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Activation Law Parameters of Viscoelastic Subglass Relaxations from Dynamic-Mechanical Moduli Measurements as a Function of Temperature

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ABSTRACT: The phenomenology of the subglass relaxation processes as a function of temperature is investigated, taking as a probe system the β relaxation behavior of a main chain segmented liquid crystalline polyester. Real (E') and imaginary parts (E'') of the modulus were measured as a function of temperature in isochronal scans performed at different frequencies. The Cole arcs obtained plotting $E''(T)$ vs $E'(T)$ revealed a non-Debye behavior of the β process, which is described by a Cole−Cole distribution of relaxation times. A procedure was outlined to determine accurate and reproducible values of the activation parameters by means of the $E'(T)$ curves. The reliability of this procedure and of the data thereof was substantiated by the derivation of the activation law and its parameters by means of the reduced variables approach.

Introduction

Polymeric materials exhibit a great variety of secondary relaxation processes, at temperatures below the glass transition, involving local motions of very short chain segments or group rotations.[1−3] The local modes involved in secondary relaxations are always found to be thermally activated, or, equivalently, the temperature dependence of their mean relaxation time τ is described by the Arrhenius equation (eq 1)

$$\tau(T) = \tau_0 \exp(\Delta E/RT) \tag{1}$$

where τ_0 is a prefactor representing the reciprocal of an attempt frequency and ΔE is the activation energy of the process.[2,3]

In contrast, the temperature dependence of the mean relaxation time for cooperative relaxation modes, as involved in the glass transition process, is described by the Williams−Landel−Ferry (WLF) equation (eq 2)

$$\tau(T) = A \exp[B/(T - T_\infty)] \tag{2}$$

where A is a prefactor, B is the pseudoactivation energy, and T_∞ is the temperature at which the extrapolated relaxation time diverges.[3]

The single time relaxation model is not able to properly describe the specific features of the viscoelastic response of the polymers as a function of frequency or temperature, because they generally exhibit non-Debye behavior.[2,3] Consequently, several empirical models, as for example the Cole−Cole, Davidson−Cole, Fuoss−Kirkwood, and Havriliak−Negami models, were introduced.[4−8] Each model implicitly assumes a relaxation time distribution $f(\tau)$ from which a mathematical expression for the frequency dependence of all viscoelastic quantities can be derived. For example, the logarithmic distribution of relaxation times $\phi(\ln \tau)$ in the Cole−Cole formalism is given[2] in eq 3

$$\varphi(\ln \tau) = \frac{\sin(\beta\pi)}{2\pi\left[\cosh\left(\beta \ln \frac{\tau}{\tau_0}\right) + \cos(\beta\pi)\right]} \tag{3}$$

and the viscoelastic functions for the storage modulus (E') and loss modulus (E'') are given in eqs 4 and 5

$$E'(\omega,\tau) = E_U + \frac{(E_R - E_U)[1 + (\omega\tau)^\beta \cos(\beta\pi/2)]}{1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}} \tag{4}$$

$$E''(\omega,\tau) = (E_U - E_R)\frac{(\omega\tau)^\beta \sin(\beta\pi/2)}{1 + 2(\omega\tau)^\beta \cos(\beta\pi/2) + (\omega\tau)^{2\beta}} \tag{5}$$

where E_U and E_R represent the limiting values of the storage modulus at infinite and zero frequency, respectively.

Depending on the model, the $E'(\omega,\tau)$ or $E''(\omega,\tau)$ equations include one or more shape parameters to account for the features of the experimental viscoelastic curves. For instance, in the Cole−Cole model, stretching of E' and broadening of E'' arise from a decrease of β to values lower than 1 (the β value of the single time relaxation model is 1).

