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Dielectric Principal Relaxation Above and Near the Glass Transition

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SUMMARY

A theoretical interpretation of the temperature dependence of position and shape of the relaxation-frequency-spectrum is given for the dielectric principal relaxation of amorphous polymers. Assuming the spectrum obeys the HAVRILIAK-NEGAMI-formula, its change versus temperature (above T_g) can be described quantitatively by three WLF-like equations differing mutually in the value of one constant only.

INTRODUCTION AND FUNDAMENTAL RELATIONS

It is well established that a polar amorphous polymer exhibits a principal (α-) and one or more secondary relaxation processes being reflected in the frequency dependence of the dielectric loss-factor $\varepsilon''(\omega)$ showing a peak for each process.

The essential information on a process is provided by the frequency ω_m of the loss maximum and by the form of the ε'' vs. $\log \omega$ plot both of them depending on the temperature T.

The $\log \omega_m$ vs. T^{-1} plot is strongly curved for the α-relaxation and can be described by a semi-empirical formula introduced by WILLIAMS, LANDEL and FERRY (1955), the well known WLF-equation.

Identifying ω_m with a mean relaxation frequency

$$\omega_m = \bar{s} \tag{1}$$

and applying the theory of free volume to $\bar{s}$ COHEN and TURNBULL (1959) have given a theoretical interpretation of the WLF-equation.

Measurements at very low frequencies are necessary for the determination of ω_m near the glass-transition. Because of experimental reasons in that case the technique of alternating currents (ac) must be replaced by a quasistatic one (dc), whereby normally the HAMON-approximation (1952) is used for the conversion of dc-into ac-data.

Referring to the shape of the loss curve HAVRILIAK and NEGAMI (1966) proposed a four-parameter model function (HN-function)

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$$\varepsilon''(\omega) = \Delta\varepsilon\,[r(\omega)]^{-\gamma}\,\sin[\gamma\vartheta(\omega)] \qquad (2)$$

$$\text{where}\quad \begin{cases} r(\omega) = \left[1 + 2\left(\frac{\omega}{s_0}\right)^{\beta}\cos\frac{\beta\pi}{2} + \left(\frac{\omega}{s_0}\right)^{2\beta}\right]^{1/2} \\ \vartheta(\omega) = \arctan\dfrac{\sin\frac{\beta\pi}{2}}{\left(\frac{\omega}{s_0}\right)^{\beta} + \cos\frac{\beta\pi}{2}} \end{cases} \qquad (2a)$$

$\Delta\varepsilon$ – intensity of the process
s_0 – characteristic frequency (generally in the vicinity of ω_m)
β, γ – form-parameters (referring to the shape of the ε'' vs. $\log\omega$ plot

The parameters are calculable by least square fitting of eq. (2) to the experimental data. In the case of dc-data this procedure requires additionally a Fourier-transform of eq. (2) (SCHLOSSER et al. 1981). An excellent fitting was demonstrated for numerous polymers.

On the other hand it is convenient to represent the ε'' vs. $\log\omega$ plot by a spectrum L(s) of DEBYE-terms which is defined by the equation (BÖTTCHER and BORDWIJK 1978)

$$\varepsilon''(\omega) = \Delta\varepsilon\int_{-\infty}^{\infty} L(s)\,\frac{\omega/s}{1 + (\omega/s)^2}\,d\ln s \qquad (3)$$

L(s) – (logarithmic) distribution of the relaxation frequencies.

Comparing the two representations of the function $\varepsilon''(\omega)$, the eq. (2) is an empirical one whereas eq. (3) reflects a physical background, therefore, being more appropriate for the further considerations.

The calculation of the spectrum L(s) requires the inversion of the integral (3). This can be done with the help of an analytic formula (KÄSTNER and SCHLOSSER 1957), involving the HN-representation of $\varepsilon''(\omega)$ leading explicitely to the HN-spectrum:

$$L(s) = \frac{1}{\pi}\,\frac{\sin[\gamma\psi(s)]}{\left[1 + 2\left(\frac{s}{s_0}\right)^{\beta}\cos\beta\pi + \left(\frac{s}{s_0}\right)^{2\beta}\right]^{\gamma/2}} \qquad (4)$$

$$\text{where}\quad \psi(s) = \frac{\pi}{2} - \arctan\frac{\left(\frac{s}{s_0}\right)^{-\beta} + \cos\beta\pi}{\sin\beta\pi} \qquad (4a)$$

Further, it will be suitable to replace the parameters s_0, β, γ (characterizing the spectrum) by the relaxation frequencies s_m, s' and s" which denote on the frequency scale the position of the maximum L_{max} and of the lower and upper half-width of the spectrum:

$$L(s_m) = L_{max} \qquad L(s') = L(s'') = \frac{L_{max}}{2} \qquad (5)$$

Because of their sensibility to the form of the spectrum the parameters half-width b_s and asymmetry-coefficient u_s defined by the equations

$$b_s = \lg s'' - \lg s'$$

$$u_s = \frac{(\lg s'' - \lg s_m) - (\lg s_m - \lg s')}{\lg s'' - \lg s'} \qquad (6)$$

are often used instead of s_m, s' and s'' .

