

## A nonlinear regularization method for the calculation of relaxation spectra

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*Abstract:* It is well known that the relaxation spectrum characterizing the linear viscoelastic properties of a polymer melt or solution is not directly accessible by an experiment. Therefore, it must be calculated from data for a material function. With Tikhonov regularization the relaxation spectrum in the terminal and plateau region can be calculated from data for a material function in the corresponding region. Serious difficulties arise however, if the spectrum should be determined in a larger range. These difficulties are caused by the considerably different contributions at short and long relaxation times. We show that these difficulties can be avoided by a nonlinear regularization method.

*Key words:* Relaxation spectrum – Tikhonov regularization – nonlinear regularization

### 1. Introduction

The relaxation spectrum is a fundamental quantity in the linear theory of viscoelastic fluids. If this spectrum is known, other material functions can be calculated without difficulties. In addition, this spectrum is often used to study the rheological properties of polymer blends. Unfortunately, it is not directly accessible by an experiment and it must be calculated from data for a material function. As this calculation requires the inversion of a Fredholm integral equation of the first kind the determination of the relaxation spectrum is an ill-posed problem and specific methods such as Tikhonov regularization (see, e.g., Groetsch (1984)) must be used to solve it.

The application of regularization methods in rheology has been proposed and discussed by Wiff and Gehatia (1975), Wiff (1978), Friedrich and Hofmann (1983), Honerkamp and Weese (1989), Honerkamp (1989) and Elster and Honerkamp (1991). Elster et al. (1992) have shown that Tikhonov regularization is a useful tool for the calculation of the relaxation spectrum in the terminal and plateau region from data characterizing a material function in the corresponding region. However, in many cases the time temperature superposition principle (see, e.g., Ferry (1980)) can be employed leading to master-curves which characterize a material function in a

larger range. In this case, the calculation of the relaxation spectrum in the corresponding range is connected with serious difficulties. These difficulties are caused by the considerably different contributions in the relaxation spectrum: for short relaxation times there is a huge contribution characterizing the rheological properties in the transition and glassy region and for long relaxation times there is a very small contribution which describes the rheological properties in the terminal and plateau region. In this article we propose a nonlinear regularization method by which the difficulties can be avoided.

The following section includes a short description of the determination of relaxation spectra with Tikhonov regularization. The difficulties which arise when this method is applied to rheological data are illustrated in Sect. 3. In Sect. 4 it is shown that these difficulties can be avoided by a nonlinear regularization method. This method was used to calculate the relaxation spectra of several polystyrene samples. The results are presented in Sect. 5.

### 2. Determination of relaxation spectra with Tikhonov regularization

As pointed out in the introduction, the relaxation spectrum  $h(\tau)$  is related to experimental accessible

material functions by Fredholm integral equations of the first kind. For the storage modulus  $G'(\omega)$  and the loss modulus  $G''(\omega)$  these relations are given by (see, e.g., Ferry (1980))

$$G'(\omega) = \int_{-\infty}^{+\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} h(\tau) d(\ln \tau) \quad (1a)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} h(\tau) d(\ln \tau) . \quad (1b)$$

When Tikhonov regularization is used for the determination of the relaxation spectrum from data for the dynamic moduli, an estimate for the spectrum  $h(\tau)$  is defined by the minimum of the quantity

$$\begin{aligned} V(\lambda) = & \sum_{i=1}^n \frac{1}{\sigma_i'^2} \left[ G_i'^{\sigma} - \left( \int_{-\infty}^{+\infty} \frac{\omega_i^2 \tau^2}{1 + \omega_i^2 \tau^2} h(\tau) d(\ln \tau) \right) \right]^2 \\ & + \sum_{i=1}^n \frac{1}{\sigma_i''^2} \left[ G_i''^{\sigma} - \left( \int_{-\infty}^{+\infty} \frac{\omega_i \tau}{1 + \omega_i^2 \tau^2} h(\tau) d(\ln \tau) \right) \right]^2 \\ & + \lambda \int_{-\infty}^{+\infty} \left( \frac{d^2}{d\tau^2} h(\tau) \right)^2 d(\ln \tau) , \end{aligned} \quad (2)$$

where  $G_1'^{\sigma}, \dots, G_n'^{\sigma}, G_1''^{\sigma}, \dots, G_n''^{\sigma}$  denote the experimental data for  $G'(\omega_1), \dots, G'(\omega_n), G''(\omega_1), \dots, G''(\omega_n)$  and  $\sigma_1', \dots, \sigma_n', \sigma_1'', \dots, \sigma_n''$  are the corresponding errors. With an appropriate value for the so-called regularization parameter  $\lambda$ , the first and the second term on the righthand side of Eq. (2) force the result to be compatible with the data. The third term leads to a smooth estimate for the spectrum  $h(\tau)$ .

