The relaxation time spectrum of nearly monodisperse polybutadiene melts*)

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Abstract: The relaxation behavior of polymers with long linear flexible chains of uniform length has been investigated by means of dynamic mechanical analysis. The relaxation time spectrum ($H(\lambda)$) follows a scaling relationship with two self-similar regions, one for the entanglement and terminal zone, and a second one for the transition to the glass. This can be described in its most general form (termed "BSW spectrum") as $H(\lambda) = H_e \lambda^{n_e} + H_g \lambda^{-n_g}$ for $\lambda < \lambda_{max}$ and $H(\lambda) = 0$ for $\lambda_{max} < \lambda$, where H_e, H_g, n_e, n_g are material constants and λ_{max} is the molecular weight dependent cut-off of the self-similar behavior. In this study, the dynamic mechanical response has been measured and analyzed for four highly entangled, nearly monodisperse polybutadienes with molecular weights from 20000 to 200000. The data are well represented by the BSW spectrum with scaling exponents of $n_e = 0.23$ and $n_g = 0.67$. The values of the exponents obtained in this work are about the same as those found for polystyrene samples in a previous study. This suggests that the two types of polymers have a similar relaxation pattern. However, at this point further refinement of the experiments is needed before being able to draw definite conclusions about the universality of the exponents.

Key words: Relaxation time spectrum; monodisperse polymer; self-similarity; polybutadiene melt

Introduction

Polymers with long linear flexible chains of uniform length relax in a very distinct pattern which can be probed experimentally through the dynamic moduli G', G'' (Onogi et al. (1970), Schindlauer et al. (1985), Marin, Graessley (1977)). Distinct regions can be identified for the i) flow regime at low frequencies (denoted "terminal zone" of the relaxation time spectrum), ii) the entanglement regime at intermediate frequencies, iii) transition regime towards the glass, and iv) the glassy region. This experimental study will concentrate on regions i – iii, for which the experimental parameters are the plateau modulus (G_N^0), a longest relaxation time (λ_{max}), a relaxation time for the onset of the glass transition (Rouse time) (λ_0), a slope for G'' in the entanglement regime ($-n_e$), and a slope of G' and G'' in the transition to the glass (n_g).

Many proposals have been made for describing the flow and entanglement behavior from first principles by postulating a model of the molecular motion (Rouse (1953), de Gennes (1979), Doi, Edwards (1986), Bird et al. (1987), des Cloizeaux (1990)). These molecular theories have given much insight into the origin of the macroscopically observed parameters, even if a quantitative agreement with experimental data does not seem to be achievable without a range of correction terms.

Much further insight may be gained by studying polymer relaxation experimentally. However, the understanding of linear viscoelastic data has been obscured by their conventional format. They were mostly observed in the form of the dynamic moduli

$$G'(\omega) = \int_0^\infty H(\lambda) \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda} \, , \qquad (1)$$

$$G''(\omega) = \int_0^\infty H(\lambda) \frac{\omega\lambda}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda} \, , \qquad (2)$$

or in the form of the relaxation modulus

$$G(t) = \int_0^\infty H(\lambda)e^{-t/\lambda}\frac{d\lambda}{\lambda} , \qquad (3)$$

while we really need to know the relaxation time spectrum $H(\lambda)$. A direct Fourier transform of the data is not possible since the experimental data are limited to a certain frequency window, i.e., they are truncated at high and, also, often at low frequencies.

Major advances have been made recently in the determination of the relaxation time spectrum (called "spectrum" from here on) from experimental data. The conversion from the frequency to the time domain takes advantage of the fact that G'' probes the spectrum locally while G' is a more integral measure of the relaxation. The resulting spectrum is valid in the time window which corresponds to the experimental frequency window. The calculated spectrum may be represented in continuous form or as a sum of discrete Maxwell modes (Baumgaertel, Winter (1992)).