All the mathematical expressions describing the viscoelastic functions include the mean relaxation time τ as a parameter. From the fit of $E''(\omega,\tau)$ or $E'(\omega,\tau)$ as a function of frequency, measured at different temperatures, it is possible to obtain the temperature dependence of τ, or, in other words, the activation law $\tau(T)$ and related parameters. This procedure is usually followed to determine the activation energy ΔE of a relaxation process described by eq 1 or the pseudoactivation energy B and the temperature T_∞ of a relaxation process described by eq 2. In contrast, the representations of E' and E'' as a function of T at constant frequency are normally taken into account just to visualize the viscoelastic relaxation processes. However, the representations of E' and E'' as a function of T at constant frequency contain in principle more information, concerning the specific features of the relaxation process, than the representations of E' and E'' measured at constant temperature, although it is definitely more difficult to extract this information from the experimental data.

In this paper, we discuss some features of E' and E'', as a function of temperature, taking as a probe system the β relaxation of a main chain segmented liquid crystalline polyester **I**, with the following structure:

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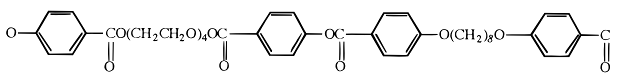

I

The activation parameters of the β relaxation are extracted from the representations of E' and E'' as a function of T at constant frequency, performing the proper curve fit procedure. The method described in the following is a general one and can be applied to the subglass relaxations of polymeric materials.

Experimental Section

Polyester **I** was prepared according to ref 9 and is characterized by number average molar mass $M_n = 12\,000$ gmol^{-1} and first polydispersity index $M_w/M_n = 2.0$. The samples for the dynamic-mechanical analysis were prepared introducing the powder polymer sample into a rectangular mold. The entire assembly was then placed between press plates with a nominal pressure of 4.9×10^7 Pa and allowed to stand at room temperature for 20 min. The temperature was then raised to 160 °C (above the isotropization temperature of polymer **I**) and the pressure released to 4.9×10^6 Pa. After 15 min, the sample was quenched into cold water and recovered in the LC state as rectangular $20 \times 5 \times 2$ mm sheets. The modulus was measured with a dynamic mechanical analyzer Perkin-Elmer DMA-7, employing the three-point bending flexural geometry. A static-to-dynamic stress ratio of 120% and a scanning rate of 2 K/min were chosen. The strain was sufficiently small to be within the linear viscoelastic range. Isochronal scans were performed using frequencies ranging from 0.8 to 40 Hz and collecting around 500 points in each scan. The data analysis was performed employing the Igor Pro software licensed by Wavemetrics Inc.

Results and Discussion

Polyester **I** displays a nematic mesophase[9] with the nematic−isotropic transition temperature at 150 °C. Depending on the thermal history, it can be obtained as a nematic glass or as a semicrystalline sample. Rapid cooling from the isotropic state to room temperature affords the nematic glass whereas prolonged annealing at 50 °C allows the sample to partly crystallize. Figure 1 displays the real $E'(T)$ and imaginary parts $E''(T)$ of the modulus of polyester **I**, measured by dynamic-mechanical analysis at $2\pi\omega = 3$ Hz, for the β relaxation in the 170−260 K temperature range. The storage modulus E' at 170 K is about 2.6×10^9 Pa and decreases steadily with increasing temperature until a value of about 1.2×10^9 Pa at 260 K. As the mathematical expressions for $E'(T)$ and $E''(T)$ are not available, these types of curves are generally conceived as just fingerprints of the relaxation phenomena. In fact, only the mathematical expressions for the τ dependence of E' and E'' are known, once the specific rheological model is assumed (see for example eqs 4 and 5 for the Cole−Cole model), whereas the temperature dependence of E' and E'' is provided only after the activation law and related parameters are established.

Looking at eqs 4 and 5, it should be observed that the actual parameter which controls the viscoelastic functions is the product $\Theta = \omega\tau$. Accordingly, $E'(\omega,\tau)$ and $E''(\omega,\tau)$ can be written as $E'(\Theta)$ and $E''(\Theta)$. It does not matter if a Θ variation is due to a frequency or temperature (that is τ) change. In fact, in an isothermal frequency scan, τ is kept constant and Θ changes because ω changes whereas in an isochronal temperature scan, ω is kept constant and Θ changes because τ changes. However, as in the former case Θ is proportional to ω, Θ is swept over the same number of decades as ω, and only a small part of $E'(\omega)$ and $E''(\omega)$ curves can be visualized because of the restricted frequency range accessible to the mechanical measurements. This situation is reversed in the latter case, when isochronal temperature scans are performed, because the T change produces a very large τ variation, according to eqs 1 or 2. For example, in a thermally activated process with an activation energy of 19 kcal/mol, if T varies from 160 to 260 K, as in Figure 1, τ is swept over 8 decades.

