different mechanisms proposed for the anthryl and pyrenyl polypeptides.

Conclusions

A sequential polypeptide carrying a one-dimensional array of anthryl chromophores was synthesized and characterized by experimental and theoretical CD spectroscopy. No ground-state dimer or higher aggregates was detected in the absorption and fluorescence excitation spectra. The fluorescence spectrum consisted of the monomer and the excimer fluorescence. It was shown that the excimer is formed after a very fast and efficient energy migration along the one-dimensional array. The EFS may be located where the helical structure is largely destroyed.

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Registry No. p(L_2A) homopolymer, 122334-92-3; p(L_2A) SRU, 122357-51-1; Ac-DL-antAla, 82317-69-9; Ac-D-antAla·(−)-ephedrine, 106819-06-1; Ac-L-antAla, 109120-02-7; L-antAla-OMe, 122334-86-5; L-antAla-OMe·HCl, 122334-87-6; BOC-Lys(Z)-OH, 2389-45-9; BOC-Lys(Z)-antAla-OMe, 122334-88-7; BOC-Lys(Z)-antAla-OH, 122334-89-8; BOC-Lys(Z)-OSu, 34404-36-9; H-Lys(Z)-OSu·HCl, 64419-78-9; BOC-Lys(Z)-antAla-Lys(Z)-OSu, 122334-90-1; H-Lys(Z)-Lys(Z)-antAla-OSu·HCl, 122357-50-0; (−)-ephedrine, 299-42-3.

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Determination of the Relaxation Spectrum by a Regularization Method

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ABSTRACT: The determination of the relaxation spectrum using data from small amplitude oscillatory shear flow is investigated. Starting with the application of a linear regression method, the difficulties connected with the determination of the relaxation spectrum are illustrated. A new method based on classical Tikhonov regularization is proposed. The method has been tested using simulated experimental results. Finally it has been applied to the determination of the relaxation spectrum of a polybutadiene sample.

1. Relaxation Spectrum

The basic quantity in the linear theory for viscoelastic polymeric fluids is the relaxation module $G(t)$. It relates the stress tensor $\tau(t)$ to the rate of deformation tensor $\dot{\gamma}_{ij}(t) = \nabla_i v_j + \nabla_j v_i$ (where v is the velocity field) in the constitutive

$$\tau(t) = \int_{-\infty}^{t} G(t - t')\,\dot{\gamma}(t')\,\mathrm{d}t' \qquad (1.1)$$

and it is directly measurable by a sudden shear displacement of the material ($\gamma(t) = \gamma_0\,\Theta(t)$, $\dot{\gamma}(t) = \gamma_0\,\delta(t)$). In the Rouse model[1] one obtains $G(t)$ as a sum of exponential terms

$$G(t) = \sum_{\alpha=1}^{M} e^{-t/\tau_\alpha} \qquad (1.2)$$

where the τ_α are specific relaxation times. A generalization of eq 1.2, which is also compatible with the expressions other models suggest for $G(t)$, is

$$G(t) = \sum_{\alpha=1}^{M} h_\alpha e^{-t/\tau_\alpha} \qquad (1.3)$$

where the relaxation times $\{\tau_\alpha;\ \alpha = 1, ..., M\}$ are, for example, considered to be equally distributed on a logarithmic scale within an interval $[\tau_a, \tau_b]$. The $\{h_\alpha\}$ specifies the weight of each of these relaxation times.

The introduction of the relaxation spectrum $\{\tau_\alpha, h_\alpha\}$ corresponds with the discretization of the relaxation spectrum usually defined by the integral equation

$$G(t) = \int_{-\infty}^{+\infty} h(\tau)\, e^{-t/\tau}\,\mathrm{d}\ln\tau \qquad (1.4)$$

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where the existence of $h(\tau)$ is a physical requirement motivated, as indicated above, by microscopic models of the fluid.

The relaxation spectrum $\{\tau_\alpha, h_\alpha\}$ is a very useful quantity because from it the behavior of a linear viscoelastic fluid in any other standard experiment can be predicted.

In small amplitude oscillatory shear flow with frequency ω and a rate of deformation tensor component

$$\dot{\gamma}_{xy} = \mathrm{Re}\,(\gamma_0 i\omega e^{i\omega t}) \tag{1.5}$$

a stress tensor component $\tau_{xy}(t)$ is generated according to eq 1.1, which can be written as

$$\tau_{xy}(t) = \mathrm{Re}\,\{\gamma_0 e^{i\omega t}(G'(\omega) + iG''(\omega))\} \tag{1.6}$$

With the representation in eq 1.3 the storage modulus G' and the loss modulus G'' can be written as

$$G'(\omega) = \sum_{\alpha=1}^{M} h_\alpha \frac{\omega^2\tau_\alpha{}^2}{1 + \omega^2\tau_\alpha{}^2} \tag{1.7a}$$

$$G''(\omega) = \sum_{\alpha=1}^{M} h_\alpha \frac{\omega\tau_\alpha}{1 + \omega^2\tau_\alpha{}^2} \tag{1.7b}$$

