$  spectrums and (ii) the Rouse and local segmental contributions simply add in the modulus. If chain modes and the segmental relaxation modes are well-separated in frequency, the former assumption is reasonable.



**FIG. 2.** Data in Fig. 1 after subtraction of solvent and local segmental contributions to the dynamic moduli: (a) 6% PS ( $5.48 \times 10^6$  Daltons) solution, and (b) 8% PS ( $20.07 \times 10^6$  Daltons) solution. The lines with the slope of 1/2 represent the power law used to extract the Rouse behavior.

However, it is not obvious by inspection when sufficient separation has been attained. Moreover, the breakdown of time-temperature superpositioning in the transition zone belies such separation, since thermorheological complexity is a consequence of the differing temperature dependence of the two modes [Roland *et al.* (2001); Santangelo and Roland (1998); Plazek (1996); Plazek *et al.* (1995)]. Another intrusion of the chain modes into the high frequency dynamics comes from  $\eta_0$ , which can be shown to make a measurable contribution to the dynamic modulus even at the glass transition temperature [Plazek and O'Rourke (1971)]. Furthermore, from an analysis of stress birefringence data, Okamoto *et al.* (1995) concluded that the local segmental relaxation (referred to therein as the glassy component) dominates the viscoelastic response at frequencies well

into the rubbery plateau region. Clearly, a satisfactory method of deconvoluting overlapping contributions to the viscoelastic spectrum is of quite general importance.

Many workers have analyzed their experimental data by assuming additivity of the strains, whereby the viscosity [Janeschitz-Kriegl (1983); Ferry (1980)], segmental relaxation [Mott and Roland (1998); Ngai *et al.* (1996)], glassy compliance [Plazek *et al.* (1994)] and solvent contributions [Plazek *et al.* (1979)] are removed by subtraction of the appropriate compliance functions. Collectively, these results argue that overlapping contributions to the viscoelastic spectrum are additive in the compliance, not the modulus. Certainly, in the case of the viscous deformation and recoverable strain, the compliance functions are additive, as directly verified by creep-recovery experiments [Ferry (1980); Laun (1981)].

The dynamic mechanical data for the four PS solutions were reanalyzed by calculating the retardation spectra  $L(\lambda)$ , obtained from the dynamic moduli using [Ferry (1980)]

$$J'(\omega) = J_g + \int_{-\infty}^{\infty} \frac{L}{1 + \omega^2 \lambda^2} d \ln \lambda, \quad (5)$$

where  $J_g$  is the instantaneous compliance of the glass, and the storage compliance  $J'(\omega) = G'/(G'^2 + G''^2)$ . Conversion of the spectra was carried out by a nonlinear regularization method [Honerkamp and Weese (1993)]; the results were internally self-consistent. Figures 3(a) and 3(b) show the respective retardation spectra  $L(\lambda)$  of PS8.4M6 and PS20M8%. Both exhibit Rouse-mode and terminal maxima, which are separated by a region over which  $L(\lambda) \propto \lambda^{1/3}$ , the so-called Andrade terminal region [Andrade (1910); Plazek (1960); Berry (1976)]. (At shorter times, the solvent and segmental peaks are not well resolved. This may account for the absence of any “primary Andrade” creep region at shorter times, where again  $L(\lambda) \propto \lambda^{1/3}$ .) At longer times, the transition to the Andrade terminal behavior marks the onset of entangled dynamics, thereby defining of the Rouse retardation time,  $\lambda_e$ .

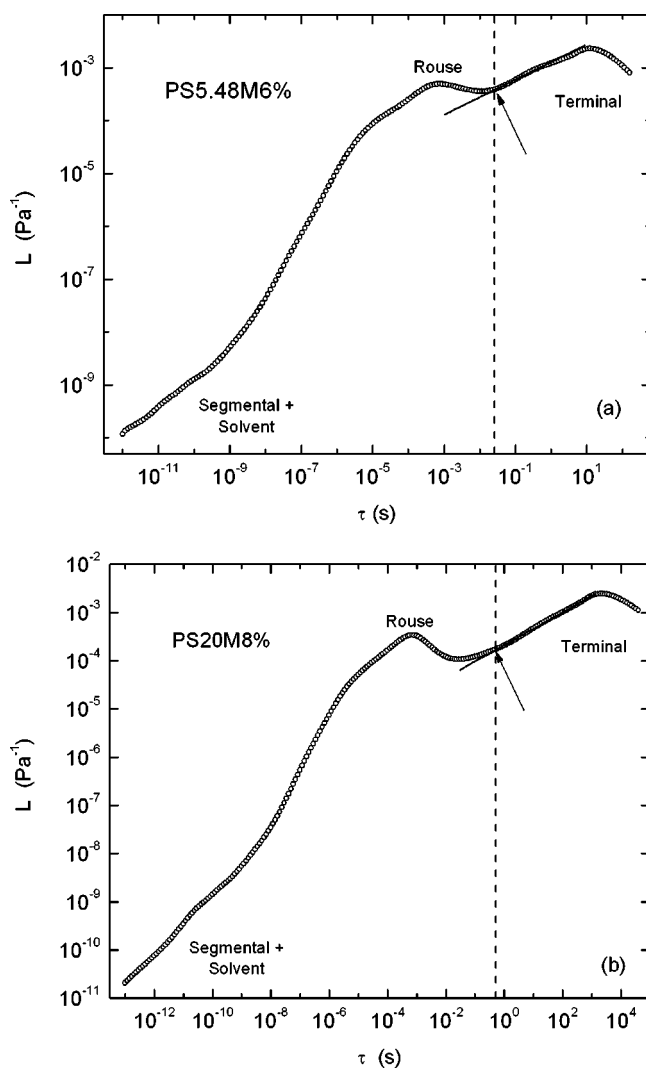
The obtained Rouse retardation times for all four solutions are listed in Table I. At fixed concentration, the entanglement time is expected to be independent of molecular weight [Ferry (1980)]. For the three solutions having the same concentration—PS3.8M6, PS5.48M6, and PS8.4M6%— $\lambda_e$  are indeed constant to within the experimental error. This is also true for the  $\tau_e$  in Table I. However, there is a substantial difference between the respective retardation and relaxation times, the former larger by an order of magnitude or more. The relation between the terminal retardation times and relaxation times of the Rouse model has been addressed by Berry (1987). At the long time end of the Rouse region (i.e., when the Rouse chain segment approaches the entanglement length), if the viscous contribution to the deformation is sufficiently small, the material can be treated as a Rouse solid, whereby  $\tau_1 = \tau_e$  and  $\lambda_0 = \lambda_e = 2.38\tau_e$  [Berry (1987)]. However, the  $\lambda_e$  in Table I exceed  $\tau_e$  by considerably more than this factor of 2.38.