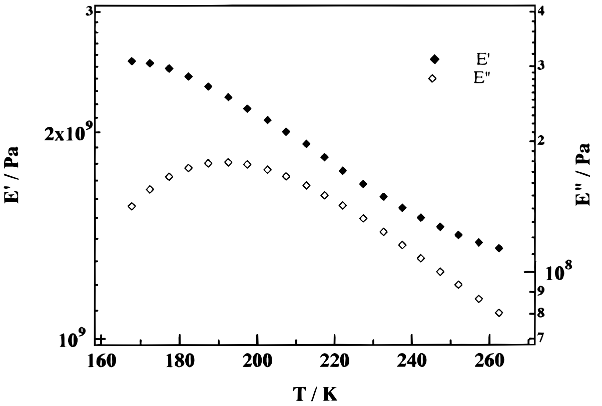

Figure 1. Dynamic storage modulus E' (◆) and loss modulus E'' (◇) as a function of temperature at 3 Hz for the β relaxation of polymer **I**.

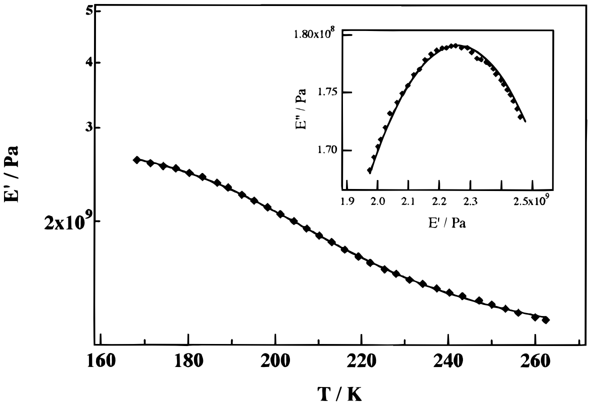

Figure 2. Dynamic storage modulus E' as a function of temperature at 3 Hz and Cole−Cole best fit curve (eq 4). The inset shows the Cole arc obtained plotting $E''(T)$ versus $E'(T)$ at 3 Hz and the best fit Cole−Cole curve (eqs 4 and 5).

The above considerations imply that the same Cole−Cole plot (E'' versus E') is obtained when E' and E'' are measured in an isothermal frequency scan or in an isochronal temperature scan, provided that no structural rearrangement or morphological change of the polymeric material occur.

The inset in Figure 2 reports the experimental Cole−Cole plot obtained from the $E''(T)$ vs $E'(T)$ data of polymer **I** measured at 3 Hz. Only a few representative experimental data points are displayed. The symmetry of the Cole arc suggests that the relaxation can be described within the Cole−Cole formalism[4] which implies the determination of the β parameter, according to eqs 4 and 5. The appropriate fitting of the raw data in the inset of Figure 2 is complicated by two factors. First of all, the temperature dependence for E' and E'' are not known because the temperature dependence of the mean relaxation time is not known *a priori*. In addition, even if this dependence would be available, it is not possible to provide the explicit function g for $E'' = g(E')$. The first problem can be solved substituting for τ in eqs 4 and 5 either one of the expressions given in eqs 1 and 2. As a first attempt, we introduced into eqs 4 and 5 the temperature dependence of τ given by the Arrhenius equation, thus introducing two new

Table 1. Best Fit Activation Parameters Obtained from the Fit of $E'(T)$ Measured at Different Frequencies for Polymer I