The calculations in the following section have been performed with the program FTIKREG developed by Weese (1992). This program is an implementation of a solution method for Fredholm integral equations of the first kind based on Tikhonov regularization. It offers the ability to determine an appropriate value for the regularization parameter and to consider positivity constraints. Both features have been used to calculate the relaxation spectra shown in Sect. 3.

### 3. Difficulties with Tikhonov regularization

In order to illustrate the difficulties in the determination of relaxation spectra with Tikhonov regularization a spectrum  $h(\tau)$  (Fig. 1a) has been chosen which could represent the linear viscoelastic proper-

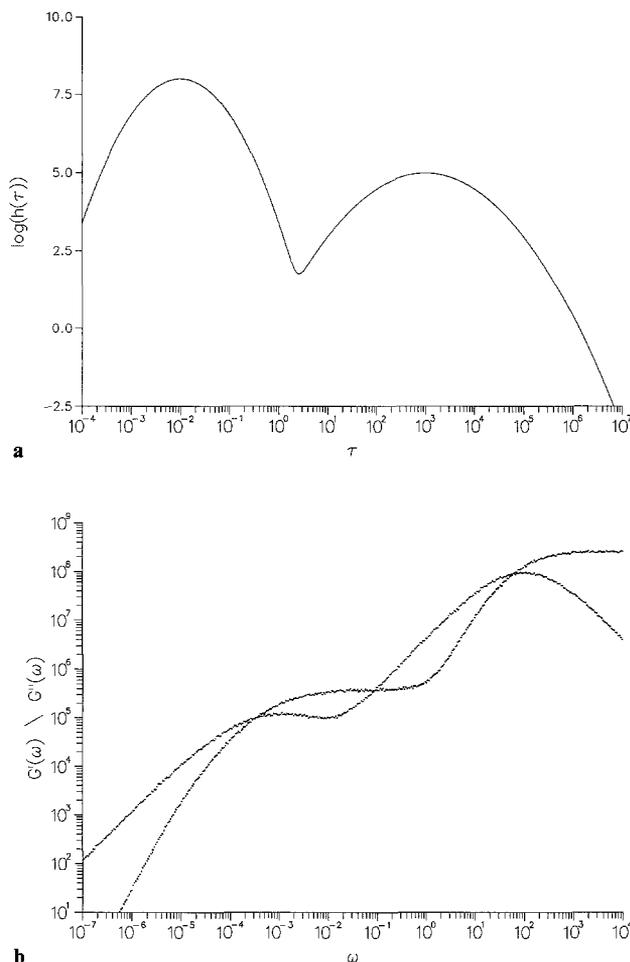


Fig. 1. Relaxation spectrum (a) and simulated data (b) used to illustrate the difficulties in the determination of relaxation spectra with Tikhonov regularization

ties of a polymer melt in the terminal, plateau, transition and glassy region. For this spectrum simulated data (Fig. 1b) have been generated by evaluating the corresponding dynamic moduli  $G'(\omega)$  and  $G''(\omega)$  at different values of  $\omega$ . Then a Gaussian random number corresponding to a relative error of 3% was added.

Figure 2 shows the result for the relaxation spectrum calculated with Tikhonov regularization from the simulated data. Though the data characterize the entire spectrum, only the large peak at short relaxation times is well represented. For long relaxation times the errors of the spectrum are so large that the result is completely unsatisfactory.

The result is even worse, if the relaxation spectrum is calculated from data in the terminal, plateau and transition region ( $10^{-7} \text{ s}^{-1} < \omega < 10^{-1} \text{ s}^{-1}$ ). In this case the data indicate a contribution of the relaxation

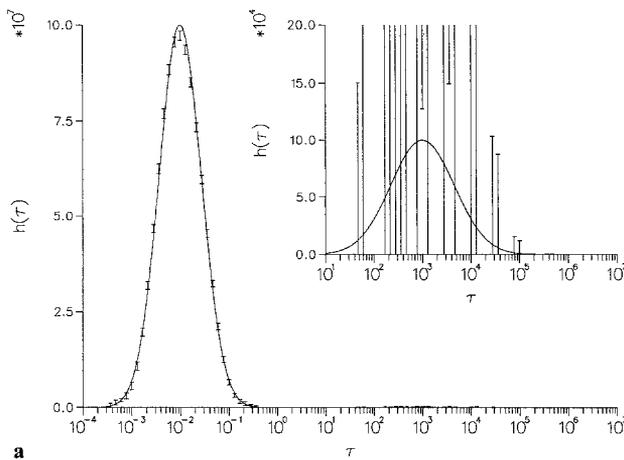
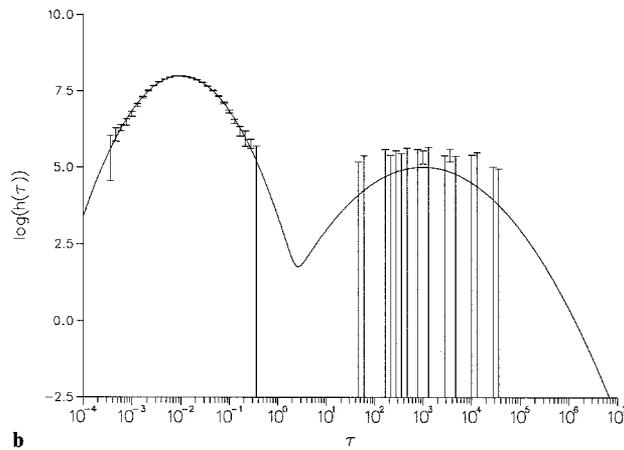

