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# The occurrence of self-similar relaxation in polymers

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## Abstract

Several observations of self-similar relaxation behavior have been reviewed and grouped. Parameters are the exponent of the self-similar spectra, the front factor and the upper and lower bound of the self-similar region. Properties of self-similar spectra have been explored for negative and for positive exponent values.

## 1. Introduction

Polymeric materials relax with a broad distribution of relaxation modes. The longer modes originate from the motion of large molecular chain segments and short modes depend on the small-scale chemical detail. Extra long relaxation modes arise from large-scale structures which some polymers are able to form due to phase separation or due to associations on molecular or particular level. The distribution of relaxation modes represents the material structure in some convoluted way. The search for a one-to-one relation between relaxation spectrum and molecular structure has attracted much attention, not only because of its practical importance but also from a fundamental point of view.

It is most remarkable that some materials relax with a very simple power law over a wide time window as will be discussed below. Such behavior

has been termed 'self-similar' or 'scale invariant' since it is the same at any time scale of observation (within the given time window). Self-similar relaxation has been associated with self-similar structures on the molecular and supra molecular level and, for suspensions and emulsions, on particulate level.

The relaxation time spectrum  $H(\lambda)$  (for example, Ref. [1]), abbreviated as 'spectrum' in the following, defines the linear viscoelastic behavior of a material. The spectrum is a non-negative function (Ref. [2]) which exists in the range of relaxation times  $0 < \lambda \leq \lambda_{\max}$ . An important material property is the longest relaxation time,  $\lambda_{\max}$ , beyond which the spectrum vanishes,  $H(\lambda) = 0$  for  $\lambda > \lambda_{\max}$ . The Laplace transform of the spectrum defines the transient component of the relaxation modulus (linear relaxation function)

$$G(t) = G_e + \int_0^{\lambda_{\max}} H(\lambda) e^{-t/\lambda} (d\lambda/\lambda), \quad (1)$$

which often serves as the viscoelastic characteristic of materials. The longest relaxation time  $\lambda_{\max}$

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prescribes the upper bound of the integral. Solid materials are distinguished by a finite equilibrium modulus,  $G_e > 0$ , while liquids have no permanent contribution,  $G_e = 0$ . This study is concerned with the transient part of the spectrum, only. When describing experiments, we will evaluate both functions  $G(t)$  and  $H(\lambda)$  in search of patterns in the relaxation behavior. Most researchers prefer to use  $G(t)$  instead of  $H(\lambda)$  since the relaxation modulus appears directly in the equation for the stress. Molecular theories also seem to have focused on  $G(t)$  and not on  $H(\lambda)$ .

Direct measurement of the spectrum is impossible, but many methods have been proposed to somehow extract  $H(\lambda)$  from the stress response to various strain histories. We will discuss self-similarity of the spectrum in conjunction with such stress-strain relations (called 'linear viscoelastic material functions'). Appropriately measured material functions can be analyzed through the classical equation of linear viscoelasticity (for example, Ref. [1])

$$T(t) = \int_{-\infty}^t G(t-t') 2D(t') dt', \quad (2)$$

with  $T(t)$  being the stress tensor and  $D(t')$  the rate of strain tensor,  $-\infty < t' < t$ . The relaxation modulus  $G(t-t')$  identifies the material. The linear viscoelastic equation applies for strains which are so small that the material can maintain its equilibrium state.

Small amplitude oscillatory shear often serves the purpose of determining  $G(t)$  or  $H(\lambda)$ . Its shear stress response is conveniently decomposed into an in-phase component with the strain and an out-of-phase component, the storage modulus  $G'$  and the loss modulus  $G''$ :

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

$$G''(\omega) = \int_0^{\lambda_{\max}} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} \frac{d\lambda}{\lambda}. \quad (3)$$

The equilibrium modulus  $G_e$  affects the storage modulus only. The longest relaxation time again defines the upper bound of the integrals. Inversion of these integrals gives  $H(\lambda)$ .