An alternative method of obtaining  $\lambda_e$  is from the deviation of the recoverable creep compliance  $J_R(t)$  in the terminal region. The recoverable creep compliance is calculated from the retardation spectrum as

$$J_R(t) = J_g + \int_{-\infty}^{\infty} L(1 - e^{-t/\lambda}) d \ln \lambda, \quad (6)$$

in which  $t$  is the creep time. Since the terminal Andrade creep  $J_A(t)$  follows the relation

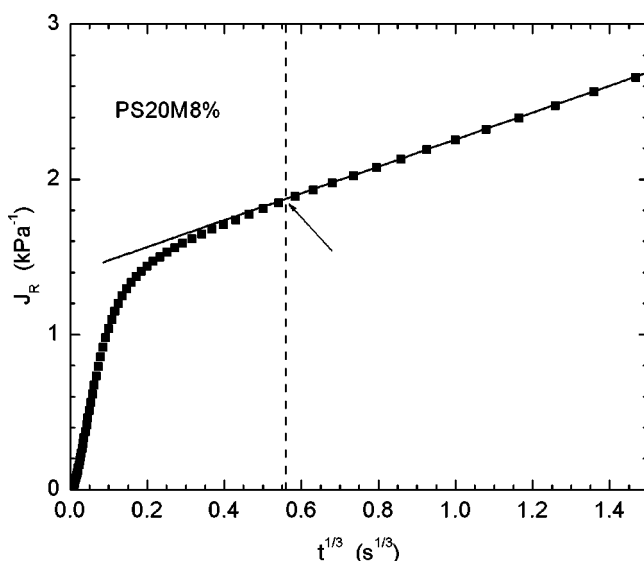
$$J_A(t) = J_A + \beta t^{1/3}, \quad (7)$$



**FIG. 3.** Retardation spectrum for (a) 6% PS ( $5.48 \times 10^6$  Daltons) and (b) 8% PS ( $20.07 \times 10^6$  Daltons) in diethyl phthalate, calculated from the dynamic modulus in Fig. 1. The deviation from the Andrade fit, denoted by the dashed line at  $\lambda = \lambda_e$ , demarcates the onset of entanglement effects, separating the Rouse and terminal zones.

where  $J_A$  and  $\beta$  are temperature-dependent constants, the onset of entanglements is revealed when  $J_R(t)$  becomes a straight line when plotted versus  $t^{1/3}$  [Plazek (1960)]. The result is shown in Fig. 4, from which we obtain  $\lambda_e = 0.56 \pm 0.02$  s for PS20M8%. This is equal to within the experimental error to the determination from  $L(\lambda)$ , and again significantly larger than the  $\tau_e$  from Eqs. (1)–(4). Similar results are obtained for PS8.4M6% (Table I). The two solutions of the lower molecular weight PS yield Andrade regions of insufficient extent for a reliable assessment to be made.

In conclusion, different procedures were used to deduce entanglement Rouse relaxation (or retardation) times from dynamic mechanical measurements. Values of  $\lambda_e$  obtained by rigorously deconvoluting the retardation spectrum are consistently larger than the  $\tau_e$  obtained from analysis of the modulus functions, although both methods yield the



**FIG. 4.** Recoverable compliance calculated from the retardation spectrum in Fig. 3(b). The deviation at shorter times from the Andrade fit yields  $\lambda_e$ .

expected molecular weight independence. Although some of this discrepancy can be ascribed to the differences in magnitude between Rouse relaxation and retardation times, we believe the discrepancy is real, and reflects an outstanding issue in polymer viscoelasticity.

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