These new methods made it possible to determine the continuous relaxation time spectrum of polystyrene standards (Baumgaertel et al. (1990)). The molecular weights varied from 39500 to 2500000, and the reference temperature for the data was 180°C. The spectrum was expressable in the simple form

$$H(\lambda) = \begin{cases} H_e\lambda^{n_e} + H_g\lambda^{-n_g} & \text{for} \quad \lambda_1 < \lambda < \lambda_{max} \\ 0 & \text{for} \quad \lambda > \lambda_{max} . \end{cases} \qquad (4)$$

In the following, we will denote Eq. (4) as the BSW-spectrum. Very short time data are not available, so that this spectrum is only valid above the shortest observation time, λ_1, of the experimental data. The first term represents the entanglement and flow regime (regions I – II), having a coefficient

$$H_e = n_e G_N^0 \lambda_{max}^{-n_e} . \qquad (5)$$

The second term represents the transition zone (region III)

$$H_g = n_g G_N^0 \lambda_0^{n_g} . \qquad (6)$$

No new parameters had to be introduced beyond the parameters which are commonly used to characterize G', G'' data. The spectrum is equal to zero above the longest relaxation time, λ_{max}. The crossover between regions II and III has simply been approximated by the linear superposition of the two power laws, Eq. (4), for regions II and III.

The BSW-spectrum, when introduced into Eqs. (1) and (2), is able to represent the G', G'' data within the experimental noise level. It should be emphasized that the conversion method, which originally was needed to find the BSW-spectrum, has no significance from here on. The parameters of the BSW-spectrum can be determined directly from the G', G'' data.

The range of validity of the BSW-spectrum and the value of the exponents n_e and n_g need to be explored further. A wider range of linear viscoelastic data has to be made available. For this purpose, we measured the dynamic moduli of several polybutadiene melts of high molecular weights and narrow molecular weight distribution. The data were analyzed in terms of the BSW-spectrum.

Experimental

Material and Characterization

Experiments were performed with four specifically synthesized polybutadiene samples of different molecular weights. The polymers were synthesized using a standard anionic technique. The polymerization was done in cyclohexane at 50°C. Both the monomer and solvent were purified before polymerization. The initiator was s-BuLi. At the end of a 2-h reaction the polymerization was terminated using anhydrous methanol. To prevent oxidation Ethanox 330 was added at 0.5% by weight of the polymer. Cyclohexane was removed by first allowing free evaporation and then stripping at reduced pressure, both at room temperature. These polymerization conditions were employed for the bench-top synthesis of these samples. GPC analysis and proton NMR were performed to determine the molecular weights, polydispersity, and 1,2-vinyl content of the samples. The glass transition temperature of the samples was measured on a DuPont DSC instrument model 2910 at a heating rate of 20 K/min. A summary of the characterization is shown in Table 1. The polydispersity of the samples is below 1.1, except for the sample with the molar mass of 201000 g/mol, which is 1.27.

Table 1. Characterization of polymer samples

Sample	Mw	Mw/Mn	% cis[#]	% trans[#]	% vinyl	% vinyl[*]	Tg (°C)
PBD-1	20700	1.04	39	53	8	8.19	−91.3
PBD-2	44100	1.04	–	–	–	8.11	−90.4
PBD-3	97000	1.07	–	–	–	8.04	−89.6
PBD-4	201000	1.27	–	–	–	7.88	−92.0

[*] measured by ^{1}H NMR
[#] measured by F.T. Raman spectroscopy

Rheological measurements

Storage and loss moduli were measured as a function of frequency using a Rheometrics Dynamic Mechanical Spectrometer, RDS 7700, with parallel plate geometry. The gap between the plates was adjusted to about 1.5 mm. Measurements were made at temperatures in the range of $-77\,°C$ to $+60\,°C$. Cooled nitrogen was continuously circulated in the environmental chamber to obtain subambient temperatures. Time-temperature superposition allowed shifting of the dynamic data into master curves.

Spectrum interpretation

A standard program (Baumgaertel, Winter (1989)) was used to express the dynamic mechanical data in the form of a discrete spectrum

$$H(\lambda) = \sum_{i=1}^{N} g_i \, \delta(1 - \lambda/\lambda_i) \, , \tag{7}$$

which is equivalent to a discrete relaxation modulus

$$G(t) = \sum_{i=1}^{N} g_i e^{-t/\lambda_i} \, . \tag{8}$$

It consists of a linear superposition of N Maxwell modes of strength g_i and relaxation time λ_i. $\delta(x)$ is the Dirac delta function. The spectrum determination was optimized with the objective to describe the data within the experimental scatter while using the smallest possible number of representative Maxwell modes. Such an approach is termed "parsimonious modeling" (PM). The corresponding discrete spectrum (PM-spectrum) will be used throughout the paper as a convenient way to represent the experimental data.

