

Dielectric Normal-Mode Relaxation of Entangled *cis*-Polyisoprene Melts: Effects of Polydispersity

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SYNOPSIS

The effects of polydispersity on the dielectric normal-mode relaxation of entangled, *cis*-polyisoprene melts are considered. We use a linear mixing rule and reptation theory in conjunction with a theoretical molecular weight distribution (MWD) of variable breadth to predict loss spectra of model *cis*-polyisoprene melts. The half-widths of the predicted spectra show a nonlinear dependence on polydispersity index, with the greatest sensitivity near the monodisperse limit. The calculations are in agreement with literature data on narrowly dispersed samples. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The study of dielectric normal-mode (NM) relaxation in entangled melts of *cis*-polyisoprene (*cis*-PI) offers the unique opportunity to probe the effects of polydispersity on the relaxation of nearly unperturbed linear chains. The strong directional correlation of the backbone components of the segmental dipoles endows the *cis*-PI chain with a nonzero net dipole moment proportional to its end-to-end vector (therefore, *cis*-PI is a type A polymer as classified by others¹⁻⁴). Measurable fluctuations in material polarization are thus linked to NM relaxation that, in entangled systems, occurs by reptation.⁵ NM relaxation emerges dielectrically as a low frequency loss peak with magnitude, shape, and position strongly dependent on the sample molecular weight distribution (MWD). A high frequency "segmental" loss-peak is also observed.¹⁻⁴ This peak, however, is insensitive to molecular weight characteristics of the sample. It originates from the fast fluctuation of the components of the segmental dipoles perpendicular to the chain contour, which lack long-range correlation.

The dielectric behavior of *cis*-PI has been extensively characterized.^{2,3,6-9} The effects of polydispersity on the NM contribution to the dielectric loss of

entangled melts have been considered by Imanishi et al.⁹ and lately by Fodor and Hill.¹⁰ Polydispersity broadens and lowers the NM loss spectra so that to first order, peaks' half-widths can be used as a measure of the breadth of the MWD. Imanishi and coworkers⁹ compared the half-widths of loss spectra of *cis*-PI samples with varying degree of polydispersity, as quantified by the ratio M_w/M_n , M_w and M_n being the weight and number average molecular weights, respectively. The half-widths below and above the peak frequency (which would differ from each other even for a monodisperse sample^{9,10}) were considered separately. Linear extrapolation of the low-frequency half-widths to $M_w/M_n = 1$ led to an intercept that agreed with reptation; but on the high frequency side the intercept was about 10% higher than expected, raising concern about the legitimacy of the reptation model.

The existence of a discrepancy in Imanishi's data was recently questioned by us.¹⁰ We argued that the inconsistency could be explained in terms of 1) unaccounted experimental scatter (which would have made extrapolation uncertain within 10%) and 2) failure of the linearity assumption (which was theoretically unjustified). We did not provide any evidence to support the latter statement, however. Clarification of this issue remains important if we are to lend credence to reptation theory.

We have recently shown that the dielectric response of moderately polydisperse *cis*-PI melts above entanglement can be quantitatively reproduced from

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the known MWD with the autocorrelation function of reptation and a linear mixing rule.¹⁰ Therefore, loss spectra of model systems with assigned MWD can now be predicted and the results compared to the data of Imanishi et al.⁹ As will be shown, the calculations support our previous claims, indicating that reptation indeed works. We also test the legitimacy of using a single polydispersity index to fully characterize a polydisperse system. MWDs with different shapes, but identical M_w and M_n , can produce loss spectra with widely different shapes and peak-frequency values. The relaxation-time spectra of such data would clearly show substantial structural differences, which could be erroneously attributed to inadequacies in the theoretical treatment.

Below we briefly review the set of equations and assumptions necessary for the predictions. Discussion of the results, comparison with experiments, and concluding remarks follow.

THEORY

The NM contribution to the dielectric loss for a type A polymer is related to the autocorrelation function of the end-to-end vector, $\Psi(t)$, as follows¹⁰

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty) \int_0^\infty \Psi(z/\omega) \cos(z) dz \quad (1)$$

where ϵ'' is the dielectric loss; ω the frequency; ($\epsilon_0 - \epsilon_\infty$) the dielectric strength (dependent on temperature, but not on molecular weight¹⁰); and z a dummy variable of integration.