In a stress growth experiment upon inception of steady shear flow on obtains

$$\tau_{xy}(t) = \dot{\gamma}_0 \eta(t) \tag{1.8}$$

with

$$\eta(\tau) = \sum_{\alpha=1}^{M} h_\alpha \tau_\alpha (1 - e^{-t/\tau_\alpha}) \tag{1.9}$$

Hence, as long as the fluid can be considered *linear* viscoelastic, the relaxation spectrum $\{\tau_\alpha, h_\alpha\}$ characterizes the material. Therefore, a method to unambiguously extract this quantity from as few as possible measurements would be very welcome.

The determination of the relaxation spectrum by a linear regression method is widespread in practice and in the literature. We explain it by denoting the experimental results for some function $g(\omega)$ at $\omega = \omega_i$, $i = 1, ..., N$ by g_i^σ. The superscript σ will indicate that the g_i^σ's are affected by standard errors σ_i. In correspondence with eq 1.7 $g_i = g(\omega_i)$ are given by the expression

$$g_i = \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha} h_\alpha \tag{1.10}$$

If we consider the example where $g = G'(\omega)$ in eq 1.7a, then the quantities $\mathbf{K}_{i\alpha}$ are given by

$$\mathbf{K}_{i\alpha} = \frac{\omega_i{}^2\tau_\alpha{}^2}{1 + \omega_i{}^2\tau_\alpha{}^2} \qquad i = 1, ..., N; \quad \alpha = 1, ..., M \tag{1.11}$$

which are the elements of a $N \times M$ matrix $\mathbf{K}$. Given the data (g_i^σ, σ_i) and the matrix $\mathbf{K}$ (i.e., the ω_i and the τ_α), one can try to find the "best" set of $\{h_\alpha\}$ by a linear regression method,[2] which determines those $\{h_\alpha\}$ for which the sum

$$\chi^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i{}^2}(g_i^\sigma - \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha} h_\alpha)^2 \tag{1.12}$$

is minimized.

Anyone who has used this method knows that there occur formidable problems. In the next section we will illustrate the problems associated with this method and explain their source. We also point out why these problems are unavoidable.

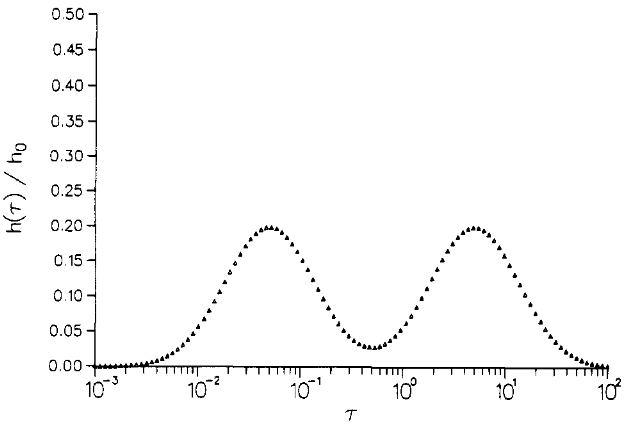

Figure 1. Original relaxation spectrum for the demonstration of the linear regression method and the regularization method.

2. Shortcomings in the Application of the Linear Regression Method

The determination of the relaxation spectrum is well-known to be an ill-posed problem[3-6] (see ref 7 for a definition of ill-posed problems and ref 8 for a more detailed discussion of ill-posed problems and examples). When applying the linear regression method to such a problem, one will be faced with the following phenomena:

(a) The results for $\{h_\alpha\}$ depend strongly on the choice of the points τ_α and on M, the number of points. Certain choices may even lead to negative values of h_α, which are disallowed. As M increases, the number of h_α's that are negative also increases. Therefore, the desire to improve the resolution in τ may lead to results that are completely unsatisfactory.

(b) The results for $\{h_\alpha\}$ alone are insufficient for the characterization of the spectrum. One must also calculate the standard errors of these quantities, and here the failure of the method becomes evident. The standard errors increase with the number of points τ_α and easily become as large or even larger than h_α.