	Arrhenius law		WLF law	
frequency/Hz	ΔE/(kcal/mol)	τ_0/s	B/K	T_∞/K
1	16.2 ± 0.2	6×10^{-19}	5640	35
3	16.5 ± 0.2	2×10^{-19}	5317	42
10	16.2 ± 0.2	7×10^{-19}	5753	34

parameters (ΔE and τ_0). The second problem can not be overcome directly, because E'' is only implicitly known as a function of E' and the explicit form $E'' = g(E')$ is not computable. However, we performed a numerical calculation with a procedure able to fit simultaneously a combined E' and E'' data set with the same parameters choosing a fit function like eq 4 for E' and eq 5 for E''. The best fit curve is also reported in the inset of Figure 2, and the best fit value for β, which is the only parameter determining the width of the Cole arc, is $\beta = 0.23$.

We would like to stress that the shape of the Cole–Cole arc is not influenced by the temperature dependence of the relaxation times of the materials. Accordingly, the result of the fit in the inset of Figure 2 immediately provides a criterion to decide if the model assumed for the distribution of relaxation times is correct. In the following analysis, the choice of the proper model is crucial and only a careful evaluation of the shape parameters, calculated fitting the experimental data reported in the Cole–Cole plot, leads to correct and reproducible results.

When the activation law is the Arrhenius one, a first estimate of the activation energy ΔE can be done calculating the area under the $E''(T)$ curve using T^{-1} as the integration variable.[2] The activation energy is given by eq 6

$$\Delta E = (E_{\mathrm{U}} - E_{\mathrm{R}})\frac{R\pi}{2}\frac{1}{\int_0^\infty E''(T)\,\mathrm{d}(1/T)} \tag{6}$$

Substituting the β value obtained from the Cole–Cole plot ($\beta = 0.23$) into eq 5, the relaxed and unrelaxed moduli values are obtained, from which calculation of ΔE from eq 6 can be performed. The activation energy for the β relaxation of polymer **I** so calculated is $\Delta E = 17.5$ kcal/mol. This value was employed as the initialization value for the determination of ΔE from several $E'(T)$ curves recorded at different frequencies. The $E'(T)$ curves were preferred over the $E''(T)$ because of their better signal to noise ratio. It is important to stress that the determination of the correct β value from the fit of the Cole arc and a reasonable initialization value of ΔE through eq 6 are essential to fit $E'(T)$. In fact, the preliminary determination of β eliminates a fit parameter and a good initialization value for ΔE eliminates the risk of a convergence toward a local minimum for the χ^2 value. The fit convergence was in all cases good (see Figure 2) and the best fit values for the activation energy and τ_0 calculated from three $E'(T)$ curves recorded at different frequencies are reported in Table 1. The best fit values obtained for the unrelaxed and relaxed moduli are $E_{\mathrm{U}} = 2.7 \times 10^9$ Pa and $E_{\mathrm{R}} = 1.1 \times 10^9$ Pa in all cases. The three values obtained for ΔE are practically equal to each other and within the range of those usually found in literature.[2]

We already noticed that the choice *a priori* of an Arrhenius equation is a tentative hypothesis. To verify whether this choice is the right one, we performed the same $E'(T)$ fit introducing into eqs 4 and 5 the temperature dependence of τ given by the WLF equation. The best fit values of the pseudoactivation energy B and T_∞ are reported in Table 1. The values of B are so large compared to the usually found ones (around one thousand) that they can be considered physically meaningless. In addition, the T_∞ values are extremely low compared to those usually found (around 50 °C below the transition temperature).[1-3] Figure 3 reports the relaxation map, that is a plot where $\log(\tau^{-1})$ is reported vs $10^3/T$, relevant to the best fit Arrhenius and WLF curves calculated from the $E'(T)$ data recorded at 3 Hz. In this plot, eq 1 is a straight line and eq 2 is a concave curve. The two curves reported in Figure 3 are extremely close to each other in the whole temperature region and the tendency of the WLF curve to merge together with the Arrhenius one is evident. As the WLF equation reduces to the Arrhenius one when $T_\infty = 0$, we can conclude that the fit convergence to extremely low T_∞ values derives from the necessity to recover an Arrhenius-like trend using the WLF equation. In conclusion, the convergence to physically meaningless values for the WLF activation parameters demonstrates that the β relaxation process is thermally activated.