The autocorrelation function of a polydisperse mixture is obtained by linearly weighing the relaxation functions of the individual species^{10,11}:

$$\Psi(t) = \sum_{i=1}^N \phi_i \psi(t/\tau_i) \quad (2)$$

$$\psi(t/\tau_i) = \frac{8}{\pi^2} \sum_{\substack{p=1 \\ p \text{ odd}}}^{\infty} \frac{\exp(-p^2 t/\tau_i)}{p^2} \quad (3)$$

where $\psi(t/\tau_i)$, ϕ_i , and τ_i are the relaxation function as predicted by reptation, volume fraction, and relaxation time of species i , respectively. The molecular weight dependence of the latter is of the power-law type, as indicated by experiments:

$$\tau_i = \tau_r (M_i/M_r)^\nu, \quad (4)$$

where, τ_r and M_r are reference relaxation time and molecular weight, respectively and, for *cis*-PI, $\nu = 3.70$.^{3,8-10,12}

The integral in Eq. (1) with Eqs. (2) and (3) as kernels can be easily carried out analytically, giving:

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty) \sum_{i=1}^n \phi_i \vartheta(\omega\tau_i) \quad (5)$$

where

$$\begin{aligned} \vartheta(\omega\tau_i) &= \int_0^\infty \Psi(z/\omega) \cos(z) dz \\ &= \frac{8}{\pi^2} \sum_{\substack{p=1 \\ p \text{ odd}}}^{\infty} \frac{\omega\tau_i}{p^4 + (\omega\tau_i)^2}. \end{aligned} \quad (6)$$

In summing the series in Eq. (6) care must be taken to ensure that an adequate number of terms are included.¹⁰ We have recently shown¹⁰ that Eqs. (4)–(6) can accurately predict the NM spectra of *cis*-PI melts above entanglement from the known MWD.

To systematically examine the effects of varying sample MWD we use two theoretical distributions. The Schultz distribution¹³ gives a fair description of typical samples with narrow MWD:

$$\phi_i = \frac{M_0 a}{M_n \Gamma(a+1)} \left(\frac{aM_i}{M_n} \right)^a \exp\left(-\frac{aM_i}{M_n}\right). \quad (7)$$

Here ϕ_i and M_i are the weight fraction and molecular weight of species i , respectively; M_n the number average molecular weight; $(M_w/M_n) = (a+1)/a$; $\Gamma(X)$ the gamma function; and M_0 the monomer molecular weight, equal to 68 g/mol for *cis*-PI.

We also use a uniform, or “box” distribution (which is of course purely theoretical, but simple):

$$\begin{aligned} \phi_i &= \phi^* \quad \text{for } M_1 \leq M_i \leq M_2 \\ \phi_i &= 0 \quad \text{otherwise.} \end{aligned} \quad (8)$$

Comparison of loss spectra calculated with Eqs. (7) and (8) allows us to examine the effects of the shape of the MWD.

The above equations can also be recast in terms of a continuous MWD, $f(M)$:

$$f(M) d \ln M = \frac{dW}{W_{\text{tot}}} \quad (9)$$

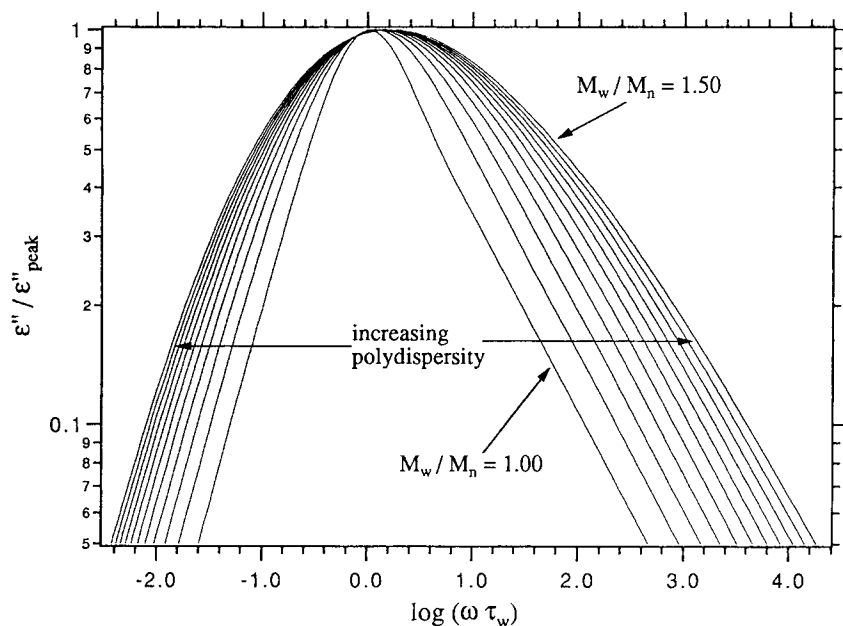


Figure 1 Predicted dielectric loss spectra from a Schultz molecular weight distributions with M_w/M_n ranging from 1.0 to 1.5 in increments of 0.05, as determined by Eq. (7). The spectra have been normalized by their peak values and the frequency has been reduced by τ_w , as discussed in the text.

where dW/W_{tot} is the weight fraction of species with molecular weight between M and $M + dM$. For sufficiently fine discretization, the discrete and continuous distributions are related as follows:

$$f(M) = \phi(M) \frac{M}{M_0} \quad (10)$$

Relations linking M_1 and M_2 to M_w and M_n for the box distribution [Eq. (8)] can easily be calculated in the continuum limit:

$$M_n = (M_2 - M_1) / \ln(M_2/M_1) \quad (11)$$

$$M_w = (M_2 + M_1) / 2. \quad (12)$$

It is interesting to examine the consequences of choosing a molecular weight distribution of the form $f(a, M/M_n)$ (such as the Schultz distribution), where a is a parameter related to the polydispersity index. Equations (4)–(6) can then be recast as follows:

$$\begin{aligned} \varepsilon''(\omega\tau^*, a, \nu) &= (\varepsilon_0 - \varepsilon_\infty) \\ &\times \int_{-\infty}^{\infty} f(a, X) \vartheta(\omega\tau^* X^\nu) d \ln X \quad (13) \end{aligned}$$

where

$$X = M/M_n \quad (14)$$

$$\tau^* = \tau_r \left(\frac{M_n}{M_r} \right)^\nu \quad (15)$$

It is clear from Eqs. (13)–(15) that, for a given functionality $f(a, X)$ and a fixed value of ν [Eq. (4)], a change in M_n (or M_w) at a fixed polydispersity will cause the loss spectrum to shift immutably either to the right (decreasing M_n) or to the left (increasing M_n) along the $\log(\omega)$ axis. Loss spectra of samples with identical polydispersity indices will have then identical shapes, but different positions along the frequency axis. Concomitantly, the distributions of relaxation times will be identical, but shifted. Only in such an idealized situation would a comparison between relaxation times spectra of different samples be truly legitimate.

RESULTS AND DISCUSSION

Comparisons between experimental loss spectra of *cis*-PI with the predictions of Eqs. (4)–(6) and the measured MWD from size exclusion chromatogra-