To show the shortcomings of the linear regression method mentioned above, we introduced a relaxation spectrum (see Figure 1)

$$h_\alpha = \frac{1}{2(2\pi)^{1/2}}(e^{-1/2(\ln\tau_\alpha - \ln\tau_x)^2} + e^{-1/2(\ln\tau_\alpha - \ln\tau_y)^2})$$

$$\tau_\alpha = \tau_\mathrm{a}\left(\frac{\tau_\mathrm{b}}{\tau_\mathrm{a}}\right)^{\alpha-1/L-1} \qquad \alpha = 1, ..., L$$

($\tau_x = 5 \times 10^{-2}$, $\tau_y = 5 \times 10^{0}$, $\tau_\mathrm{a} = 1 \times 10^{-3}$, $\tau_\mathrm{b} = 1 \times 10^{2}$, and $L = 100$). According to

$$G'(\omega_i) = \sum_{\alpha=1}^{L} h_\alpha \frac{\omega_i{}^2\tau_\alpha{}^2}{1 + \omega_i{}^2\tau_\alpha{}^2}$$

$$G''(\omega_i) = \sum_{\alpha=1}^{L} h_\alpha \frac{\omega_i\tau_\alpha}{1 + \omega_i{}^2\tau_\alpha{}^2}$$

$$\omega_i = \omega_\mathrm{a}\left(\frac{\omega_\mathrm{b}}{\omega_\mathrm{a}}\right)^{i-1/N-1}$$

we constructed simulated experimental results for the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ at $\omega = \omega_i$ using $\omega_\mathrm{a} = 1 \times 10^{-3}$, $\omega_\mathrm{b} = 1 \times 10^{3}$, $N = 30$, and

$$g'^{\sigma}_i = G'(\omega_i)\ (1 + \sigma N(0, 1)) \qquad i = 1, ..., N$$

$$g''^{\sigma}_i = G''(\omega_i)\ (1 + \sigma N(0, 1)) \qquad i = 1, ..., N$$

where $N(0, 1)$ denotes a normally distributed random

Table I
Simulated Experimental Results for the Storage Modulus G' and the Loss Modulus G''

ω_i	$G'(\omega_i)$	$G''(\omega_i)$
1.000×10^{-3}	7.981×10^{-5}	4.121×10^{-3}
1.610×10^{-3}	1.991×10^{-4}	6.964×10^{-3}
2.593×10^{-3}	5.174×10^{-4}	9.688×10^{-3}
4.175×10^{-3}	1.292×10^{-3}	1.794×10^{-2}
6.723×10^{-3}	3.389×10^{-3}	2.425×10^{-2}
1.083×10^{-2}	8.085×10^{-3}	3.798×10^{-2}
1.743×10^{-2}	1.642×10^{-2}	6.218×10^{-2}
2.807×10^{-2}	3.587×10^{-2}	8.589×10^{-2}
4.520×10^{-2}	6.477×10^{-2}	1.179×10^{-1}
7.279×10^{-2}	1.133×10^{-1}	1.454×10^{-1}
1.172×10^{-1}	1.734×10^{-1}	1.802×10^{-1}
1.887×10^{-1}	2.465×10^{-1}	1.900×10^{-1}
3.039×10^{-1}	3.158×10^{-1}	1.972×10^{-1}
4.894×10^{-1}	3.781×10^{-1}	1.670×10^{-1}
7.880×10^{-1}	4.099×10^{-1}	1.516×10^{-1}
1.269×10^{0}	4.879×10^{-1}	1.403×10^{-1}
2.043×10^{0}	5.130×10^{-1}	1.374×10^{-1}
3.290×10^{0}	5.102×10^{-1}	1.468×10^{-1}
5.298×10^{0}	5.674×10^{-1}	1.601×10^{-1}
8.532×10^{0}	6.599×10^{-1}	1.673×10^{-1}
1.374×10^{1}	7.182×10^{-1}	2.087×10^{-1}
2.212×10^{1}	7.074×10^{-1}	1.824×10^{-1}
3.562×10^{1}	8.239×10^{-1}	1.934×10^{-1}
5.736×10^{1}	9.196×10^{-1}	1.448×10^{-1}
9.237×10^{1}	8.538×10^{-1}	1.230×10^{-1}
1.487×10^{2}	9.169×10^{-1}	9.010×10^{-2}
2.395×10^{2}	9.739×10^{-1}	5.321×10^{-2}
3.857×10^{2}	9.566×10^{-1}	4.025×10^{-2}
6.210×10^{2}	9.999×10^{-1}	2.503×10^{-2}
1.000×10^{3}	9.790×10^{-1}	1.729×10^{-2}

number. With $\sigma = 0.04$ we obtained the data listed in Table I. In Figure 2a,b we present results of a determination of $\{h_\alpha\}$ from this data by the regression method with $M = 6$ and $M = 12$. One notices that the true values shown in Figure 1 are not reproduced at all.

Hence, the naive linear regression method does not lead to reliable results for the spectrum. Also, a strategy for finding the optimal set of points τ_α will not remedy this situation. What is the reason for this undesirable situation?

