The analysis of TSDC peaks with a KWW relaxation function or a distribution of relaxation times in polymers

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Summary

The analysis of Thermally Stimulated Depolarization Currents (TSDC) spectra in polymers requires the introduction of a distribution of relaxation times. Also, a decay of the induced polarization following a stretched exponential law can be used. Two different ways for introducing this effect in the TSDC equations are compared here together with the decomposition in elementary curves by a Simulated Annealing Monte Carlo procedure to find the distribution. It is found that the stretched exponential applied to computer generated curves corresponds in both cases to a nearly Debye process. Also the analysis of the α-peak of poly(ε-caprolactone) with the three approaches are compared.

Introduction

The study of the dielectric relaxation modes in polymers requires the detailed analysis of the relaxation times involved in each process in order to extract information towards a better understanding of the molecular structure. Several approaches have been taken to interpret current results on polymeric materials. The existence of a distribution of relaxation times resulting from a superposition of parallel Debye-like processes, i.e. characterized by a single relaxation time, has been traditionally used in the frequency domain (1-2). Parallel elementary relaxation mechanisms where the entities relax independently can be discrete or part of a distribution function. The empirical Havriliak-Negami distribution function (3) has been the most successful as it accounts both for broadening and asymmetry of the response curves as a function of frequency at constant temperature. Alternatively, approaches to account for the non-Debye character of the relaxation function in time domain based on a Kohlrausch-Williams-Watts (KWW) "stretched exponential" have been justified by different theoretical models (4). The non exponential relaxation behavior being explained in terms of either a superposition of Debye processes (5) or a series interpretation involving many sequential and correlated activation steps towards equilibrium in a hierarchically constrained dynamics for glass relaxations (6).

Thermally stimulated techniques are both powerful and sensitive to study the relaxation modes of dielectrically active species in amorphous and crystalline materials. The advantages of the Thermally Stimulated Depolarization Current technique reside in its high sensitivity and its capability in separating the segmental α mode corresponding to

the glass-transition of the material, from the lower temperature β-modes which are caused by local motions of the dipolar entities. In a TSDC experiment the return to a randomly oriented state of the electrical dipoles, previously aligned during the polarization step, is followed as the material is heated at a linear rate. The resulting current is recorded as a function of temperature. This non-isothermal spectrum has been analyzed in terms of a distribution of uncoupled Debye processes. An experimental decomposition of the complex curve can be attempted by the thermal sampling technique (7), which consists in applying narrow polarization windows and analyzing the resulting spectra as pure Debye processes. Another approach is to decompose the complex curve in elementary Debye curves by use of the Direct Signal Analysis (DSA) (8) or the improved Simulated Annealing Direct Signal Analysis (SADSA) (9) computer programs. The output of the program is for each energy bin, E_{0Li}, the contribution to the polarization, P_{0Li}, and a frequency factor, τ_{0Li}, for either Arrhenius, $\tau(T) = \tau_0 \exp(E/kT)$, or Vogel-Tammann-Fulcher (VTF), $\tau(T) = \tau_0 \exp(E/k(T - T_0))$, temperature dependencies of the relaxation times. Instead of using this approach, two interesting contributions (10, 11) have recently proposed to apply the non exponential decay of the built-in polarization described by the KWW stretched exponential to the TSDC equations. The resulting expressions for the depolarization current density, $J(T)$, are remarkably different. The aim of this work is to compare both results to those obtained by the SADSA method by applying them to computer generated curves whose activation parameters are known and to discuss the interpretation that follows.

Experimental and data analysis

The test of the analysis methods discussed here is made on the α-relaxation of a semi-crystalline poly(ε-caprolactone) film prepared by successive anionic polymerization in benzene (M_w=124,500, M_n= 83,000). The glass transition temperature, T_g = 207 K and the degree of crystallinity, X_c = 53% are both determined by differential scanning calorimetry at 20 K/min (12).