Results

All the dynamic data measured obeyed the time-temperature superposition principle

$$G'(\omega, T) = b_T G'(a_T \omega, T_{ref}) \, , \tag{9}$$

$$G''(\omega, T) = b_T G''(a_T \omega, T_{ref}) \, . \tag{10}$$

The temperature dependence of the horizontal shift factor a_T (see Fig. 3) was accurately described by the WLF equation (Ferry (1980))

$$\log a_T = -\frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}} \, . \tag{11}$$

Figures 1 and 2 show dynamic data master curves of the four polybutadiene standards at a reference temperature of $T_{ref} = 28\,°C$. The shifting parameters do not depend on molecular weight (a result which was expected). When plotted as tan δ (see Fig. 4), the data show the distinct regions for flow at low frequencies (terminal zone), entanglements at intermediate frequencies, and transition to the glass at high frequencies.

The sample with the highest molecular weight was measured on the Rheometrics RMS 800 and the result was compared to the data taken on the RDS 7700.
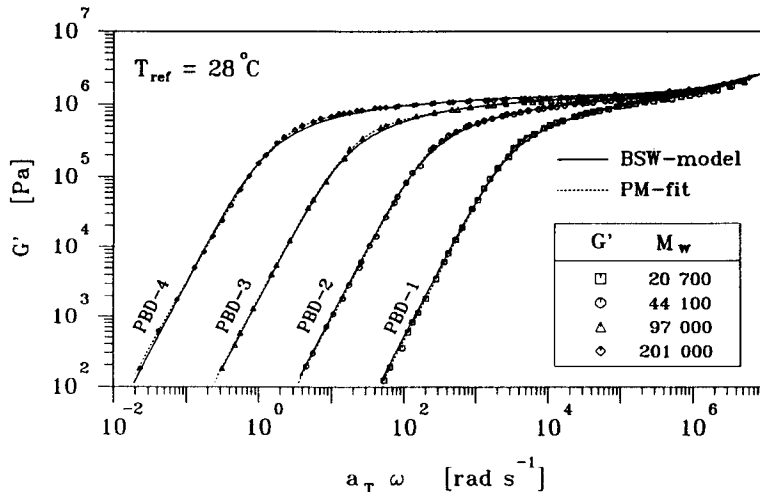

Fig. 1. Storage moduli $G'(\omega)$ of polybutadiene standards which were synthesized by using anionic polymerization. The molecular weights and the polydispersities of the samples are PBD-1: $M_w = 20700$ g/mol, $M_w/M_n = 1.04$; PBD-2: $M_w = 44100$ g/mol, $M_w/M_n = 1.04$; PBD-3: $M_w = 97000$ g/mol, $M_w/M_n = 1.07$; PBD-4: $M_w = 201000$ g/mol, $M_w/M_n = 1.27$. The experimental temperatures (°C) were 28, 10, -10, -25, -35, -45, -55, -60, -65, -70, -77 and the reference temperature is $28\,°C$
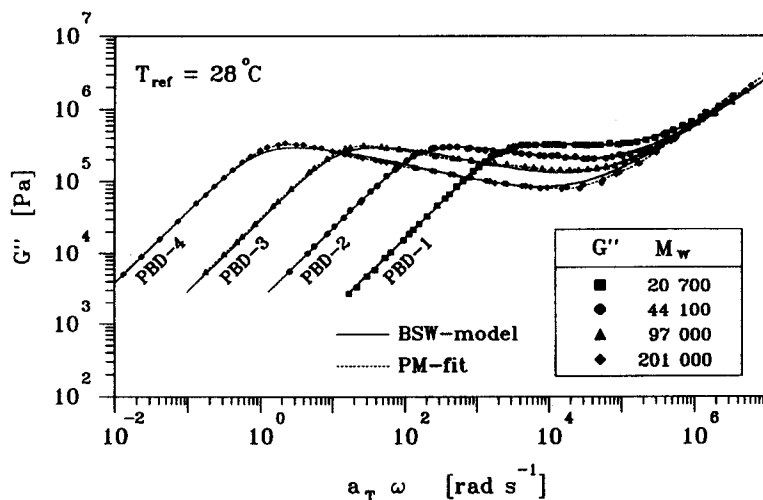
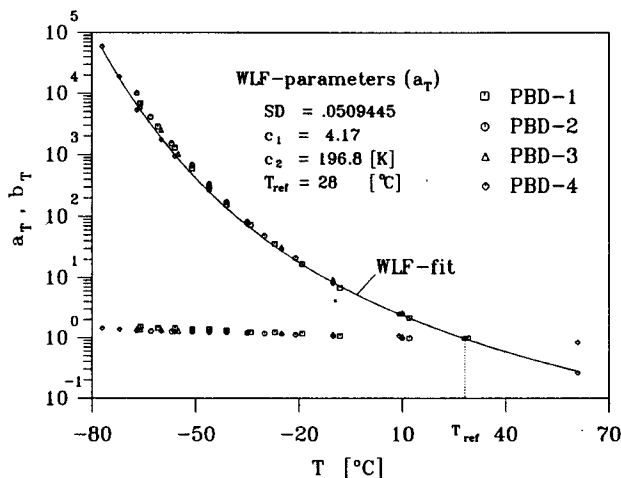Fig. 2. Loss moduli $G''(\omega)$ corresponding to the data in Fig. 1