In order to discover the source of the difficulties, we will study the $N \times M$ matrix $\hat{\mathbf{K}}$ with $\hat{\mathbf{K}}_{i\alpha} = (1/\sigma_i)\mathbf{K}_{i\alpha}$ in more detail by its singular value decomposition. We know that, for $N \geq M$, $\hat{\mathbf{K}}$ can be written as[2]

$$\hat{\mathbf{K}}_{i\alpha} = \sum_{\gamma=1}^{M} w_\gamma (\vec{u}_\gamma)_i (\vec{v}_\gamma)_\alpha \tag{2.1}$$

where the $\{\vec{u}_\gamma;\ \gamma = 1, ..., M\}$ are the orthonormalized eigenvectors of the $N \times M$ matrix $\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}^{\mathrm{T}}$ with the M largest eigenvalues and $\{\vec{v}_\gamma;\ \gamma = 1, ..., M\}$ is a complete set of orthonormalized eigenvectors of the $M \times M$ matrix $\hat{\mathbf{K}}^{\mathrm{T}} \cdot \hat{\mathbf{K}}$. The w_γ's are the nonnegative square roots of the eigenvalues of $\hat{\mathbf{K}}^{\mathrm{T}} \cdot \hat{\mathbf{K}}$, and they are called singular values of $\hat{\mathbf{K}}$. Subroutines by which the $\{\vec{u}_\gamma, \vec{v}_\gamma, w_\gamma\}$ can be determined are readily available in most computer software libraries.

With the help of these quantities, the solution $\{h_\alpha\}$ that minimizes χ^2 can immediately be written down as[2]

$$h_\alpha = \sum_{\gamma=1}^{M} \frac{1}{w_\gamma} (\vec{v}_\gamma)_\alpha (\vec{u}_\gamma \cdot \vec{b}^\sigma) \tag{2.2}$$

where we have collected the data $\{g_i^\sigma;\ i = 1, ..., N\}$ into a vector $\vec{b}^\sigma = (g_1^\sigma/\sigma_1, ..., g_N^\sigma/\sigma_N)$. The standard error for h_α is given by

$$\sigma^2(h_\alpha) = \sum_{\gamma=1}^{M} \frac{1}{w_\gamma^2} (\vec{v}_\gamma)_\alpha (\vec{v}_\gamma)_\alpha \tag{2.3}$$

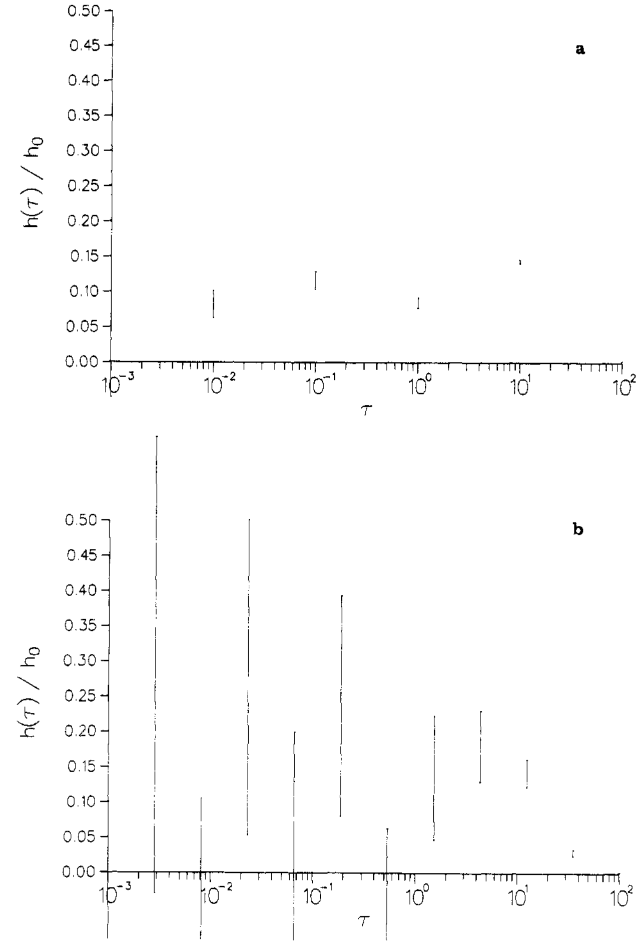

Figure 2. Normalized results for the relaxation spectrum (Figure 1) obtained with the linear regression method for (a) $M = 6$ and (b) $M = 12$.

Now it is obvious what may happen. If some singular values get too small, the errors become large because the inverse squares of the singular values contribute to the standard errors ($(\vec{v}_\gamma)_\alpha$ are of the order of 1 because $\vec{v}_\gamma$ is normalized).

Furthermore, because the inverse of the w_γ contributes also to h_α, small changes in g_i^σ may produce huge variations in h_α, if some singular values w_γ become too small. This corresponds to the large standard errors. The values $\{h_\alpha\}$ obtained from some data g_i^σ may deviate strongly from the true values.

Hence, even one small singular value—or to be more precise a small ratio of the smallest to the largest singular value, which can be considered as a condition number of the matrix—is very dangerous. It means that the matrix is a contracting mapping; somehow some information is lost, which cannot be restored by inversion.