The TSDC experiment records the depolarization current originated by the random reorientation of the dipolar segments which have been previously oriented by the application of an electric field at a temperature, T_p, where the species under study are mobile. The built-in polarization is frozen at low temperatures; the sample is then heated at a linear rate, b_h, and the current density, $J(T)$, is recorded as a function of increasing temperature. The details of the experiment have been described elsewhere (13).

The computer algorithm is a Monte Carlo procedure where the TSDC curve is expressed as the sum of N elementary monoenergetic excitations each of energy E_{0Li} and contributing P_{0Li} to the total polarization. An energy range divided in N intervals of equal width (bins) centered at E_{0Li} is chosen and the procedure finds the values of P_{0Li} and τ_{0Li} that best adjust the data by minimizing the set of square residuals using the Simulated Annealing optimization method (9).

Models

Marchal (10) introduces the stretched exponential in the expression of the time dependent polarization, $P(t) = P_0 \exp\text{-}(t/\tau_M^*)^\beta$ with a relaxation time $\tau_M^* = [\beta\omega_c^{1-\beta}\tau_M]^{1/\beta}$, where $\tau_M(T)$ is the relaxation time of the primitive species, either Arrhenius or VTF. This expression of τ_M^* was introduced by Ngai *et al.* (4) in their unified theory of dynamical processes in

complex systems. ω_c is the inverse of a characteristic time and typically varies between 10^9 to 10^{12} s^{-1}; τ_M^* is the macroscopic effective relaxation time and it is different from the τ'_M value, $\tau'_M = \tau_M [(T-T_i)(\omega_c/b_h]^{1-\beta}$, which can be measured by TSDC as $J(t) = P(t) \tau'_M = -dP/dt$.

By integrating this last equation and changing $t = (T - T_i)/b_h$, where T_i is the initial low temperature, Marchal reaches an expression for the TSD Current density, $J_M(T)$, provided that β is independent of T, which for Arrhenius relaxation times is:

$$J_M(T) = \frac{P_0}{\tau_{0M}} \tau_c^{1-\beta} \exp\left(-\frac{E_M}{kT}\right) \left(\frac{T-T_i}{b_h}\right)^{\beta-1} \exp\left\{-\frac{\tau_c^{1-\beta}}{\tau_{0M} b_h^\beta} \int_{T_i}^{T} (T'-T_i)^{\beta-1} \exp\left(-\frac{E_M}{kT'}\right) dT'\right\} \quad (1)$$

Alegría et al. (11) take a different approach and reach a quite different expression for the TSD Current density. They also start with a stretched exponential for the decay of the stored charge, $Q(t)$, but they use for describing the decay of $Q(t)$ the relaxation time $\tau_A(T)$, which is the Arrhenius or VTF expression given above, instead of $\tau_M^*(T)$ which is a much more complicated function. Then, the time derivative of the polarization is calculated, t is expressed as a function of $Q(t)$, and the expression for the TSD Current, $I_A(T)$, for Arrhenius relaxation times, is now:

$$I_A(T) = \beta \frac{Q_0}{\tau_{0A}} \exp\left(-\frac{E_A}{kT}\right) \left[\frac{1}{b_h \tau_{0A}} \int_{T_i}^{T} \exp\left(-\frac{E_A}{kT'}\right) dT'\right]^{\beta-1} \exp\left\{-\left[\frac{1}{b_h \tau_{0A}} \int_{T_i}^{T} \exp\left(-\frac{E_A}{kT'}\right) dT'\right]^\beta\right\} \quad (2)$$

Results and discussion
With expressions (1) and (2) a computer generation of KWW TSDC curves is performed for various sets of parameters. The current density could be simulated by either calculating the current with these general expressions which involve integrating over large temperature intervals or in a much faster way by numerically solving the differential equation $J(T) = -b_h\, dP/dT$ with the appropriate expressions of $P(T)$ for each model.