The zero shear viscosity and the first normal stress coefficient (for example, Ref. [1])

$$\eta_0 = \int_0^{\lambda_{\max}} H(\lambda) d\lambda \quad \text{and} \quad \psi_1 = 2 \int_0^{\lambda_{\max}} H(\lambda) \lambda d\lambda \quad (4)$$

represent the behavior in steady shear flow at low shear rates.  $\eta_0$  and  $\psi_1$  can be combined for evaluating the equilibrium compliance [1]

$$J_e^0 = \psi_1 / (2 \eta_0^2). \quad (5)$$

The spectrum defines all these material functions, however, it is weighted differently in steady shear than in the dynamic mechanical experiment. Dynamic mechanical experiments have the advantage of being spectroscopic. This is the reason why they are often preferred to measuring  $\eta_0$ ,  $\psi_1$ ,  $G(t)$ , or creep compliance  $J(t)$ .

In this study, several materials will be discussed for which the relaxation is self-similar over a range of timescales. An attempt will be made to group materials with a common origin of self-similarity.

## 2. Properties of self-similar spectra

Self-similar relaxation expresses itself in a power-law spectrum

$$H(\lambda) = H_0 (\lambda/\lambda_0)^n \quad \text{for } \lambda_l < \lambda < \lambda_u, \quad (6)$$

where  $H_0$  and  $\lambda_0$  are constants. The exponent may adopt negative or positive values, however, with different consequences and limitations. These are discussed as follows:

No material is known which would relax in a power law at all timescales (or length scales). Self-similarity only governs over a finite range of relaxation times, i.e. between a lower and an upper limit,  $\lambda_l$  and  $\lambda_u$ , which are material specific. The time window has to be sufficiently large before self-similarity becomes recognizable in material functions. As an example, the self-similar relaxation modulus might be flanked by more complicated relaxation modes at short and at long times as

demonstrated by inserting Eq. (6) into Eq. (1):

$$G(t) - G_e = \int_0^{\lambda_L} H(\lambda) e^{-t/\lambda} \frac{d\lambda}{\lambda} + \underbrace{H_0 \int_{\lambda_L}^{\lambda_u} \left(\frac{\lambda}{\lambda_0}\right)^n e^{-t/\lambda} \frac{d\lambda}{\lambda}}_{\text{self-similar part of the spectrum}} + \int_{\lambda_u}^{\lambda_{\max}} H(\lambda) e^{-t/\lambda} \frac{d\lambda}{\lambda}. \quad (7)$$

self-similar part of the spectrum

In this study we analyze self-similar behavior of materials with a sufficiently wide time window,  $\lambda_u \gg \lambda_L$ . End effects will not be addressed further in this study.

### 2.1. Self-similar relaxation with negative exponent value

For negative relaxation exponent values we will use symbol  $-n$ . The self-similar spectrum has the form

$$H(\lambda) = H_0 (\lambda/\lambda_0)^{-n} \quad \text{with } 0 < n < 1 \quad \text{for } \lambda_L < \lambda < \lambda_u. \quad (8)$$

The spectrum has only two independent parameters since several constants are lumped into the factor  $(H_0 \lambda_0^{-n})$ . The front factor  $H_0$  (Pa) and the characteristic time  $\lambda_0$  (s) depend on the specific choice of material. Various values have been assigned in the literature.

Rheological properties due to this self-similar spectrum have been mapped out by Larson [4] and Ferry [1]. If self-similarity extends over a sufficiently wide time window, approximate solutions for the relaxation modulus  $G(t)$ , Eq. (1), might be obtained by neglecting the end effects

$$G(t) - G_e = H_0 \int_0^{\infty} (\lambda/\lambda_0)^{-n} e^{-t/\lambda} \frac{d\lambda}{\lambda} = H_0 \Gamma(n) (t/\lambda_0)^{-n} \quad (9)$$

and similarly for the dynamic moduli  $G'(\omega)$ ,  $G''(\omega)$ , Eqs. (3)

$$G' = H_0 \Gamma(n) \Gamma(1-n) \cos(n\pi/2) (\lambda_0 \omega)^n, \quad (10)$$

$$G'' = H_0 \Gamma(n) \Gamma(1-n) \sin(n\pi/2) (\lambda_0 \omega)^n, \quad (11)$$