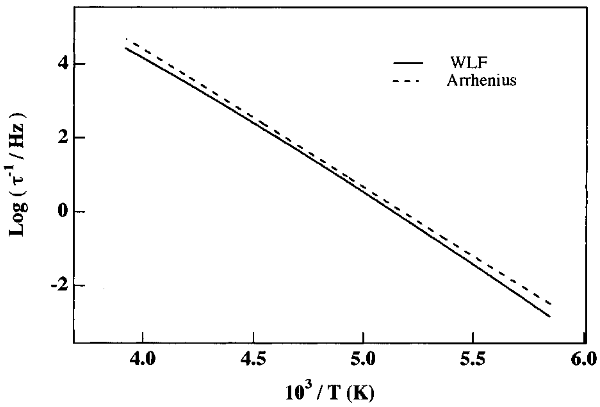

Figure 3. Arrhenius and WLF curves corresponding to the best fit activation parameters obtained from the fit of E' as a function of temperature at 3 Hz for the β relaxation of polymer **I**.

In the above analysis, to determine the values reported in Table 1, only two assumptions were made, concerning the choice of a relaxation model and the existence of a particular kind of activation law. The first assumption is largely substantiated employing the Cole–Cole arc fitting and the second is unambiguously dictated by the last considerations.

To conventionally assess the kind of activation law of the β relaxation of polymer **I** and to make an independent estimation of the activation parameters, we applied the conventional reduced variables procedure[1-3] based on the scaling behavior of the β relaxation. Data sets relevant to the storage modulus E' as a function of frequency were produced by properly analyzing several temperature scans performed at different frequency values. Figure 4 reports the experimental values of E' as a function of frequency at different temperatures from 193 to 253 K in the β relaxation region. Only some representative data sets are displayed in Figure 4. All the isothermal data sets were fit with the Cole–Cole equation (eq 4). In the fit procedure, β was kept constant and equal to 0.23, and the unrelaxed and relaxed moduli fixed to $E_{\mathrm{U}} = 2.7 \times 10^9$ Pa and $E_{\mathrm{R}} = 1.1 \times 10^9$ Pa. The fit of an isothermal data set immediately provides the τ value corresponding to the relevant temperature. In Figure 4, the best fit curves are also reported for each experimental data set.

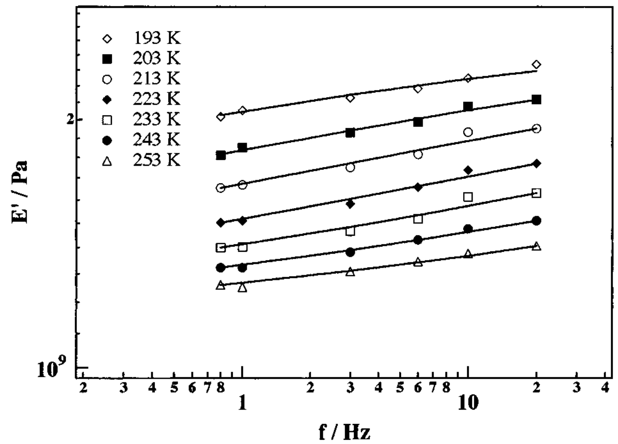

Figure 4. Dynamic storage modulus E' as a function of frequency at different temperatures for polymer **I** and Cole–Cole best fit curves (eq 4).