The curves generated with the differential equation give the same results as those obtained by numerically evaluating equations (1) and (2). The results shown in Figure 1 (a) and (b) use Marchal's expression, for Arrhenius and for VTF relaxation times temperature dependencies, respectively. The corresponding curves generated with expression (2) are shown in Figure 2 (a) (Arrhenius) and (b) (VTF). The heating rate is always 0.1 K/s, and the area under the curve is kept constant.

The differences between the curves generated with expressions (1) and (2) are to be noted. Marchal's model drastically shifts the curves to higher temperatures as the stretching parameter β increases, the variation of the temperature of the peak maxima, T_m, being larger for the Arrhenius than for VTF relaxation times. As a result of this shift, the TSDC curve is broadened as it occurs with a single Debye peak. This shift is in the same direction as the one caused by physical aging where β decreases and T_g shifts to slightly higher temperatures (14). On the contrary, the curves generated with equation (2) (Alegría et al.'s (11) derivation) are centered about the same T_m as β decreases except for the two last β values where the broadening and the asymmetry are so important that they slightly shift to lower temperatures.

The SADSA procedure is then applied to the TSDC curves generated with equation (1). The result of the fitting for Arrhenius relaxation times and $\beta = 0.5$, is shown
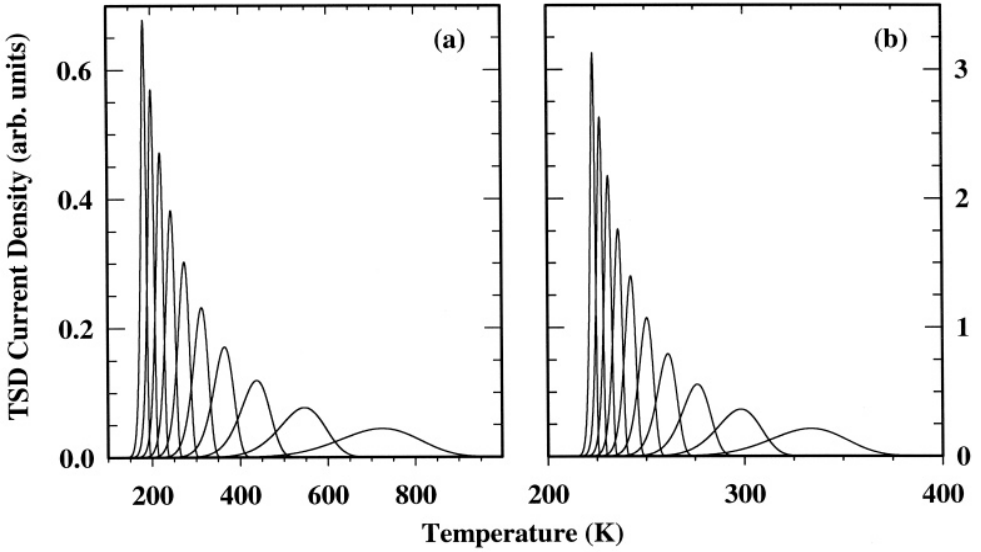
Figure 1: Simulated TSDC curves, Marchal's expression: (a) Arrhenius relaxation times, $E_M = 0.5$ eV, $\tau_{0M} = 10^{-12}$ s, $\omega_c = 10^9$ s^{-1}. (b) VTF relaxation times, $E_M = 0.1$ eV, $\tau_{0M} = 10^{-12}$ s, $\omega_c = 10^9$ s^{-1}, $T_0 = 185$ K. In both figures, $T_i = 70$ K and β varies from 1 to 0.1 by 0.1 steps from left to right.
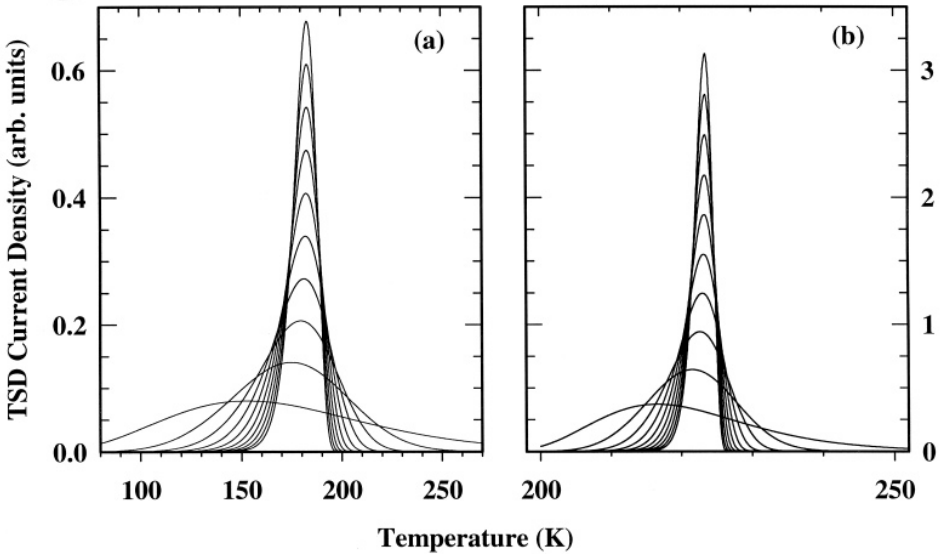