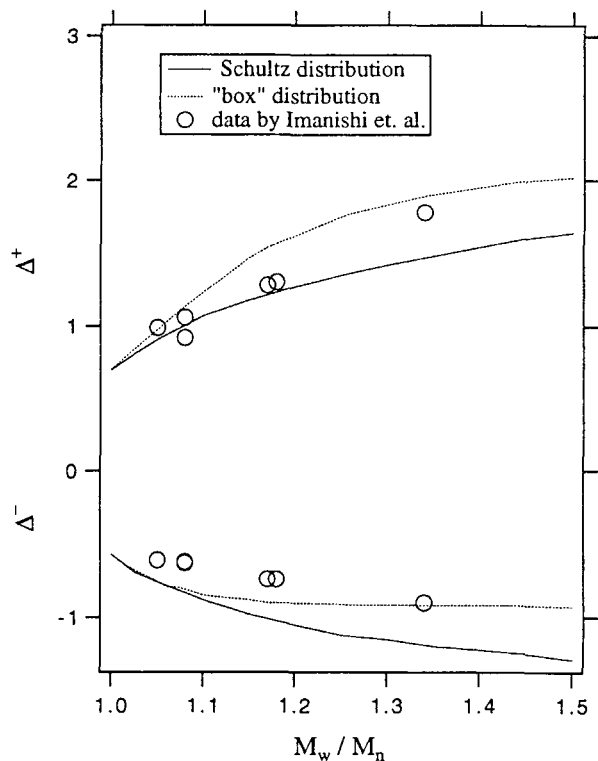


Figure 2 Half-widths, Δ^+ and Δ^- , plotted against M_w/M_n . Open circles are data by Imanishi et al.⁹ Solid line: Schultz distribution. Dotted line: "box" distribution (see text for details).

phy are reported elsewhere.¹⁰ Figure 1 shows predicted loss spectra of increasing polydispersity obtained with the Schultz distribution [Eq. (7)]. Parameter a was varied in the range $1.00 \leq M_w/M_n \leq 1.50$ in increments of 0.05. Broadening of the distribution decreases the peak values of the spectra, so that all curves were normalized by their peaks and plotted against the reduced frequency $\omega\tau_w$, τ_w being the relaxation time corresponding to M_w . Note the slight inflection on the high-frequency side of the monodisperse spectrum and how it quickly disappears with only a slight increase in polydispersity. In approaching the monodisperse limit the curves become extremely sensitive to small degrees of polydispersity. Therefore, comparison of monodisperse theories with experimental data of samples with polydispersity as low as 1.1 (often assumed to be monodisperse) should be treated with caution.

As proposed by Imanishi et al.⁹ the half-width of the spectra, Δ , can be used as a measure of polydispersity. The half width is defined as the decimal logarithm of the ratio of the frequencies where the spectrum falls to 50% of its peak value. Because of the intrinsic asymmetry of the loss curves, a more detailed description of spectral broadness can be obtained by separating the low- (Δ^-) from the high-frequency (Δ^+) contributions to Δ relative to the peak frequency. Figure 2 shows the predicted Δ^-

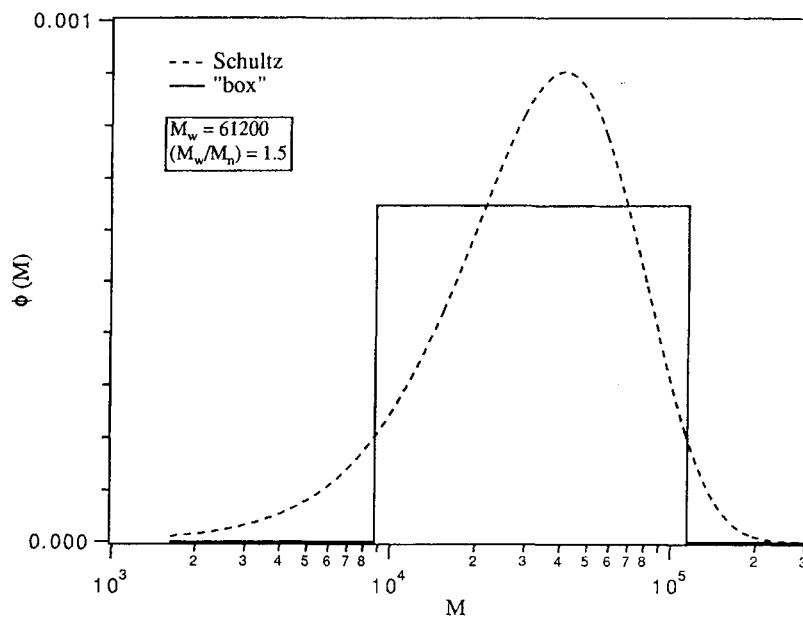


Figure 3 Schultz (dashed line) and "box" (solid line) distributions having identical values of M_w and M_n .