Now let us see whether this happens in our example. The matrix $\hat{\mathbf{K}}$ has elements

$$\hat{\mathbf{K}}_{i\alpha} = \frac{1}{\sigma_i} \frac{\omega_i^2 \tau_\alpha^2}{1 + \omega_i^2 \tau_\alpha^2} \tag{2.4}$$

With ω_i and τ_α chosen as in the example above, we obtain for $M = 6$ and $M = 12$ the singular values given in Table II. For increasing M, the condition number becomes worse, the smallest singular values become smaller, and the ratio of the smallest to the largest singular value decreases. This is due to the fact that the distance between nearest points τ_α decreases; the columns in the matrix $\hat{\mathbf{K}}$, therefore, become less independent. Near dependence of two columns of a matrix produces a small singular value

Table II
Normalized Singular Values of the Matrix $\hat{\mathbf{K}}$ for (a) $M = 6$ and (b) $M = 12$

γ	w_γ	γ	w_γ
	(a) $M = 6$		
1	274.861	4	2.069
2	10.372	5	1.022
3	4.474	6	0.352
	(b) $M = 12$		
1	278.171	7	1.013
2	23.141	8	0.621
3	10.554	9	0.381
4	4.901	10	0.229
5	2.812	11	0.135
6	1.643	12	0.069

(strict dependence leads to a zero singular value).

There may be a choice of the distribution of τ_α with a given M for which the condition number of the matrix is optimal. But the condition number of the matrix will certainly worsen with increasing M. Therefore, we have to look for another more reliable method for the determination of the spectrum.

The linear regression method is not the only one used for the determination of the relaxation spectrum. There are other usual approximation methods.[9] But care must be taken when using approximation methods involving derivatives of the storage modulus or the loss modulus, because the calculation of derivatives itself is an ill-posed problem.

3. Regularization Method

There are several methods for solving ill-posed problems.[10,11] The most commonly used is the regularization method of Tikhonov and Phillips. The basic concept of this method is described in the following section.

3.1. Basic Concept of Regularization. In the last chapter we have pointed out that the small denominators w_γ in

$$h_\alpha = \sum_{\gamma=1}^{M} \frac{1}{w_\gamma}(\vec{v}_\gamma)_\alpha(\vec{u}_\gamma \cdot \vec{b}^\sigma) \tag{3.1}$$

are the source of the difficulties. We can easily introduce a regularized version of h_α, namely

$$h_\alpha^\lambda = \sum_{\gamma=1}^{M} \frac{w_\gamma}{w_\gamma^2 + \lambda}(\vec{v}_\gamma)_\alpha(\vec{u}_\gamma \cdot \vec{b}^\sigma) \tag{3.2}$$

which converges to h_α if the regularization parameter λ converges to 0 but does not contain these dangerous denominators if $\lambda \neq 0$. For $w_\gamma^2 \gg \lambda$ we have

$$\frac{w_\gamma}{w_\gamma^2 + \lambda} \sim \frac{1}{w_\gamma} \tag{3.3a}$$

and for $w_\gamma^2 \ll \lambda$ we have

$$\frac{w_\gamma}{w_\gamma^2 + \lambda} \sim \frac{w_\gamma}{\lambda} \tag{3.3b}$$

Hence, h_α^λ is certain to differ from h_α for $\lambda \neq 0$ and cannot minimize the quantity (compare eq 1.12)

$$\chi^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(g_i^\sigma - \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha}h_\alpha)^2 \tag{3.4}$$

On the other hand, $\{h_\alpha^\lambda\}$ is the solution of the minimization problem

$$\chi_\lambda^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(g_i^\sigma - \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha}h_\alpha)^2 + \lambda \sum_{\alpha=1}^{M} h_\alpha^2 = \text{minimum} \tag{3.5}$$

This can easily be verified. After differentiation of χ_λ^2 with respect to h_α, the necessary condition for $\{h_\alpha^\lambda\}$ minimizing χ_λ^2 leads to

$$\frac{1}{2}\frac{\partial \chi_\lambda^2}{\partial h_\alpha} = \lambda h_\alpha - \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(g_i^\sigma - \sum_{\beta=1}^{M} \mathbf{K}_{i\beta}h_\beta)\mathbf{K}_{i\alpha} = 0 \tag{3.6}$$

which can also be written as

$$(\lambda 1 + \hat{\mathbf{K}}^{\mathrm{T}}\hat{\mathbf{K}})\vec{h} = \hat{\mathbf{K}}^{\mathrm{T}}\vec{b}^\sigma \tag{3.7}$$

Hence, the solution reads

$$h_\alpha^\lambda = \sum_{\beta,i}((\lambda 1 + \hat{\mathbf{K}}^{\mathrm{T}}\hat{\mathbf{K}})^{-1})_{\alpha\beta}\hat{\mathbf{K}}^{\mathrm{T}}_{\beta i}b_i^\sigma \tag{3.8}$$

which, with the singular value decomposition of $\hat{\mathbf{K}}$, leads to eq 3.2.