**a**

**b**

Fig. 2. Result for the relaxation spectrum calculated with Tikhonov regularization from the simulated data. The result is plotted on a semi-logarithmic (a) and on a double logarithmic (b) scale

spectrum at short relaxation times, but they characterize the spectrum only for  $\omega_{\max}^{-1} = 10^{+1} \text{ s} < \tau < \omega_{\min}^{-1} = 10^{+7} \text{ s}$  (Elster et al. (1992)). Therefore, the spectrum calculated with Tikhonov regularization (Fig. 3) does not characterize the large peak at short relaxation times. In addition, for long relaxation times the errors of the spectrum are very large and there is no range in which the regularization method leads to satisfying results.

Finally, the relaxation spectrum has been calculated from data in the terminal and plateau region ( $10^{-7} \text{ s}^{-1} < \omega < 10^{-2} \text{ s}^{-1}$ ). In this case the small peak can be reconstructed (Fig. 4) and the regularization method leads to good results.

The examples (Figs. 2–4) indicate that the difficulties in the determination of relaxation spectra with Tikhonov regularization are caused by the con-

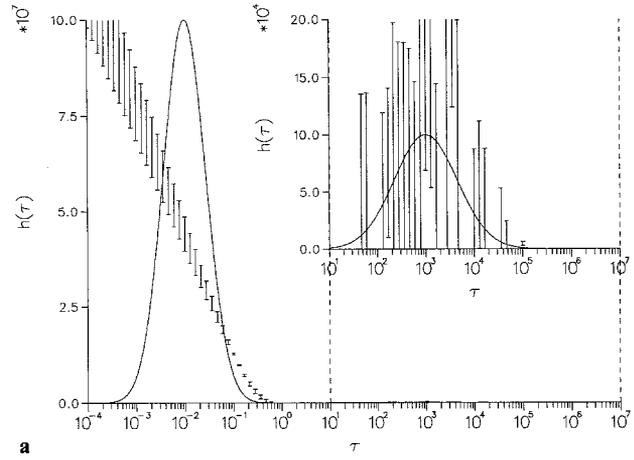
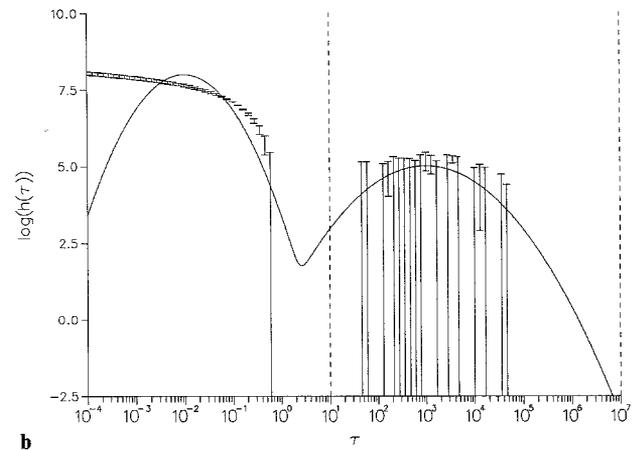
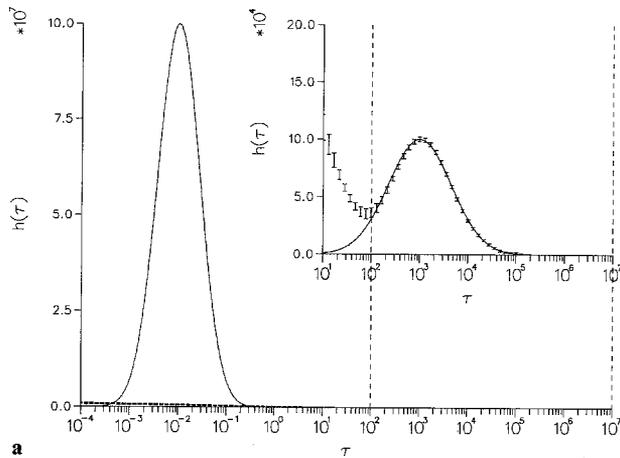

**a**

**b**

Fig. 3. Result for the relaxation spectrum calculated with Tikhonov regularization from the simulated data in the terminal, plateau and transition region. The result is plotted on a semi-logarithmic (a) and on a double logarithmic (b) scale. The dashed lines mark the range in which the data characterize the spectrum