where  $\Gamma(x)$  is the gamma function. These solutions of the idealized problem are a good approximation for the behavior within a time window  $\lambda_L < t < \lambda_u$  or the corresponding frequency window  $1/\lambda_u < \omega < 1/\lambda_L$ . Truncation effects can be seen near the edges  $\lambda_L$  and  $\lambda_u$ . The upper limit may diverge to infinity,  $\lambda_u \rightarrow \infty$ , without making the power-law spectrum inconsistent.  $\lambda_u \rightarrow \infty$  is the attribute of liquid-solid transitions (ref. [3]) as is discussed below.

Self-similar behavior is most obvious when it occurs in this form, i.e. with a negative exponent and a self-similar region which extends over several decades in time or frequency.  $G(t)$ ,  $G'(\omega)$ ,  $G''(\omega)$ , and  $H(\lambda)$  all adopt power-law format and their self-similarity has been used interchangeably in the literature. Less obvious is the self-similar behavior for positive exponent values.

### 2.2. Self-similar relaxation with positive exponent value

For positive exponent values, we use symbol  $m$  with  $m > 0$ . The spectrum has the same format as in Eq. (8),  $H(\lambda) = H_0 (\lambda/\lambda_0)^m$ , however, the positive exponent results in a completely different behavior. One important difference is that the upper limit of the spectrum,  $\lambda_u$ , has to be finite in order to avoid divergence of the linear viscoelastic material functions. This prevents the use of approximate solutions of the above type, Eqs. (9)-(11).

Spectra with a positive exponent may be explored for the ideal case of power-law relaxation over all times up to the longest relaxation time,  $\lambda_{\max}$ :

$$H(\lambda) = H_0 (\lambda/\lambda_{\max})^m \quad \text{with } m > 0 \quad \text{for } 0 < \lambda < \lambda_{\max} \quad (12)$$

and  $H(\lambda) = 0$  for  $\lambda_{\max} < \lambda$ . In this context,  $\lambda_{\max}$  is always finite and is chosen here as the characteristic time of the spectrum. Material functions of steady shear flow

$$\eta_0 = \int_0^{\lambda_{\max}} H(\lambda) d\lambda = \frac{H_0 \lambda_{\max}}{1+m},$$

$$\psi_1 = 2 \int_0^{\lambda_{\max}} H(\lambda) \lambda d\lambda = \frac{2H_0 \lambda_{\max}^2}{2+m} \quad (13)$$

have explicit solutions. However, even for this ideal spectrum, the relaxation modulus has to be evaluated numerically. It does not have any simple form which could be recognized as self-similar behavior.

### 3. Observations of self-similar relaxation behavior

Self-similar relaxation, in one way or another, has been observed experimentally for a variety of materials (specific molecular structure and composition) and, independently, it also was predicted by several molecular dynamics models of polymeric liquids. The above ideal cases of self-similar behavior, Eqs. (8) and (12), are the basis for comparing rheological observations as reported in the literature. Common properties will be discussed in terms of linear viscoelastic material functions. Regularities in the patterns will be interpreted as behavior of a more general type.

Observations of self-similarity will be reported chronologically. Two major groups can be distinguished roughly, one in which the self-similarity develops as an expression of molecular connectivity (supra molecular structures), and the other in which molecular dynamics plays the major role.

#### 3.1. Connectivity transitions

##### 3.1.1. Transition to high-frequency glass behavior

Tobolsky [5] found that the power-law spectrum, Eq. (8), with a negative exponent captures the observed relaxation behavior of polymeric liquids and solids at the transition from the entanglement regime to the glass. Experimental values for the exponent are in between  $-0.6$  and  $-0.7$ . The Laplace transform of this spectrum gives a power-law relaxation modulus as shown in Eq. (9).