In order to demonstrate the temperature-dependence of the spectrum, dielectric measurements were carried out in a large range of temperatures on polychlorostyrene (PClS) as an example, because of its α-relaxation being not disturbed by neighbouring relaxation processes. The characteristic relaxation frequencies s_m, s' and s'' obtained by an analysis of the experimental data are marked by points in Fig. 1.

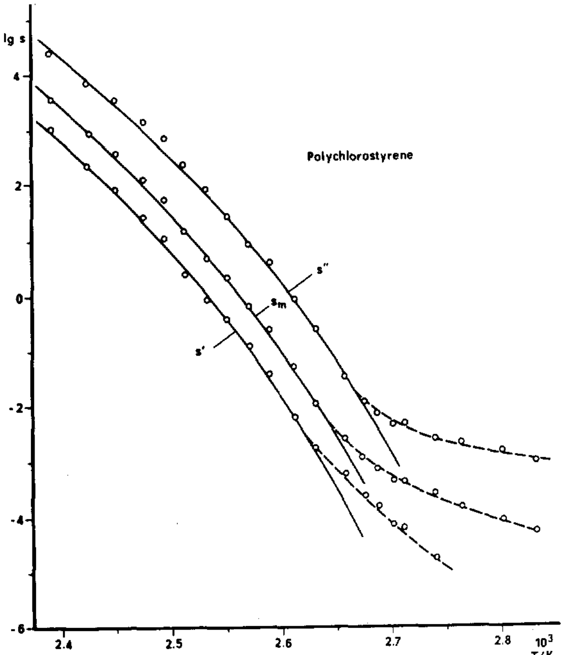

Fig.1

Temperature dependence of the characteristic relaxation frequencies s_m, s' and s''

o Experimental values
— Theoretical curves (s in sec^{-1})

Fig. 2 shows these results in terms of the half-width b_s and the asymmetry-coefficient u_s.

The figures represent the temperature dependence of the position and the form of the spectra generally found for the α-relaxation of amorphous polymers. The interpretation will be presented in the next section.

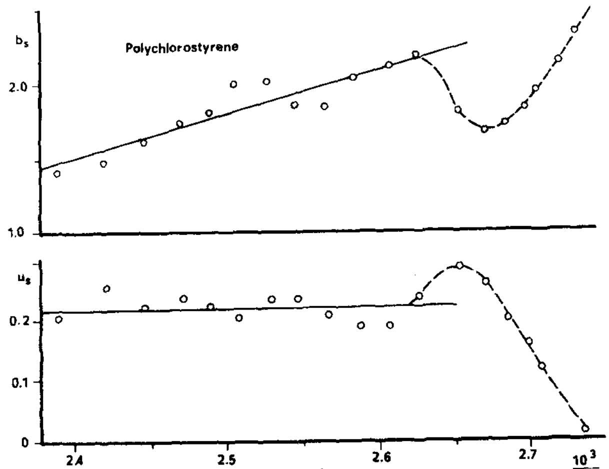

Fig. 2

Temperature dependence of b_s and u_s

o Experimental values
— Theoretical curves

INTERPRETATION OF THE TEMPERATURE DEPENDENCE OF THE SPECTRUM

In order to explain the temperature dependence of the spectrum it seems to be obvious (for $T > T_g$) to transfer the free-volume theory, up to this time successfully applied to the mean relaxation frequency $\bar{s}$, to the relaxation frequencies s_m, s' and s''.

For the maximum-frequency s_m the basic relation of the free volume theory should hold:

$$s_m = s_\infty \exp\{B/f\} \tag{7}$$

where $\quad B = V^x/V \qquad f = \bar{V}_f/V$

B – constant (V^x is the free volume at least necessary for the rearrangement of a segment; V is the mean volume of a segment)
f – relative free volume ($\bar{V}_f$ is the mean free volume)
s_∞ – limit value of s_m for $f \to \infty$

The free volume depends on the temperature, for $T > T_g$ obeying the linear relation

$$f(T) = \Delta\beta\,(T - T_o), \qquad T > T_g \tag{8}$$

where $\quad \Delta\beta = \beta_2 - \beta_1 \qquad$ (8a)

as can be concluded from the linear thermal expansion of the specific volume (dilatometric measurement).

$\Delta\beta$ – expansion coefficient of the relative free volume (β_2 and β_1 are the expansion coefficients of the relative specific volume above and below T_g, respectively)

T_0 - extrapolated value of temperature for which $f = 0$.

Introducing eq. (8) in eq. (7) one gets for $\lg s_m(T)$ the expression

$$\lg s_m(T) = \lg s_\infty - \frac{A}{T - T_0} \tag{9}$$

where
$$A = 0.434\ B/\Delta\beta \tag{9a}$$

which is identical with the WLF-relation. The s_m-values at least at three temperatures are necessary for the determination of the three constants $\lg s_\infty$, A and T_0.