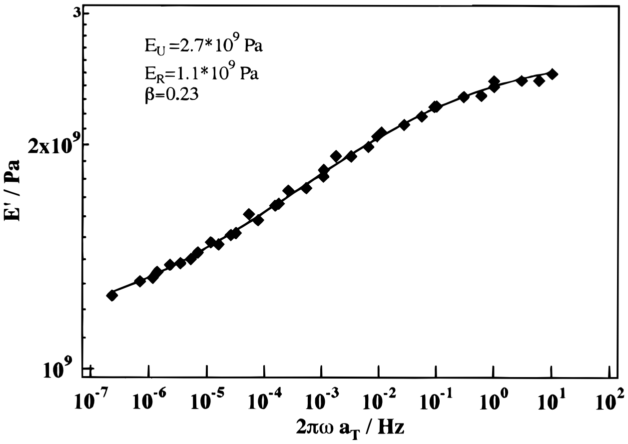

Figure 5. Master curve for the dynamic storage modulus E' reduced at 173 K and Cole–Cole best fit curve (eq 4).

Choosing the temperature T_0 of a particular isothermal data set, with relaxation time τ_0, as the reference temperature, it is possible to generate a master curve for E' by shifting along the frequency axis the curves displayed in Figure 4. The shift factor a_T, giving the correct superposition of a curve measured at temperature T with the reference curve, is calculated as $a_T = \tau(T)/\tau_0$. Figure 5 reports the master curve for E' reduced at $T_0 = 173$ K as a function of the reduced frequency $2\pi\omega a_T$ together with the best fit curve, whereas the relaxation map is illustrated in Figure 6. In this relaxation map, log(τ) exhibits a linear dependence as a function of the inverse temperature, as typically observed for a thermally activated process described by the Arrhenius equation. The continuous line in Figure 6 corresponds to the best fit Arrhenius curve from the $\tau(T)$ points calculated using the reduced variables method. The best fit value obtained for the activation energy is $\Delta E = 16.3$ kcal/mol. In the same figure, the dashed line is the best fit Arrhenius curve estimated from the analysis of the temperature scan recorded at 3 Hz (see Table 1). The coincidence between the two curves indicates that not only the activation energy estimated employing the two different approaches is equal but also the two prefactors. This latter point implies that an excellent estimation of the relaxation time values is also provided by the analysis of the temperature scans. However, it should be stressed that the method described should be considered as an alternative approach that provides a useful cross-check of the activation parameter values determined with the method of the reduced variables.

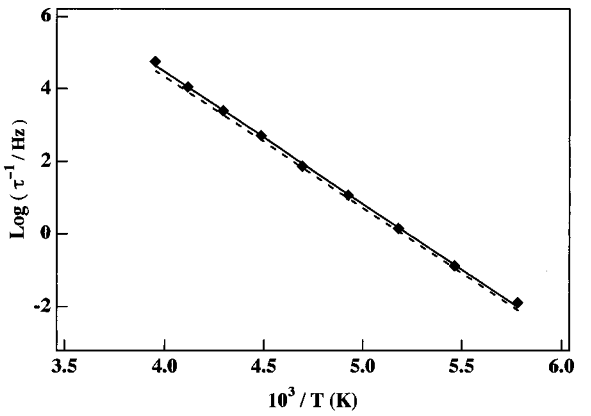

Figure 6. Relaxation time τ as a function of temperature determined with the reduced variable method for polymer **I** together with the best fit Arrhenius curve from the data points (continuous line) and the best fit Arrhenius curve estimated from $E'(T)$ at 3 Hz (dashed curve).

Conclusions

The phenomenology of the β relaxation process was investigated for a nematic glass of a main-chain (MC) liquid crystalline (LC) polyester, as a model system. Curve fitting of Cole arcs obtained from temperature scans allowed the determination of the proper model describing the non-Debye behavior of the β relaxation process. The proper fit of the $E'(T)$ curves demonstrates that the β relaxation process is governed by an Arrhenius activation law. The analysis of the modulus in isochronal temperature scans leads to reproducible values of the activation law parameters. In addition, these activation law parameters are demonstrated to be accurate from the comparison with the corresponding values obtained using the conventional procedure, where several isothermal curves are reduced. The method discussed in this paper is particularly useful because it allows assessment of the kind of activation law governing the relaxation process and precise determination of the activation law parameters, measuring only one isochronal curve. We are presently extending this approach to the glass transition process. A cross check with the method of the reduced variables is, when possible, recommended to have an independent evaluation of the activation law parameters.

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