The search for a minimum of χ_λ^2, given in eq 3.5, leads to a well-defined solution (eq 3.8 or eq 3.2), free of the difficulties described in section 2, if λ has an appropriate value. The reminder of this discussion is devoted to the question of how to choose λ, but first we ask for the meaning of our new strategy to calculate the spectral weights $\{h_\alpha\}$ from the experimental data (g_i^σ, σ_i).

The quantity χ_λ^2, given in eq 3.5, is a combination of two terms, of the old χ^2 and of a term that can be interpreted as the squared norm of $\vec{h} = (h_1, ..., h_M)$. For small λ, the minimization of χ_λ^2 is nearly a minimization of χ^2; for larger λ, the fitting procedure takes into account not only the mean-square deviation of g_i^σ from $\sum_{\alpha=1}^{M}\hat{\mathbf{K}}_{i\alpha}h_\alpha$ but also the norm of $\vec{h}$ with a nonnegligible weight. Therefore, minimizing χ_λ^2 is a compromise between looking for a solution leading to the best fit to the data and selecting a solution, which is not too complicate. The regularization parameter λ is weighing the importance of these two criteria to select a solution.

Using the regularization method considered above, we associate a complicate solution to have a large norm. One could also think of a complicate solution to be wildly oscillating and of a more simple one to be very smooth. This leads to a different frequently used regularization method not considered in this paper.

It is well-known, that values obtained by a linear regression method are an unbiased estimate for the true values. But when solving ill-posed problems, such a method leads to very large standard errors, as we have shown in section 2. The regularization method was introduced to reduce the size of these errors. As a consequence, the resulting estimate h_α^λ is no more an unbiased estimate for the true values. Therefore, care must be taken, when looking at the usual confidence regions. They show only the size of the statistical error given a distinct regularization parameter λ.

3.2. Choice of the Regularization Parameter. The main problem when using a regularization method is the determination of an appropriate regularization parameter. There are several strategies in the theory of Tikhonov regularization[12,13] to determine λ. Other methods are based on ridge estimation such as the one proposed by Mallows,[14] which we follow in this paper. The application to regularization problems is, e.g., found in ref 15. There λ is chosen so that

$$t(\lambda) = \sum_{i=1}^{N}\left(\frac{g_i}{\sigma_i} - \sum_{\alpha=1}^{M}\hat{\mathbf{K}}_{i\alpha}h_\alpha^\lambda\right)^2 \tag{3.9}$$

is a minimum, where the $\{g_i\}$'s are the true values without error given by eq 1.10.

Of course, one does not know the $\{g_i\}$, but considering $t(\lambda)$ as a realization of a stochastic variable $T(\lambda)$, one can

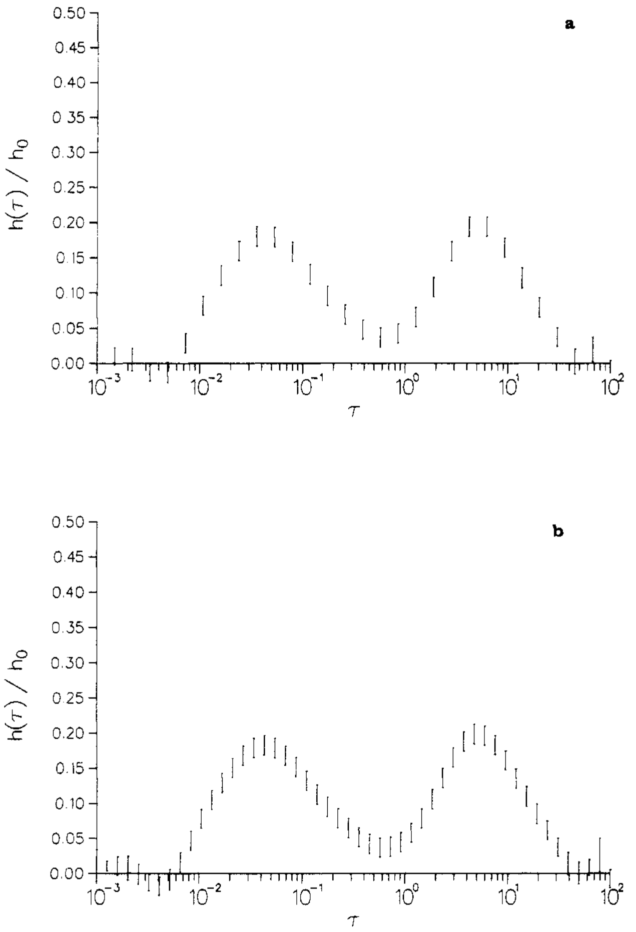

Figure 3. Normalized results for the relaxation spectrum (Figure 1) obtained with the regularization method for (a) M = 30 and (b) M = 50.