The curve $s_m(T)$ in Fig. 1 (full line) shows the excellent fitting to the experimental s_m-values of PClS where the parameters s_∞ , A and T_0 are chosen as

$$\lg s_\infty/\mathrm{sec}^{-1} = 14.49 \quad A/K = 1224.2 \quad T_0/K = 305.8 \tag{9b}$$

At the glass transition the normal deviation of the experimental data from the WLF-plot is observed, caused by the volume relaxation which is not ended during the time of experiment.

In order to extend the preceding considerations to the temperature dependence of the whole spectrum we introduce a distribution around the most probable segmental volume (related to the relaxation frequency s_m). In particular the segmental volumes V' and V'' (with $V' > V > V''$) may be related to the frequencies s' and s''.

In analogy to eq. (7) the relaxation frequencies of these segments should obey the relations

$$\begin{aligned} s' &= s_\infty \exp\{B'/f'\} \\ s'' &= s_\infty \exp\{B''/f''\} \end{aligned} \tag{10}$$

The constants B' and B'' defined according to the free-volume concept as

$$B' = \frac{V^{x'}}{V'} \quad ; \quad B'' = \frac{V^{x''}}{V''} \tag{11}$$

(compare eq. (7a)) in our model are proposed to be independent of the segmental size. Therefore we get the identity

$$B' = B'' = B \tag{12}$$

where B depends only on the type of the substance.

Contrary to this fact the relative free volume defined as the proportion of the mean free volume and the segment volume changes for different segments:

$$f' = \frac{V_f}{V'} \quad ; \quad f'' = \frac{V_f}{V''} \tag{13}$$

whereby f' and f'' are related to f using eq. (7a) according to:

$$f' = \frac{V}{V'} f \quad ; \quad f'' = \frac{V}{V''} f . \tag{14}$$

Introducing eq. (8) in eqs. (14) we get the temperature dependence of f' and f'' as

$$f'(T) = \Delta\beta'(T - T_0)$$
$$f''(T) = \Delta\beta''(T - T_0) \qquad (15)$$

with the expansion coefficients

$$\Delta\beta' = \frac{V}{V'}\Delta\beta \quad ; \quad \Delta\beta'' = \frac{V}{V''}\Delta\beta \quad . \qquad (15a)$$

Finally, to make a statement regarding s'_∞ and s''_∞ we use the experimental fact that the half-width b_s decreases continuously with the increase of the temperature. Therefore the conclusion should be justified that $b_s \to 0$ for $T \to \infty$, or

$$s'_\infty = s''_\infty = s_\infty \, . \qquad (16)$$

With the relations (12), (15) and (16) we get for the eqs. (10) the final result of the temperature dependences of s' and s'', respectively:

$$\lg s'(T) = \lg s_\infty - \frac{A'}{T - T_0}$$
$$\lg s''(T) = \lg s_\infty - \frac{A''}{T - T_0} \qquad (17)$$

where $A' = 0.434\ B/\Delta\beta'$; $A'' = 0.434\ B/\Delta\beta''$. (17a)

The temperature dependence of s' (and s'') obeys a WLF-like equation differing from eq. (9) by the value of one constant (A' and A'', respectively) only. The determination of A' and A'' requires the knowledge of s' and s'' at least at one temperature.

The curves $s'(T)$ and $s''(T)$ according to eqs. (17) at PClS ($A'/K = 1288.6$; $A''/K = 1122.5$) drawn by full lines in Fig. 1 show the good fitting to the experimental points in the temperature range $T > T_g$.

The introduction of eqs. (17) and (9) in eqs. (6) leads to the expressions which are expected from the theory for $b_s(T)$ and $u_s(T)$:

$$b_s(T) = \frac{A' - A''}{T - T_0} \quad ; \quad u_s = \frac{2A - (A' + A'')}{A' - A''} \qquad (18)$$

It is remarkable that the coefficient of asymmetry does not depend on the temperature.

The theoretical curves according to eqs. (17) are shown in Fig. 2 as full lines with sufficient fitting to the experimental points.

Still, it should be noticed that we can get the relation between the constants A, A', A'' and the relative volumes of the segments V'/V and V''/V by the equations (9a), (15a) and (17a) as

$$\frac{V'}{V} = \frac{A'}{A} \quad ; \quad \frac{V''}{V} = \frac{A''}{A} \quad . \qquad (19)$$

Because the preceding considerations should be valid for any other segment, moreover, the complete distribution of the segments is available by L(s) determined at one temperature only. It is of interest that this distribution is independent of the temperature.

The deviations of s' and s'' from their theoretical plots (predicted for $T > T_g$) appearing within the glass transition range can be discussed in a qualitative manner only at present. At decreasing temperature near T_g it can be observed that $s'(T)$, $s_m(T)$ and $s''(T)$ deviate subsequently from their WLF-like plots, the deviations being reflected also by a decrease of b_s and a rise of u_s within a range of a few degrees of Kelvin. This can be understood in terms of a gradual freezing which spreads from the larger to the smaller segments. Further investigations are necessary in order to clarify this field.

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