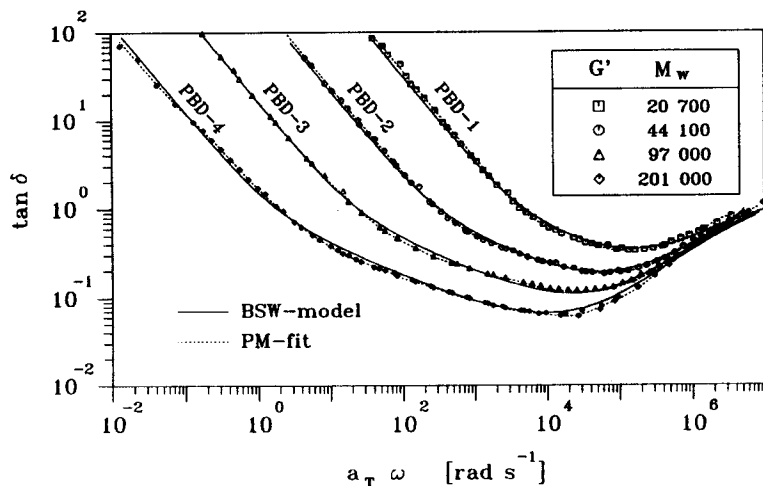Fig. 3. Temperature shift factors a_T and b_T for time-temperature superposition of experimental data

This was done to insure that the data, especially in the entanglement regime, are consistent when taken on different instruments. The data agree well between the two instruments as shown in Fig. 5.

There was some concern about sample stability. Therefore, the highest molecular weight sample was vacuum stripped at 80 °C for 34 h and measured again on the RDS 7700. As can be seen in Fig. 5, the sample was found to be unaffected by vacuum stripping. Some slight crosslinking may have occurred between the 1,2-vinyl units due to the exposure at the elevated temperature, as evidenced by the slight discrepancy of the data in the terminal region for the vacuum-stripped sample.
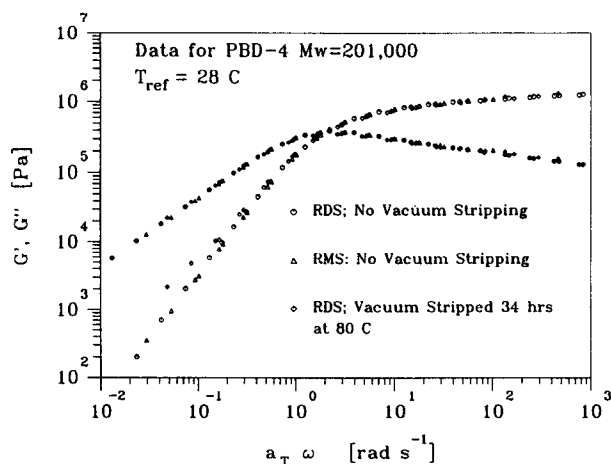

Fig. 4. Loss tangent, tan $\delta(\omega)$, corresponding to the data in Figs. 1 and 2

Fig. 5. Dynamic mechanical data from two instruments with variations in sample preparation. Sample: polybutadiene standard with $M_w = 201\,000$

Interpretation

The data of Figs. 1 and 2 can be converted into relaxation spectra $H(\lambda)$. The continuous relaxation spectra are shown by the continuous lines in Fig. 6. These BSW-spectra represent the data very closely, as demonstrated with the continuous lines in Figs. 1, 2, and 4.