Table III[a]
Experimental Results for the Storage Modulus G' and the Loss Modulus G'' of a Narrow Distribution Polybutadiene Melt with $\bar{M}_w = 5.78 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1.05$[16]

ω_i, s^{-1}	$G'(\omega_i)$, Pa	$G''(\omega_i)$, Pa
2.493×10^0	2052	34526
3.670×10^0	4156	50445
5.373×10^0	8847	73294
7.864×10^0	18834	105329
1.144×10^1	37737	149699
1.695×10^1	74730	206936
2.451×10^1	136257	266220
3.608×10^1	223611	313420
5.218×10^1	324937	345321
7.680×10^1	432105	359952
1.144×10^2	534678	343388
1.654×10^2	619214	327629
2.433×10^2	701325	307419
3.539×10^2	772708	290069
5.238×10^2	841878	278292
7.529×10^2	897344	264055
1.114×10^3	956262	249131

[a] The values refer to a temperature of 23 °C.

show that an unbiased estimator for the expectation value of $T(\lambda)$ is

$$\hat{T}(\lambda) = \vec{b}^{\sigma}\cdot(1 - \mathbf{P}(\lambda))^2\cdot\vec{b}^{\sigma} - N + 2\,\mathrm{Tr}\,(\mathbf{P}(\lambda)) \tag{3.10}$$

with

$$(\mathbf{P}(\lambda))_{ij} = (\hat{\mathbf{K}}(\hat{\mathbf{K}}^{\mathrm{T}}\cdot\hat{\mathbf{K}} + \lambda 1)^{-1}\hat{\mathbf{K}}^{\mathrm{T}})_{ij} = \sum_{\gamma=1}^{M} (\vec{u}_{\gamma})_i \frac{w_{\gamma}^{2}}{w_{\gamma}^{2} + \lambda} (\vec{u}_{\gamma})_j \tag{3.11}$$

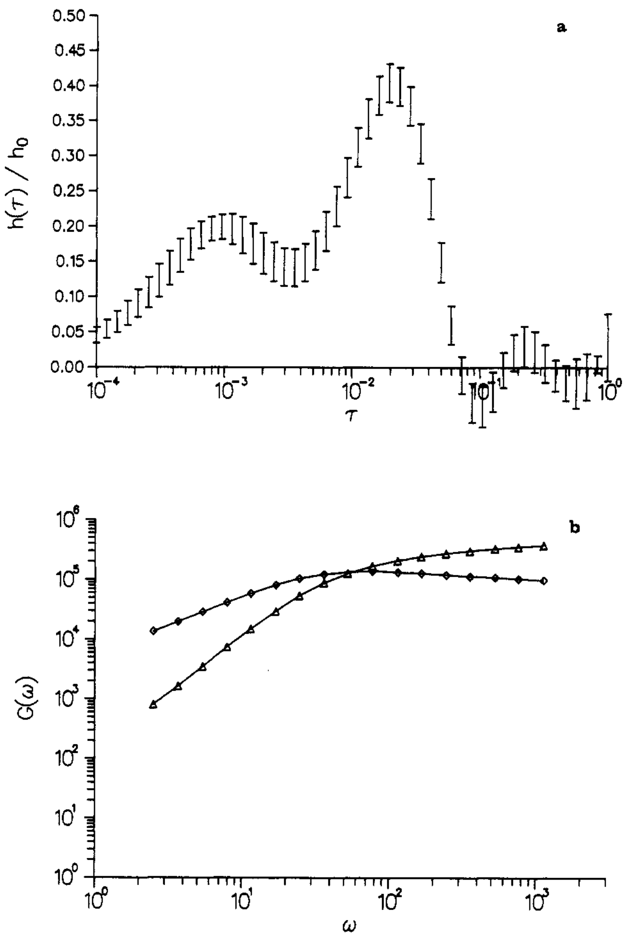

Figure 4. (a) Normalized results for the relaxation spectrum of the polybutadiene sample obtained with the regularization method. (b) Storage modulus G' and loss modulus G'' obtained for the calculated relaxation spectrum. The symbols denote the measured values for G' (△) and G'' (◇) listed in Table III.

The criterium (eq 3.9) is very plausible and can easily be considered because $\hat{T}(\lambda)$ can explicitly be expressed (up to terms independent of λ) as

$$\hat{T}(\lambda) = \sum_{\gamma=1}^{M} \frac{\lambda^2}{(w_{\gamma}^{2} + \lambda)^2} (\vec{u}_{\gamma}\cdot\vec{b}^{\sigma})^2 + 2\sum_{\gamma=1}^{M} \frac{w_{\gamma}^{2}}{w_{\gamma}^{2} + \lambda} \tag{3.12}$$

Hence, one has to compute $\vec{u}_{\gamma}$ and w_{γ} to calculate $\hat{T}(\lambda)$ by eq 3.12. A minimization of $\hat{T}(\lambda)$ then leads to a value $\lambda = \lambda^*$, which will be used in eq 3.2 in order to obtain the final result $h_{\alpha}^{\lambda^*}$ as estimation for the weights of the relaxation times τ_{α}.