Figure 2: Simulated TSDC curves, Alegría *et al.* expression: (a) Arrhenius relaxation times, $E_A = 0.5$ eV, $\tau_{0A} = 10^{-12}$ s; (b) VTF relaxation times, $E_A = 0.1$ eV, $\tau_{0A} = 10^{-12}$ s, $T_0 = 185$ K. β varies in both Figures from 1 to 0.1 by 0.1 steps from top to bottom.

in Figure 3 (a) where the agreement between the generated points and the fitted curve is shown to be excellent as quantified by the sum of square residuals (SSR), $\chi^2 = 2.7 \times 10^{-10}$. In Figure 3(b) the energy histogram is plotted and represents the contribution of each

energy bin to the total polarization. This histogram shows the existence of a predominant process at 0.483 eV and $\tau_{0L} = 3.0 \times 10^6$ s. The contribution of the other energy bins, that were included in the energy window, are about 10^8 times less intense than the main one, i.e. the relaxation is a Debye peak as it can be fitted with a single pair of E_{0L} and τ_{0L}. The resulting relaxation time is 198 s to be compared with $\tau'_M (T_m) = 197$ s, which is calculated with the values used in the curve simulation. Similar results are found in the case of VTF relaxation times for $\beta = 0.5$ and with the parameters indicated in the caption of Figure 1. The predominant bin is located at 0.097 eV and the corresponding preexponential factor is $\tau_{0L} = 1.3 \times 10^6$ s. The lateral bins are 10^4 times less intense. The VTF temperature is found to be 185 K. The agreement between the generated points and the fitted ones is also excellent here ($\chi^2 = 6.7 \times 10^{-10}$). The computed relaxation time is now 43 s as compared to $\tau'_M (T_m) = 76$ s.