The discrete Maxwell modes of the parsimonious model (PM-modes) of the four samples are shown as distinct points in Fig. 6. The PM-spectrum describes the data even more closely than the continuous BSW-spectrum. This is demonstrated with the dashed lines in Figs. 1, 2, and 4.

The parameters for the spectra are $G_N^0 = 1.41$ MPa, $n_e = 0.23$, $\lambda_0 = 8.71 \times 10^{-8}$ s, $n_g = 0.67$.
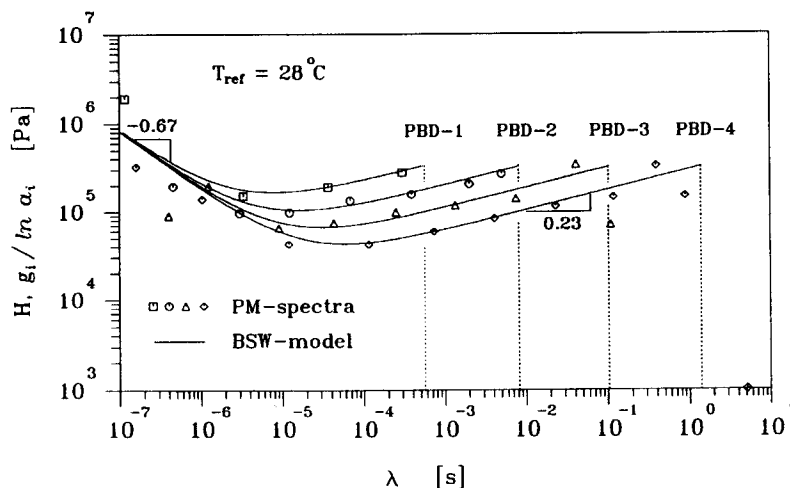
The longest relaxation times were found to be $\lambda_{max} = 6.34 \times 10^{-4}$ s, 8.37×10^{-3} s, 0.122 s, 1.45 s for the four PB standards. They follow a relation

$$\lambda_{max} = \lambda_0 (M/M_0)^{3.4} , \qquad (12)$$

as shown in Fig. 7. The exponent is in agreement with values in the literature.

The plateau modulus for the samples of molecular weights 20700 and 44100 are 1.10 MPa and 1.21 MPa, respectively. These values agree well with the those obtained by Raju et al. (1981), Colby et al. (1985), Aranguren and Macosko (1988), and Carella and Graessley (1984). The values of the next two molecular weights of 97000 and 201000 were slightly higher at 1.45 MPa and 1.38 MPa, respectively. The plateau modulus of 1.41 MPa used for the BSW model is somewhat higher than the values found by the authors above, but gave the best fit of the data for all the samples measured. The G'' slope, which is the scaling parameter in the BSW spectrum, has a value which has also been found by Carella and Graessley (1984). Data of Colby et al. (1991) suggest a somewhat higher value of n_e.

For most linear flexible polymers, the entanglement molecular weight M_0 is related to the plateau modulus G_N^0

$$M_0 = g_N \frac{\varrho R T}{G_N^0} . \qquad (13)$$

The numerical factor g_N is close to unity for most linear flexible polymers, and ϱ is the density of the polymer. The plateau modulus G_N^0 is assumed to be independent of the molecular weight and of the mo-

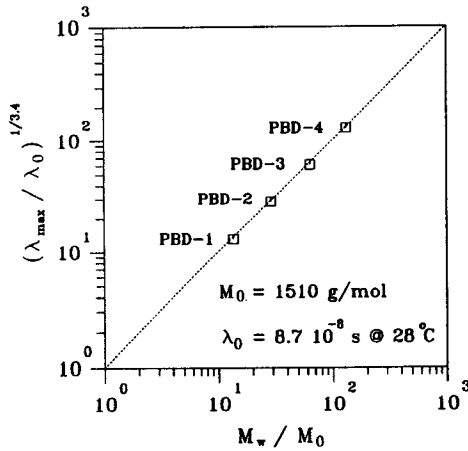Fig. 6. Continuous BSW-spectra and discrete PM-spectra of the four PB standards of Figs. 1 and 2

Fig. 7. Molecular weight dependence of the longest relaxation time

lecular weight distribution, as long as all polymer chains are longer than the critical chain length. This assumption is supported by theoretical considerations which propose that the entanglement density is unaffected by molecular weight, thus leading to a constant plateau modulus.