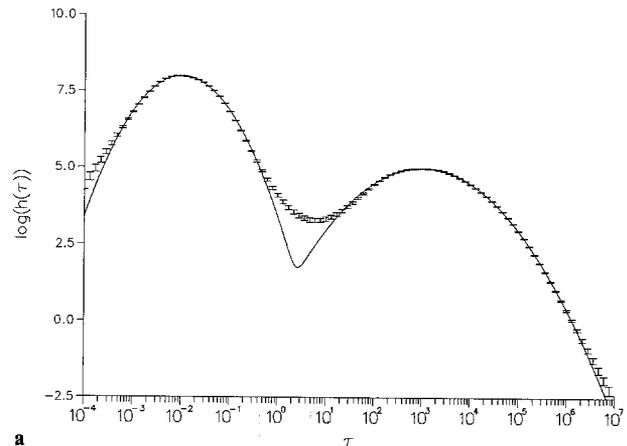
siderably different contributions at short and long relaxation times. From a mathematical point of view this is a peculiar property of the relaxation spectrum and it can be expected that the difficulties can be avoided by taking this property into consideration.

#### 4. A nonlinear regularization method

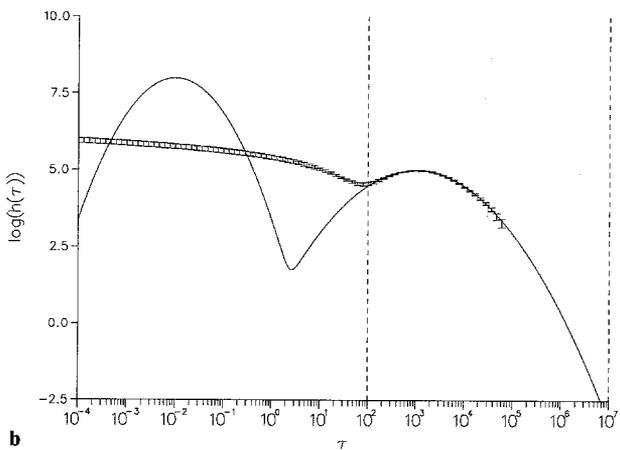
Because of the considerably different contributions at short and long relaxation times, the relaxation spectrum is usually plotted on a double logarithmic scale (see, e.g., Ferry (1980)). This is also the basic concept of the nonlinear regularization method: the logarithm of the spectrum  $\tilde{h}(\tau) = \log h(\tau)$  is calculated instead of the spectrum  $h(\tau)$  itself.



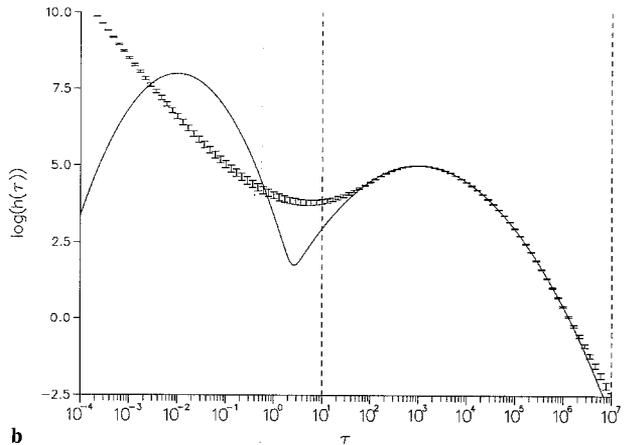
a



a



b



b

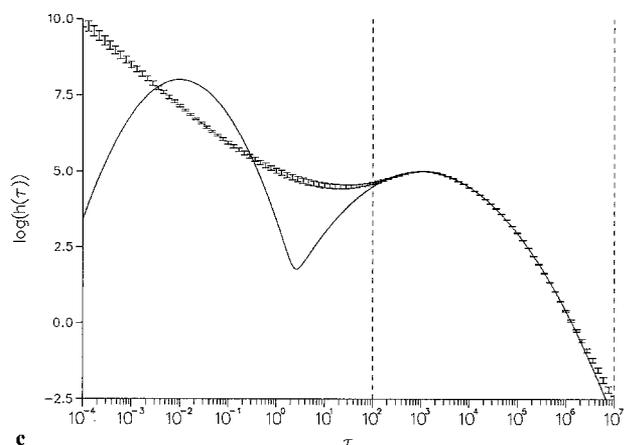
Fig. 4. Result for the relaxation spectrum calculated with Tikhonov regularization from the simulated data in the terminal and plateau region. The result is plotted on a semi-logarithmic (a) and on a double logarithmic (b) scale. The dashed lines mark the range in which the data characterize the spectrum