A slightly modified form of the spectrum (Ref. [6]) is commonly used for describing the glass transition behavior of polymeric solids:

$$G(t) = G_e + (G_g - G_e) (1 + t/\lambda_c)^{-n}. \quad (14)$$

This empirical equation fits the glass transition as well as the glass behavior.  $G_e$  and  $G_g$  are the equilibrium modulus and the modulus of the glass, i.e. the limits of the modulus at very long times and very short times.  $\lambda_c$  is the characteristic time for the dynamically induced crossover from the entanglement behavior to the glass.

For highly entangled polymeric liquids, Tobolsky [5] proposed to combine the power-law spectrum for the glass transition with a 'box' spectrum for the entanglement region,  $\lambda > \lambda_c$ . This box spectrum could not be verified experimentally and, thus, will not be discussed here. The experimentally observed shape of the spectrum for the entanglement region is fundamentally different as will be shown below.

##### 3.1.2. Phase-separated block-copolymers

Microphase separation is known to increase the low-frequency moduli of block copolymers (Refs. [7-9]). For a di-block copolymer at low rates of shear, Bates [10] and Koppi et al. [11] observed power-law relaxation, eq. (8), with an exponent of  $-0.5$ . The power-law relaxation is not associated with the instant of transition itself but it prevails at temperatures far into the micro-phase-separated region. It is property of the ordered structure. The power-law relaxation data of Koppi et al., for instance, were taken 60 K below the order-disorder transition temperature.

##### 3.1.3. Phase-separated polymer blends

Strongly phase-separated polymer blends, above the melting temperatures and glass transition temperatures of the components, can show a power-law relaxation behavior at low frequencies or long times (Refs. [12,13]). The phenomenon occurs far away from the coexistence temperature. It cannot be associated with the phase transition but is a property of the phase-separated structure. At very long times (outside the experimental frequency window), the material is expected to flow like a typical liquid.

### 3.1.4. Cross-linking polymers near their gel point

The extent of cross-linking, denoted as  $p$  with  $0 < p < 1$ , is a measure of the growing molecular sizes during chemical gelation. The critical extent of cross-linking,  $p_c$ , marks the gel point. The approach of and transition through the gel point can be recognized by the growth and decay of the longest relaxation time,  $\lambda_{\max}$ . This is accompanied by a straightening of the relaxation modulus which, in the close vicinity of the gel point, reduces to a power law (Refs. [14-16]):

$$H(\lambda) = H_0 (\lambda/\lambda_0)^{-n} \quad \text{and}$$

$$G(t) = H_0 \Gamma(n) (t/\lambda_0)^{-n} \quad \text{for } \lambda_0 < \lambda < \lambda_{\max}. \quad (15)$$

Beyond the gel point, the spectrum shortens again ( $\lambda_{\max}$  decays). The self-similar spectrum (CW-spectrum) is only characteristic for the critical region near the gel point.

The upper limit of the self-similar behavior coincides with the longest relaxation time,  $\lambda_u = \lambda_{\max}$ , which depends on the distance from the gel point,  $|p - p_c|$ :

$$\lambda_{\max} \sim |p - p_c|^{-\alpha}, \quad \alpha = s + z, \quad (16)$$

The critical exponent for the longest relaxation time,  $\alpha$ , is given as the sum of the critical exponents,  $s$  and  $z$ , of the viscosity and the equilibrium modulus near the gel point (Refs. [3,17-20]). In the limiting case of the critical gel (a sample being exactly at the gel point,  $p = p_c$ ), the longest relaxation time diverges to infinity,  $\lambda_{\max} \rightarrow \infty$ , and the self-similar behavior is found for the terminal zone. The lower limit of the CW-spectrum,  $\lambda_0$ , denotes the crossover to the glass behavior (for short precursor molecules) or to entanglement behavior (for long precursor molecules).

Soft critical gels have a low strength,  $S = H_0 \Gamma(n) \lambda_0^n$ , and a high relaxation exponent,  $n \rightarrow 1$  (Ref. [21]). This can be achieved by several different methods, for instance by choosing low molecular weight precursors (Ref. [18,22,23]), by adding an inert diluent (Refs. [21,24]), or by selecting a low stoichiometric ratio (Refs. [16,25,26]). Vice versa, stiff critical gels (high  $S$  and low  $n \rightarrow 0$ ) can be made by choosing undiluted polymers of high molecular weight (Refs. [14-16,21,24]). Muthukumar [27] at-

tributed this observed molecular weight effect to screening.