4. Results

Taking again the synthetic data listed in Table I, we solved the minimization problem

$$\chi_{\lambda}^{2} = \sum_{i=1}^{N} \left\{ \frac{1}{(\sigma_i')^2} (g_i'^{\sigma} - \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha}' h_{\alpha})^2 + \frac{1}{(\sigma_i'')^2} (g_i''^{\sigma} - \sum_{\alpha=1}^{M} \mathbf{K}_{i\alpha}'' h_{\alpha})^2 \right\} + \lambda \sum_{\alpha=1}^{M} h_{\alpha}^{2} = \text{minimum}$$

$$\mathbf{K}_{i\alpha}' = \frac{\omega_i^2 \tau_{\alpha}^2}{1 + \omega_i^2 \tau_{\alpha}^2} \qquad \mathbf{K}_{i\alpha}'' = \frac{\omega_i \tau_{\alpha}}{1 + \omega_i^2 \tau_{\alpha}^2}$$

$$\sigma_i' = \sigma g_i'^{\sigma} \qquad \sigma_i'' = \sigma g_i''^{\sigma}$$

$$\tau_{\alpha} = \tau_a \left(\frac{\tau_b}{\tau_a} \right)^{\alpha-1/M-1} \qquad \alpha = 1, ..., M$$

with $\tau_a = 1 \times 10^{-3}$, $\tau_b = 1 \times 10^2$, $\sigma = 0.04$, and $M = 30$, and $M = 50$, where λ was determined as described in section 3.2. The results are shown in Figure 3a,b and are in good agreement with the true relaxation spectrum (Figure 1). Furthermore, the result is independent of the number of relaxation times M introduced.

Finally, we determined the relaxation spectrum of a narrow distribution polybutadiene melt with $\bar{M}_w = 5.78 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1.05$ using data from Berger.[16] The values for the storage modulus and the loss modulus listed in Table III refer to a temperature of 23 °C. With $\sigma = 0.04$, $M = 50$, $\tau_a = 1 \times 10^{-4}$, and $\tau_b = 1 \times 10^0$, we obtained the relaxation spectrum shown in Figure 4a. Figure 4b shows the resulting storage modulus and loss modulus, which is in good agreement with the measured values.

As expected, nearly all h_α's are positive. Furthermore, there can be identified two peaks in the relaxation spectrum at $\tau \approx 8 \times 10^{-4}$ and $\tau \approx 2 \times 10^{-2}$ s. For small τ_α ($\approx 1 \times 10^{-4}$) the corresponding h_α's tend toward 0, and for large τ_α ($\gtrsim 1 \times 10^{-1}$) the h_α's seem to be compatible with 0. There remain questions concerning the resolution of the obtained relaxation spectrum. Furthermore, the dependence of the accuracy of the obtained values on the number N of measured values and on the range in which measured values for $G'(\omega)$ and $G''(\omega)$ are available should be studied in the future.

5. Conclusions

It has been shown, that the results for the relaxation spectrum using a naive linear regression method are not satisfactory at all. Pointing out the reason for this, we proposed a solution method for the determination of the relaxation spectrum based on classical Tikhonov regularization. The method was tested using simulated experimental data, and the results obtained were in good agreement with the known relaxation spectrum. The application to real experimental data always leads to plausible results.

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Polymorphic Structures and Molecular Vibrations of Syndiotactic Polystyrene

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ABSTRACT: Two crystal modifications, α and β, of syndiotactic polystyrene (SPS) were found by means of vibrational spectroscopic and X-ray diffraction methods. It has been revealed that the α phase, crystallized from the melt or by annealing glassy samples, consists of molecules having the all-trans (TT) skeletal conformation and the β phase, crystallized from solutions or by holding glassy samples in an atmosphere of solvent vapor, consists of the TTGG skeletal conformation. The infrared bands characteristic of these specific conformations were observed and compared with those of isotactic polystyrene with TG conformation. The thermal crystallization from the glassy state and a solid-state phase transition from β to α phase were followed by the infrared spectral change and DSC thermogram. The TT form is found to be more stable than the TTGG form under ambient conditions.

Introduction

Isotactic polystyrene (abbreviated as IPS) is representative of stereoregular polymers. Since the first invention by Natta et al. in 1955,[1] many studies have been reported on the structure of IPS and related low molecular weight compounds in crystalline and noncrystalline states. It is now well-known that in the crystalline state the IPS molecule assumes a (3/1) helical form with a regular repetition of trans (T) and gauche (G) conformations of the skeletal C–C bonds.[2,3] Another skeletal conformation having a nearly extended form consisting of a repetition of nonstaggered trans C–C bonds (with the internal rota-

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