For the calculation of the logarithm of the spectrum  $\bar{h}(\tau)$  from data for the dynamic moduli  $G'(\omega)$  and  $G''(\omega)$  not the Eq. (1), but the equations

$$G'(\omega) = \int_{-\infty}^{+\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} 10^{\bar{h}(\tau)} d(\ln \tau) \quad (3a)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} 10^{\bar{h}(\tau)} d(\ln \tau) \quad (3b)$$

must be considered. These equations are nonlinear integral equations and a nonlinear regularization method must be applied to determine the logarithm of the spectrum from experimental data. Nevertheless, the



c

Fig. 5. Results for the relaxation spectrum calculated with the nonlinear regularization method from all and from part of the simulated data. The dashed lines mark the range in which the data characterize the spectrum

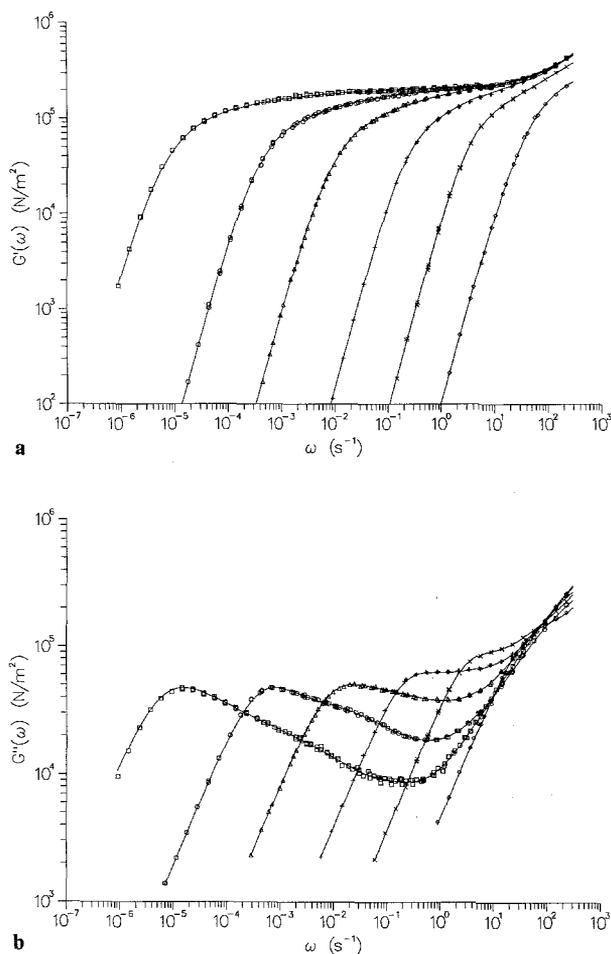


Fig. 6. Mastercurves for the dynamic moduli  $G'(\omega)$  (a) and  $G''(\omega)$  (b) of the six nearly monodisperse PS samples ( $\diamond$  PS 1,  $\times$  PS 2,  $+$  PS 3,  $\triangle$  PS 4,  $\circ$  PS 5,  $\square$  PS 6). The solid lines mark the values for the dynamic moduli recalculated from the relaxation spectra obtained by nonlinear regularization (Fig. 7, error bars)

basic concept of Tikhonov regularization can be employed and an estimate for the logarithm of the spectrum  $\tilde{h}(\tau)$  is obtained by minimizing

$$\begin{aligned}
 V(\lambda) = & \sum_{i=1}^n \frac{1}{\sigma_i'^2} \left[ G_i' \sigma - \left( \int_{-\infty}^{+\infty} \frac{\omega_i^2 \tau^2}{1 + \omega_i^2 \tau^2} 10^{\tilde{h}(\tau)} d(\ln \tau) \right) \right]^2 \\
 & + \sum_{i=1}^n \frac{1}{\sigma_i''^2} \left[ G_i'' \sigma - \left( \int_{-\infty}^{+\infty} \frac{\omega_i \tau}{1 + \omega_i^2 \tau^2} 10^{\tilde{h}(\tau)} d(\ln \tau) \right) \right]^2 \\
 & + \lambda \int_{-\infty}^{+\infty} \left( \frac{d^2}{d\tau^2} \tilde{h}(\tau) \right)^2 d(\ln \tau) . \quad (4)
 \end{aligned}$$

Table 1. Molar mass and polydispersity index of the nearly monodisperse PS samples

Sample	$M \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PS 1	39	1.05
PS 2	70	1.06
PS 3	128	1.05
PS 4	275	1.07
PS 5	770	1.07
PS 6	3000	1.05

In addition, an appropriate value for the regularization parameter must be determined. For this purpose the SC-method can be used which has originally been proposed by Honerkamp and Weese (1990) for linear regularization methods.

The technical details as well as the numerical realization of the nonlinear regularization method are rather complicated. For that reason the easy-to-use program NLREG (for NonLinear REGularization) has been developed by Weese (in preparation). This program was used to perform numerical calculations.