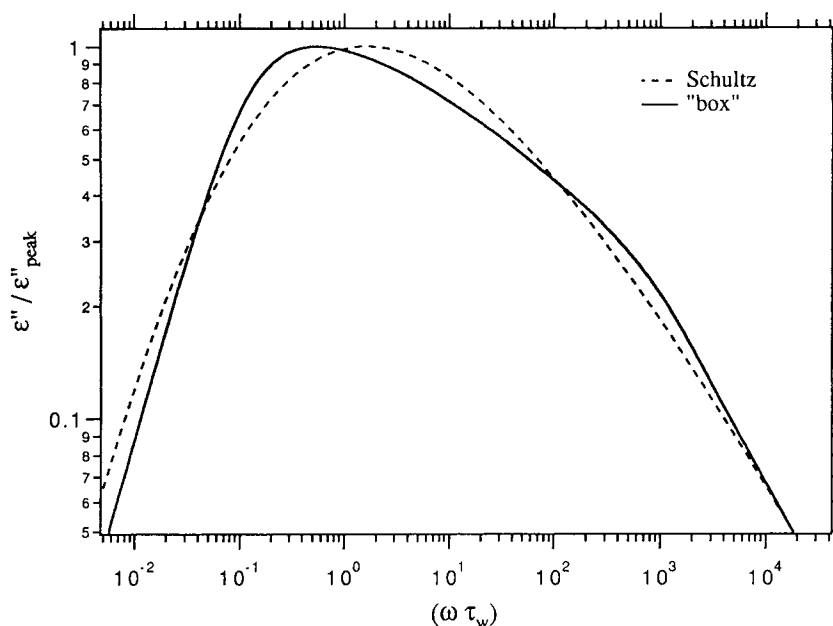


Figure 4 Loss spectra predicted from the “box” (solid line) and a Schultz (dashed line) distributions shown in Figure 3. The spectra have been normalized as in Figure 1.

and Δ^+ (determined from Fig. 1) plotted against M_w/M_n . Superposed on the predictions are the data of Imanishi et al.⁹ Detailed quantitative agreement between theory and experiments was not expected, due to anticipated differences between the assumed and the actual (unknown) molecular weight distributions. The experimental trends are captured by the theory, however. The predictions clearly show that linear extrapolation of the Δ^+ data to $M_w/M_n = 1$ can lead to inaccurate estimates of Δ^+ in the monodisperse limit. (Note, especially, the pronounced change in the trend below about $M_w/M_n = 1.05$.) This justifies the discrepancy reported by Imanishi et al.⁹

The use of a single parameter to characterize a polydisperse system may be questionable, even for narrow molecular weight distributions. Distributions with identical M_w and M_n could, in fact, be highly dissimilar, leading to marked differences in observable properties for nominally identical samples. Figure 3 shows a Schultz distribution [Eq. (7)] and a “box” [Eq. (8)] distribution both characterized by $M_w = 61.2$ kg/mol and $M_w/M_n = 1.50$. The loss spectra for each case are shown in Figure 4. The spectra have been normalized by their peak values and plotted against $\omega\tau_w$. The half-widths calculated from the box distribution are also shown in Figure 2. The trends are similar to the Schultz case and,

interestingly, although Δ^+ and Δ^- individually show appreciable variation with the type of distribution, the global half-widths $\Delta = |\Delta^+| + |\Delta^-|$ do not, being nearly identical to within a few percent. It can be seen that the Δ^- predictions lie above the experimental data. This is an indication that the experimental MWDs were much steeper on the high molecular weight side than the equivalent Schultz distribution that we have used.

CONCLUSION

We have analyzed the effects of small degrees of polydispersity and the shape of the molecular weight distribution on the dielectric loss spectrum. Predictions with distributions of variable breadth captured the trends in the data of Imanishi and coworkers⁹ on *cis*-PI samples of narrow MWD. In particular, the previously reported discrepancy between experimental half-widths and the monodisperse prediction of reptation was shown to originate in an improper linear extrapolation procedure, inadequate to capture the extreme sensitivity of the loss spectra to polydispersity near the monodisperse limit.

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