### 3.1.5. Physical gelation

The spectrum of polyvinyl chloride plastisols (Ref. [28]) and thermoplastic elastomers (Refs. [29,30]) during solidification (due to a quench below the respective crystallization temperature) follows the same evolution as the spectrum of chemically cross-linking polymers. The longest relaxation time grows in the approach of the gel point and the spectrum straightens out into a power-law form. Beyond the gel point, the spectrum shortens again and a permanent contribution,  $G_e$ , builds up.

## 3.2. Molecular dynamics

### 3.2.1. Spectrum for Rouse chains

Rouse [31] proposed a model for the motion of linear macromolecules and derived a spectrum which can be written in form of a discrete relaxation modulus

$$G(t) = g_0 \sum_{i=1}^{\infty} e^{-t^2/\lambda_i}. \quad (17)$$

At short times ( $t/\lambda_0 \ll 1$ ) or at high frequencies ( $\omega \lambda_0 \gg 1$ ), this modulus reduces to power-law format with a negative power-law exponent of  $-0.5$ .  $\lambda_0$  is the longest relaxation time of the spectrum. Zimm [32] extended the model, including 'hydrodynamic interaction' between segments of the same chain, and derived an exponent of  $2/3$ . Detailed descriptions of these theories can be found in the books by Ferry [1], Bird et al. [33] and Doi and Edwards [34]. Rouse and Zimm behavior has been found with a range of low molecular weight polymer melts and solutions (Ref. [1]).

The power-law behavior of the Rouse model becomes more obvious when realizing that the above discrete spectrum is very closely resembled by a continuous spectrum

$$H(\lambda) = g_0 (\lambda/\lambda_0)^{-0.5} \quad \text{for } \lambda \leq \lambda_0. \quad (18)$$

A simple cut-off is sufficient at long times, e.g.  $H(\lambda) = 0$  for  $\lambda_0 < \lambda$ . The  $(-0.5)$ -exponent is prescribed by the Rouse model. The equivalence of eqs. (17) and (18) can be seen when calculating  $G'$  and  $G''$  for both spectra and plotting them against each



other. The difference is much smaller than any  $G'$ ,  $G''$  experiment would be able to detect. An equivalent power law would represent the Zimm spectrum, however, with an exponent of  $-2/3$ .

### 3.2.2. Spectrum of polymers with long linear flexible molecules

Doi [35] predicted the relaxation function of polymers on the basis of a fixed tube model as proposed by de Gennes [36]. Doi's discrete spectrum can be expressed in continuous form with a positive relaxation exponent of 0.5 and a cut-off at the longest relaxation time  $\lambda_{\max}$ :

$$H(\lambda) = 0.5 G_N^0 (\lambda/\lambda_{\max})^{0.5} \quad \text{for } \lambda_0 < \lambda \leq \lambda_{\max}, \quad (19)$$

and  $H(\lambda) = 0$  for  $\lambda > \lambda_{\max}$ .  $G_N^0$  is the so-called plateau modulus. The theory predicts a 3rd power molecular weight dependence of the longest relaxation time which is not very far from the experimentally observed value of 3.4. It gives much insight into the dynamics of macromolecules but, as recognized by Doi and Edwards [34], predictions are not quantitative in the entanglement region where much experimental information is available.

### 3.2.3. Spectrum of polymers with branched molecular architecture

A polymer melt with comb-like molecules was found to exhibit power-law relaxation at intermediate frequencies (Ref. [37]). Due to a value of  $-0.5$  for the relaxation exponent, the behavior was attributed to Rouse-like relaxation.

Molecules with fractal structure have been predicted to have a power-law relaxation spectrum at low frequencies (Refs. [38-40]).

Microgels were found to relax with a power-law spectrum over up to 5 decades in frequency (Ref. [41]). The behavior might be attributed to the fractal structure of the molecules.