Figure 5 shows the results for the relaxation spectra obtained with the nonlinear regularization method from all and part of the simulated data shown in Fig. 1b. The results show that the difficulties illustrated in the preceding section can be avoided: in the range in which the data characterize the relaxation spectrum a good estimate for the original spectrum is obtained.

## 5. Results for some polystyrene samples

In this section the nonlinear regularization method is used to determine the relaxation spectra of six nearly monodisperse PS samples and of a commercial PS sample. For the commercial PS sample, data for the dynamic moduli and the relaxation modulus were available. It is therefore possible to compare the results for the relaxation spectrum obtained from different material functions. The agreement of the results can be considered as a test of the nonlinear regularization method.

### 5.1 Results for six nearly monodisperse PS samples

The data used in this section have been published by Schausberger et al. (1985). They characterize the dynamic moduli of six nearly monodisperse PS samples with molar masses between  $39 \cdot 10^3$  and  $3000 \cdot 10^3$  (Table 1) and were measured at temperatures between  $150^\circ$  and  $270^\circ$  C. For the determination of the master-

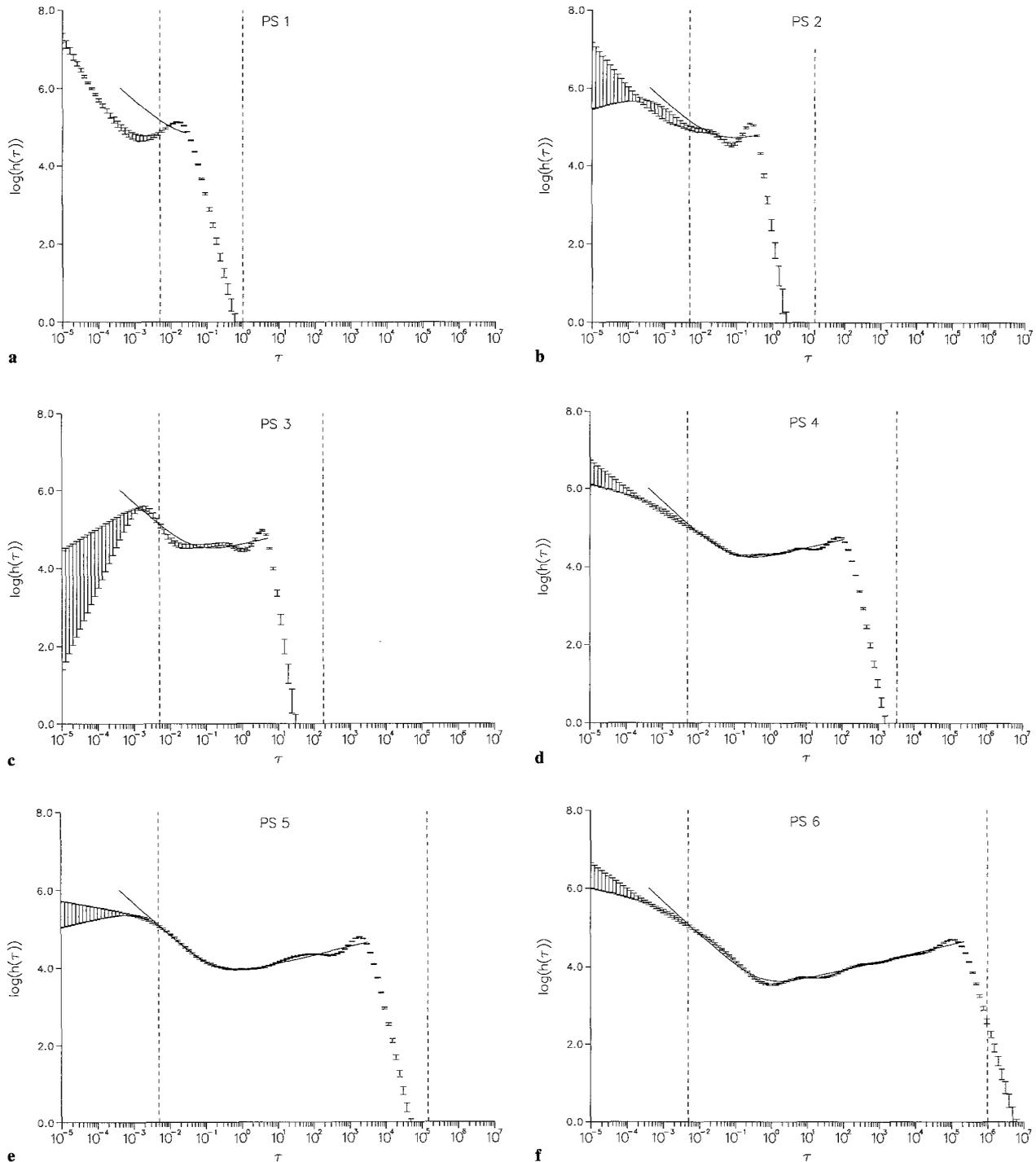


Fig. 7. Relaxation spectra of the six nearly monodisperse PS samples calculated with the nonlinear regularization method (error bars). For comparison, the corresponding BSW-spectra are also shown (solid line). The dashed lines mark the range in which the data characterize the spectrum

curves the shift procedure proposed by Honerkamp and Weese (1973) was used. This shift procedure is a mathematical method for the calculation of mastercurves and scaling factors from experimental data

showing a scaling behavior as, for example, the time-temperature superposition principle. The resulting mastercurves for the dynamic moduli are shown in Fig. 6. They refer to a temperature of  $T_0 = 150^\circ\text{C}$ .