The same kind of results hold for a wide range of β values which covers the usual variation of β reported in the literature for polymeric materials. The results reported above imply that the TSDC curves generated by equation (1), either with Arrhenius or VTF relaxation times, are Debye-like peaks as when one tries to extract a distribution of relaxation times only one energy bin is significantly contributing to the total polarization. The relaxation times found by the SADSA procedure are in good agreement with Marchal's $\tau'_M (T_m)$ which is an indication about the consistency of the model. The similarity of the KWW generated curves to Debye-peaks is somewhat unexpected as in the isothermal case a β value as low as 0.5 implies a very noticeable widening (5).
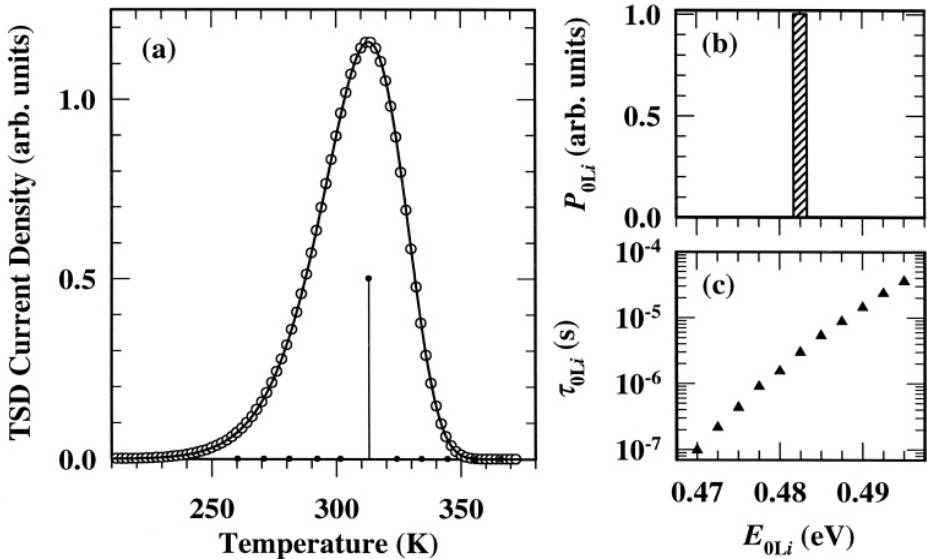

Figure 3: Results of SADSA for a computer generated curve with expression (1) and Arrhenius relaxation times with: $E_{0M} = 0.5$ eV, $\tau_{0M} = 10^{-12}$ s, $\omega_c = 10^9$ s^{-1}, $\beta = 0.5$: (a) generated points and results of the fitting; (b) energy histogram; (c) variation of τ_{0Li} with the energy bin value.
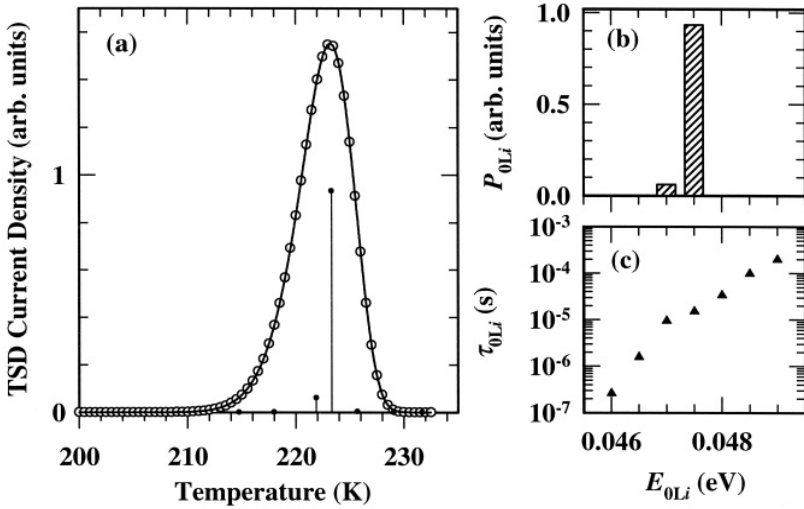
Figure 4: Results of SADSA for a computer generated curve with Alegría *et al.*'s model and VTF relaxation times, with: $E_{0A} = 0.1$ eV, $\tau_{0A} = 10^{-12}$ s, $\beta = 0.5$, $T_0 = 185$ K : (a) generated points and results of the fitting; (b) energy histogram; (c) variation of τ_{0Li} with the energy bin value.