With these molecular parameters, the BSW-spectrum may be rewritten as

$$H(\lambda) = G_N^0 \left\{ n_e \left(\frac{M_0}{M}\right)^{3.4n_e} \left(\frac{\lambda}{\lambda_0}\right)^{n_e} + n_g \left(\frac{\lambda}{\lambda_0}\right)^{-n_g} \right\}$$

$$\text{for} \quad \lambda_1 < \lambda < \lambda_0 (M/M_0)^{3.4} \tag{14}$$

and

$$H(\lambda) = 0 \quad \text{for} \quad \lambda > \lambda_0 (M/M_0)^{3.4} . \tag{15}$$

Discussion

The plateau modulus cannot be measured directly. It is defined as an extrapolation of the entanglement contribution (region II) to G, G', or G'' at short times or high frequency. Its various definitions (Ferry (1980))

$$G_N^0 = \lim_{t \to 0} G_{II}(t) = \lim_{t \to 0} \int_0^\infty H_{II}(\lambda) e^{-t/\lambda} \frac{d\lambda}{\lambda} , \tag{16}$$

$$G_N^0 = \lim_{\omega \to \infty} G_{II}'(\omega) = \lim_{\omega \to \infty} \int_0^\infty H_{II}(\lambda) \frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda} , \tag{17}$$

$$G_N^0 = \frac{2}{\pi} \int_0^\infty G_{II}''(\omega) \frac{d\omega}{\omega}$$

$$= \frac{2}{\pi} \int_0^\infty \int_0^\infty H_{II}(\lambda) \frac{\omega\lambda}{1+(\omega\lambda)^2} \frac{d\lambda}{\lambda} \frac{d\omega}{\omega} \tag{18}$$

can all be expressed as

$$G_N^0 = \int_0^\infty H_{II}(\lambda) \frac{d\lambda}{\lambda} , \tag{19}$$

where subscript II denotes the contribution of the entanglement regime (or the neglect of any glass transition at short times or high frequencies). The above condition is obviously satisfied by the BSW-spectrum: For $H_{II}(\lambda) = n_e G_N^0 \lambda_{max}^{-n_e}$ we obtain

$$G_N^0 \equiv \int_0^{\lambda_{max}} n_e G_N^0 (\lambda/\lambda_{max})^{n_e} \frac{d\lambda}{\lambda} . \tag{20}$$

More interesting is the decomposition of the BSW-spectrum into two contributions, one for flow and entanglement behavior, and one for the transition to the glass (see Fig. 8). The consequences of the decomposition for the dynamic moduli are informative (Fig. 9). The moduli without the glass transition, G_{II}' and G_{II}'' give the dashed lines in continuation of the data. Log G_{II}'' has a slope of $-n_e$ at high frequencies.

The dotted lines in Fig. 9 denote the glass transition component of the spectrum G_{II}' and G_{II}''. Too little data are available to decide on a definite value of n_e. From a practical point of view, it is important to note that the dotted lines will intersect the data at a low frequency. This has been avoided by truncating the lower end of that spectrum (see curvature at low frequencies).

The continuous spectrum does not lend itself to analytical solutions for linear viscoelastic material functions such as $G(t)$, $G'(\omega)$, or $G''(\omega)$. For evaluation of these functions, it is easiest to express the BSW-spectrum in a discrete set of densely spaced Maxwell modes. The individual contributions of these Maxwell modes are simple analytical functions which may be added up to obtain solutions for the linear viscoelastic material functions. The discrete representations of the BSW spectrum

$$G(t) = \sum_{i=1}^{N_e} g_{1,e} a_e^{n_e(i-1)} \exp \left\{ \frac{-t}{a_e^{i-1} \lambda_{max}} \right\}$$

$$\underbrace{\phantom{G(t) = \sum_{i=1}^{N_e} g_{1,e} a_e^{n_e(i-1)} \exp}}_{\text{flow and entanglement regime}}$$

$$+ \sum_{i=1}^{N_g} g_{1,g} \, a_g^{n_g(i-1)} \exp \left\{ \frac{-t}{a_g^{i-1} \lambda_0} \right\} \qquad (21)$$

$$\underbrace{\hspace{5cm}}_{\text{glass transition regime}}$$

contain the spacing of the discrete modes

$$a = \lambda_{i+1}/\lambda_i \ ; \quad a = 0.9 \ , \qquad (22)$$

which was chosen here to be constant and of a value of about $a \rightarrow 1$, in order to make the spacing narrow. The leading Maxwell modes are defined by $(g_{1,e}; \lambda_{max})$ and $(g_{1,g}; \lambda_0)$.