### 3.2.4. Broadly polydisperse polyethylene melts

Broadening of the molecular weight distribution results in a smearing out of the crossover from the flow regime to the entanglement regime. As a consequence, the relaxation modulus seems to be of power-law type at intermediate timescales (Refs. [42,4]). The power-law modulus, however, is not a locally sensitive measure of relaxation. Data of

other (more sensitive) material functions of broadly polydisperse polymers, such as the dynamic moduli,  $G'$  and  $G''$ , could not be modeled satisfactorily with a power-law spectrum.

### 3.2.5. Spectrum of polymer melts with highly entangled linear molecules of uniform length

Recent advances in the determination of relaxation time spectra from dynamic mechanical data made it possible to revisit the problem of Doi [35] and determine the spectrum experimentally. The result is a self-similar relaxation time spectrum (BSW spectrum) in the entanglement and flow zone, i.e., at the long timescales of the polymer melt (Refs. [43,44])

$$H(\lambda) = m G_N^0 (\lambda/\lambda_{\max})^m \quad \text{for } \lambda_c < \lambda \leq \lambda_{\max}, \quad (20)$$

and  $H(\lambda) = 0$  for  $\lambda_{\max} < \lambda$ . The scaling exponent  $m$  and the plateau modulus  $G_N^0$  are material specific parameters. Experimental values between  $m = 0.2$  and  $0.25$  were found for a range of polymers of different chemistry. The longest relaxation time of the measured moduli,  $\lambda_{\max}$ , increases with the 3.4th power of the molecular weight (Refs. [43,44]). The lower limit of the self-similar spectrum,  $\lambda_c$ , is given by the crossover to the high-frequency glass behavior.

The high-frequency behavior is independent of polymer molecular weight and can be described by the empirical spectrum which Tobolsky [5] has suggested. Without detailed experimental information on the crossover from the entanglement to the high-frequency glass behavior, we chose the most simple case of a linear superposition of the two limiting power laws:

$$H(\lambda) = m G_N^0 \left[ \left( \frac{\lambda}{\lambda_c} \right)^{-n} + \left( \frac{\lambda}{\lambda_{\max}} \right)^m \right] \quad \text{for } \lambda \leq \lambda_{\max}. \quad (21)$$

A typical example of dynamic mechanical data,  $G'$  and  $G''$ , and the corresponding spectrum is shown in Figs. 1--3.

The BSW-spectrum very closely represents data of a variety of chemically different polymers as long as the distribution of molecular mass is sufficiently narrow (as achieved in polymer standards). It does not seem to be important here that real samples are

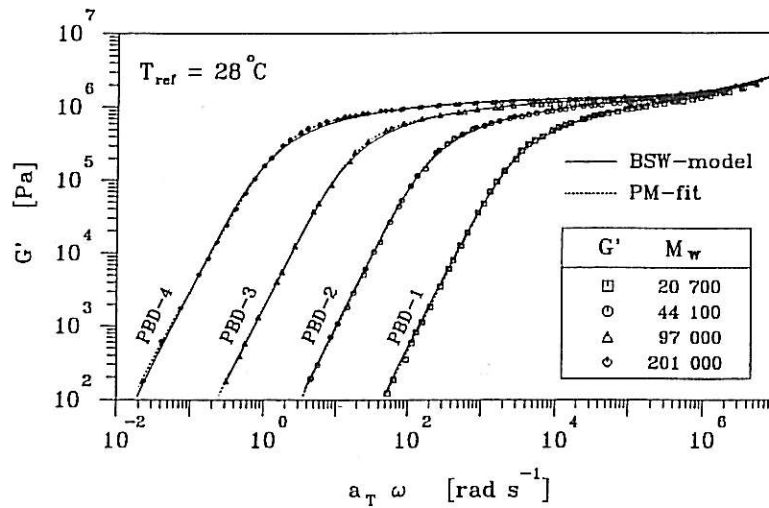


Fig. 1. Storage modulus of nearly monodisperse polybutadiene melts (Ref. [44]). Lines are calculated with the spectra of Fig. 3: the continuous spectra of Eq. (21) and discrete spectra (parsimonious model) as determined by the IRIS program (Ref. [55]).