Table 2. Values obtained by the nonlinear regularization method for the regularization parameter  $\lambda$  and the relative error  $\sigma$

Figure	$\lambda$	$\sigma$
7a	$2.03 \cdot 10^{-3}$	2.17%
7b	$1.10 \cdot 10^{-4}$	2.00%
7c	$8.07 \cdot 10^{-5}$	1.94%
7d	$7.93 \cdot 10^{-4}$	1.53%
7e	$1.59 \cdot 10^{-3}$	1.72%
7f	$3.67 \cdot 10^{-3}$	2.84%
9a	$1.96 \cdot 10^{-5}$	1.10%
9b	$3.33 \cdot 10^{-3}$	0.64%

The relaxation spectra have been calculated with the nonlinear regularization method described in Sect. 4. The results are shown in Fig. 7. In addition, Table 2 includes the values obtained for the regularization parameter  $\lambda$  and the estimates of the relative error  $\sigma$ .

When discussing the results it should be kept in mind that only in the range marked by the dashed lines do the data characterize the relaxation spectra. The contributions at shorter (and longer) relaxation times depend on the regularization method, but they are needed to compensate the contributions of those parts of the relaxation spectra which cannot be resolved (Elster et al. (1992)). In this range all relaxation spectra show the typical properties of nearly monodisperse polymer samples: at long relaxation times there is a peak which characterizes the terminal relaxation time. With increasing molar mass this peak moves towards longer relaxation times. At short relaxation times all spectra indicate an enormous contribution which is due to the glass transition.

The relaxation spectra calculated with the nonlinear regularization method (Fig. 7, error bars) can be compared with the BSW-spectra (Fig. 7, solid line) of Baumgaertel et al. (1990). The BSW-spectra do not show a typical peak at long relaxation times. In addition, the longest relaxation time of the BSW-spectra is slightly larger than the terminal relaxation time of the spectra obtained by nonlinear regularization. Disregarding these differences, both spectra show roughly the same features. For the samples PS 4, PS 5, and PS 6 the agreement between both spectra is even quite good.

### 5.2 Results for a commercial PS sample

For the commercial PS sample, data for the dynamic moduli and the relaxation modulus were available. The data have been measured by Rheometrics on a

RMS 800 at temperatures between 122° and 250°C. The corresponding mastercurves are shown in Fig. 8. They refer to a temperature of  $T_0 = 180^\circ\text{C}$ .

The relaxation spectrum could be calculated from the data for the dynamic moduli as well as from the data for the relaxation modulus. The results are shown in Fig. 9. The values for the regularization parameter  $\lambda$  and the estimates of the relative error  $\sigma$  are listed in Table 2.

As the commercial PS sample has a broad molar mass distribution the relaxation spectra show no peak at long relaxation times. Especially satisfactory is the excellent agreement of both relaxation spectra in the range in which they can be compared (Fig. 9c).