When discretizing the continuous spectrum, the sudden cut-off is replaced by a more gradual decay

near $\lambda = \lambda_{max}$. As part of this gradual transition, an additional weak Maxwell mode needs to be introduced with a time constant greater than λ_{max}. The definition of a longest relaxation time becomes unclear. However, the representation of the data is equally satisfactory with the gradual decay as with the sudden cut-off.

Conclusions

The polybutadiene standards follow the same relaxation pattern as the previously studied polystyrene standards. The BSW-spectrum closely represents this relaxation behavior.

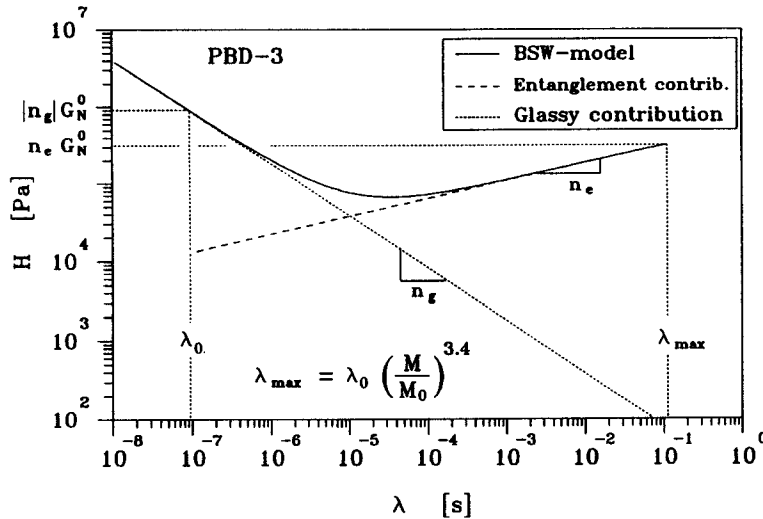Most parameters in the BSW-spectrum are well-founded in molecular theory, i.e., plateau modulus

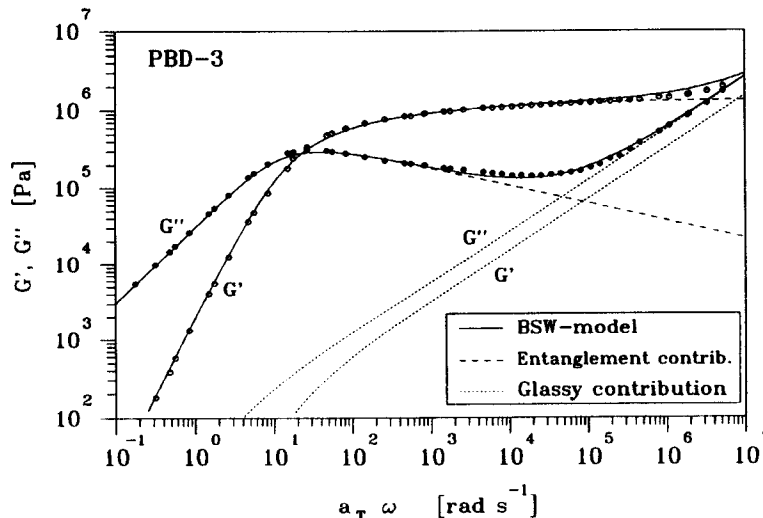Fig. 8. Decomposition of the spectrum in the entanglement and glass transition zone

Fig. 9. Contributions of the entanglements and of the glass transition to the dynamic mechanical behavior

and longest relaxation time. The origin of the scaling parameter n_e is not known yet. Many experiments indicate that n_e is a material constant with a value of about $0.2 - 0.25$ for PB and PS. The experimental error (transducer compliance, mainly) is still too high for making a conclusive statement. There remains a possibility that n_e may slightly increase with molecular weight; n_e seems to slightly depend on the polymer.

More data are needed at high frequencies. The onset to the glass transition, however, is well-represented with a power-law spectrum with a negative exponent.

Future studies should concentrate on further improvement of dynamic mechanical instruments with the objective of more accurately measuring the phase angle δ.

Acknowledgement

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