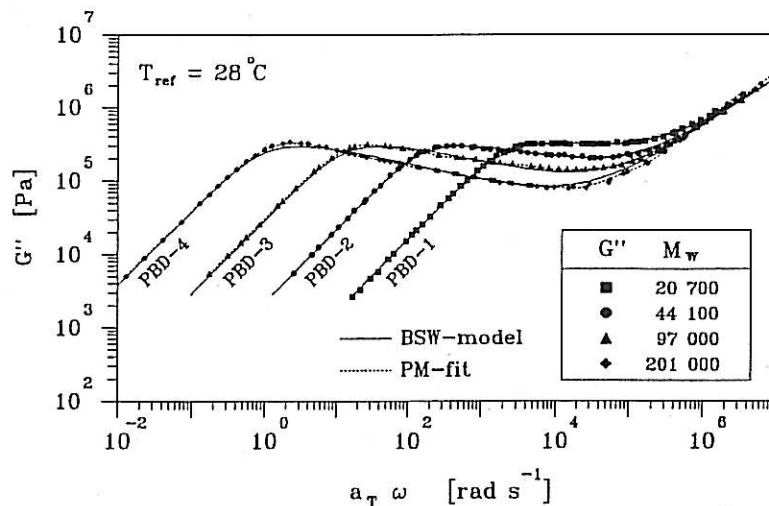


Fig. 2. Loss modulus of nearly monodisperse polybutadiene melts (Ref. [44]). Lines are calculated with the spectra of Fig. 3: the continuous spectra of Eq. (21) and discrete spectra (parsimonious model) as determined by the IRIS program (Ref. [55]).

not perfectly monodisperse. Prerequisite, however, is a sufficiently high molecular weight so that  $\lambda_{\max} \gg \lambda_c$ .

#### 4. Discussion

Very different molecular and supra molecular structures can relax with a power-law distribution

of relaxation modes. A one-to-one correlation between relaxation and structure seems to be out of reach at the current state of knowledge. At least, data interpretation will require additional information about the molecular properties (such as transition temperatures, chemical stability, cross-linking or not, multicomponent or single component). Two special cases, however, allow more definite

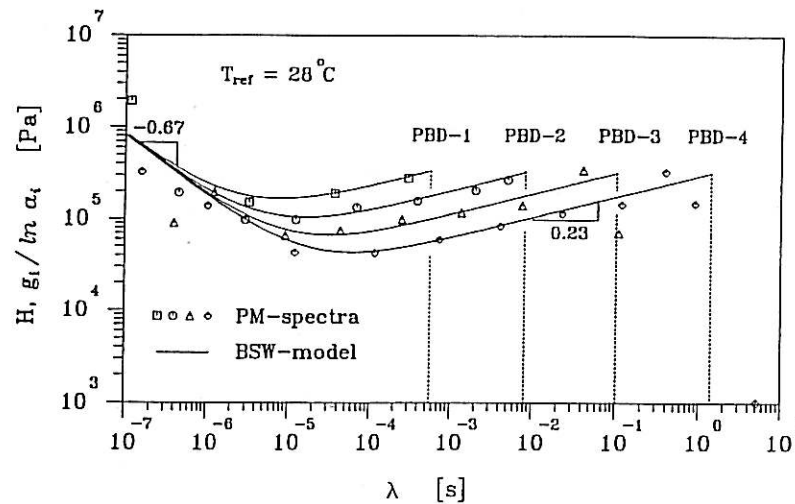


Fig. 3. BSW-spectra of nearly monodisperse polybutadiene melts (Ref. [44]), see Eq. (21)). The discrete modes refer to a modulus  $G(t) = \sum_{i=1}^N g_i e^{-t/\lambda_i}$  with spacings  $a_i$  between the modes. The parsimonious model (PM) of Baumgärtel et al. [55] seeks an optimum number of relaxation modes,  $N$ , in order to avoid overfitting or underfitting of the data,

conclusions: the polymer melt with long linear flexible molecules of uniform length and the materials at a liquid–solid transition of second order. Each of these materials has a unique spectrum which allows identification of the underlying structure.