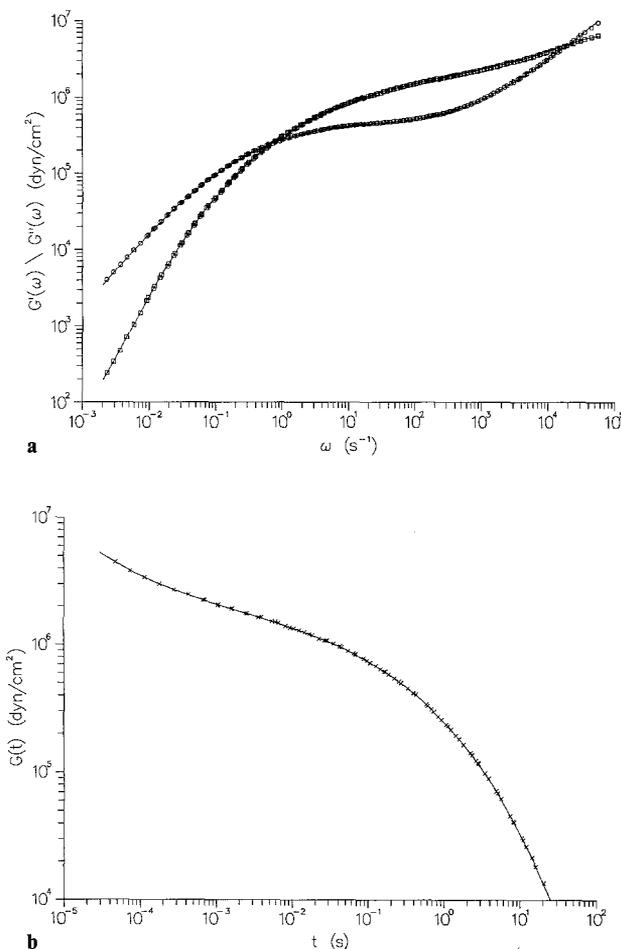


Fig. 8. Mastercurves for the dynamic moduli  $G'(\omega)$  and  $G''(\omega)$  (a) and the relaxation modulus  $G(t)$  (b) of the commercial PS sample. The solid lines mark the values for the dynamic moduli recalculated from the relaxation spectra shown in Fig. 9

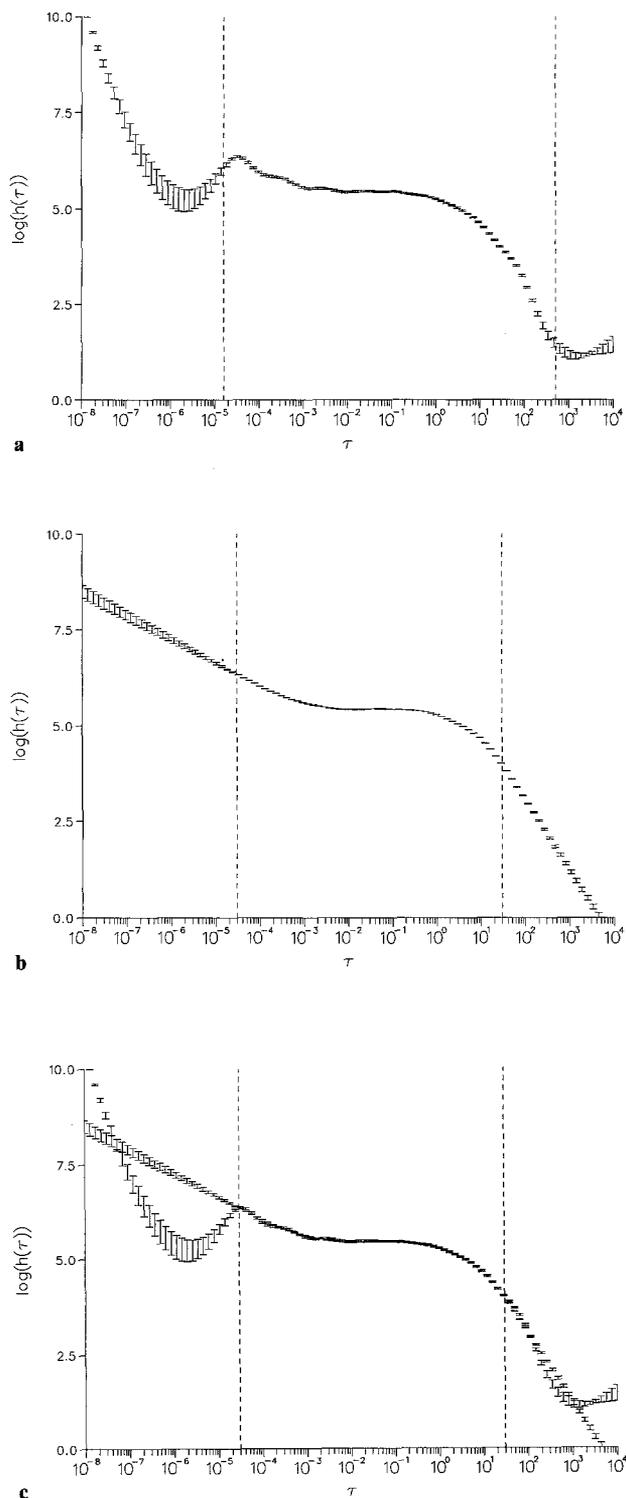


Fig. 9. Relaxation spectrum of the commercial PS sample calculated with the nonlinear regularization method from data for the dynamic moduli (a) and from data for the relaxation modulus (b), respectively. For comparison, both spectra are also shown in one plot (c). The dashed lines mark the range in which the data characterize the spectrum

## 6. Conclusions

Using simulated data it has been shown that the difficulties in the determination of relaxation spectra with Tikhonov regularization can be overcome by applying a nonlinear regularization method. With the nonlinear regularization method it was possible to calculate the relaxation spectra of six nearly monodisperse polystyrene samples from data for the dynamic moduli. Furthermore, the relaxation spectrum of a commercial polystyrene sample has been computed from data for the dynamic moduli and from data for the relaxation modulus. In the range in which both data sets characterize the relaxation spectrum consistent results have been obtained.

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