The most simple molecular architecture for a polymer, that of long linear flexible chains of uniform length, already results in a very complicated relaxation behavior with a broad distribution of relaxation times. However, the linear viscoelastic properties are known to follow a unique pattern (Refs. [45–49]). Therefore, the corresponding relaxation time spectrum should also be unique. This spectrum has been proposed to be self-similar and to have a positive exponent (BSW-spectrum). Small deviations from ideal monodispersity broaden the crossover from the flow to the entanglement regime (and hence affect the zero shear compliance; see Ref. [50]), but they do not seem to affect the main part of the spectrum in any significant way.

The BSW-spectrum has been found empirically by inverting rheological data and by checking its predictions against experiments. The inversion of the modulus data does not have a unique solution. However, the simplicity of the BSW-spectrum is appealing to us, even if we realize that other, more

complicated spectra may result in an equally close representation of the data.

The experimentally found spectrum is surprisingly close to the spectrum which Doi [35] has derived from a molecular model. Only two changes are necessary: the value of the relaxation exponent has to be reduced from  $m = 0.5$  to about  $m = 0.2$ – $0.25$ , and the molecular weight dependence of the longest relaxation time has to be increased from the 3rd to the 3.4th power. This shows the sensitivity of the viscoelastic behavior to small changes in the spectrum. The changes are necessary but their physical origin is not known.

Dynamic mechanical data as shown in Figs. 1 and 2 can normally be assigned to that specific molecular structure. However, experimental details have to be taken into account. Recently, Granick et al. [51] found a very similar looking modulus with molecules of low molecular weight when shearing them in an extremely narrow gap.

The second distinct spectrum (CW-spectrum) was found with materials during chemical or physical gelation (which are paradigms for second order liquid–solid transitions). The broadening of the spectrum in the approach of the gel point, the self-similarity of the long relaxation modes at the gel point, and the shrinking of the spectrum beyond



the gel point make a unique pattern. The broadening of the spectrum is an expression of increasing connectivity. Molecular motions are coupled over wider and wider distances. The distance diverges at the gel point and becomes small again as the solidification proceeds. This structural evolution is reflected in the linear viscoelastic properties. Viscoelasticity and structure are closely correlated near the liquid-solid transition.

The divergence of the longest relaxation time in physical gelation is limited by the average life time of the physical junctions. The long life time of crystalline junctions resulted in a behavior comparable to chemical gelation. Little is known about physical gels with junctions of shorter life time. Examples would be percolating suspensions, polymer melts with hydrogen bonding between molecules, emulsions, etc.

Self-similar relaxation at intermediate timescale has been found with many different structures and for a variety of reasons. Self-similar relaxation of fractal molecules and microgels can be attributed to their self-similar molecular structure. However, microphase separated block copolymers and (macro)phase separated polymer blends exhibit self-similar relaxation without having a self-similar structure. In addition, broadening of the spectrum might give the appearance of a self-similar behavior. This has been seen with polymer melts of broadly distributed molecular weight. Self-similar relaxation is a very interesting consequence of molecular or supra molecular dynamics which should be explored further.

It should be mentioned that the self-similar behavior is not restricted to relaxation phenomena. A power-law retardation spectrum has been reported for the creep of metals (Refs. [52-54]). Its analysis would be beyond the scope of this study.

## 5. Conclusions

Self-similar scaling of the relaxation dynamics is more an exception than the rule for polymers. If it occurs, it is a striking phenomenon since it gives rise to very distinct patterns in linear viscoelastic relaxation data. These common patterns have been

recognized for several classes of materials. One of the main parameters is the relaxation exponent.

The sign of the relaxation exponent, positive or negative, makes a fundamental difference in the self-similar behavior. A negative exponent has been found with many materials at intermediate timescales, however, it seems to be specific for second order liquid-solid transitions when observed in the terminal relaxation region. Only one of the reviewed self-similar materials has a positive exponent. That is the polymer melt with long linear flexible molecules of uniform length. Its entanglement and flow behavior follows a power-law pattern which is a surprisingly simple result.

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