The same analysis is then performed with the curves generated with expression (2) and the results are shown in Figure 4 for VTF relaxation times, and $\beta = 0.5$. Here again, the histogram consists of a predominant bin whose contribution to the total polarization is 93%, and a small lateral bin in the energy window chosen. The other contributions are negligible. The VTF energy is 0.0475 eV and the preexponential factor $\tau_{0L} = 1.5 \times 10^5$ s. The best fit is for $T_0 = 185$ K. The agreement between the generated points and the fitted ones is also excellent here ($\chi^2 = 4.1 \times 10^{-10}$). There is a significant difference of these values of E_{0L} and τ_{0L} when compared to the values used for the curve simulation as they are, respectively, half and overestimated by 7 orders of magnitude. Moreover, if the M-L algorithm is used to fit these curves to a Debye peak the agreement found is also excellent for the curves generated with equations (1) or (2). There is a difference between the SADSA results: Alegría's expression always lead to strongly decreasing values of the energy with β while with Marchal's expression the energy decreases very slightly as β decreases. Moreover, the computed $\tau_A (T_m)$ with the simulation parameters is within 60% of that calculated with the values obtained from the SADSA procedure for $\beta = 0.5$. As Alegría *et al.* use the variation of the TSDC spectra when b_h varies, our simulations and analysis were carried for $0.01 \leq b_h \leq 1$ K/s. The simulated curves show the same behavior as those reported on Figures 2 and 4. If $\log(b_h/T_m^2)$ is plotted against $1/T_m$ the values found for E_A are within 2% of the values used in the simulation with Arrhenius dependences for $\beta \geq 0.3$. This result is a thorough check on the consistency of the model.

The important result is that the curves generated with both expressions (1) and (2) can be fitted by a distribution which is almost monoenergetic, i.e. with a single relaxation time; this result was expected only in the case where the β parameter used to simulate the curves would be equal or close to 1 and not in the whole β range.

In the case of a TSDC experimental curve such as the dielectric manifestation of the primary glass transition in poly(ε-caprolactone) the α-peak is represented in Figure 5 (a). Several fittings are performed to this experimental data always using VTF relaxation times. The SADSA procedure gave the results shown by the continuous curve with a $\chi_L^2 = 7.5 \times 10^{-9}$ which is very good for an experimental curve as it is only one order of magnitude larger than that found for computer generated curves. The energy histogram (figure 5(b)) shows a narrow distribution of relaxation times with a half width less than 0.04 eV, a central value of 0.155 eV for the energy, a VTF temperature of 152.5 K and $\langle \tau_{0L} \rangle = 4.0 \times 10^{-12}$ s. The distribution is slightly asymmetric as seen in Figure 5 (b). The relaxation time corresponding to the central bin is $\tau_L(T_m) = 36$ s. If the peak is adjusted now by the conventional Marquardt-Levenberg (M-L) non-linear least squares fitting to equation (1), fittings of acceptable quality are obtained, $\chi_M^2 = 1.1 \times 10^{-6}$. This value is 150 times larger than that obtained with the SADSA procedure; the best fit parameters are $E_{0M} = 0.0275$ eV, $\tau_{0M} = 6.7 \times 10^{-11}$ s, $\omega_{cM} = 7.1 \times 10^{12}$ s^{-1}, $\beta_M = 0.445$ and $T_{0M} = 172.5$ K. With these values $\tau'_M(T_m) = 76$ s, which is about twice the value obtained with the SADSA parameters. If equation (2) is used with the M-L algorithm the best fit is surprisingly identical in its trace to that obtained with equation (1) but the final parameters: $E_{0A} = 0.125$ eV, $\tau_{0A} = 4.4 \times 10^{-14}$ s, $T_{0A} = 170.5$ K and $\beta_A = 0.265$, are quite different. These parameters yield a fitting of the same quality as the fit to Marchal's expression as the SSR is again $\chi_A^2 = 1.1 \times 10^{-6}$. Moreover, the calculated $\tau_A(T_m) = 34$ s, is in this case in very good agreement with the SADSA value.

In order to further proof the results yielded by the different analysis an estimate of the fractional free volume, f, at $T_m \approx T_g$ in the poly(ε-caprolactone) sample, is carried
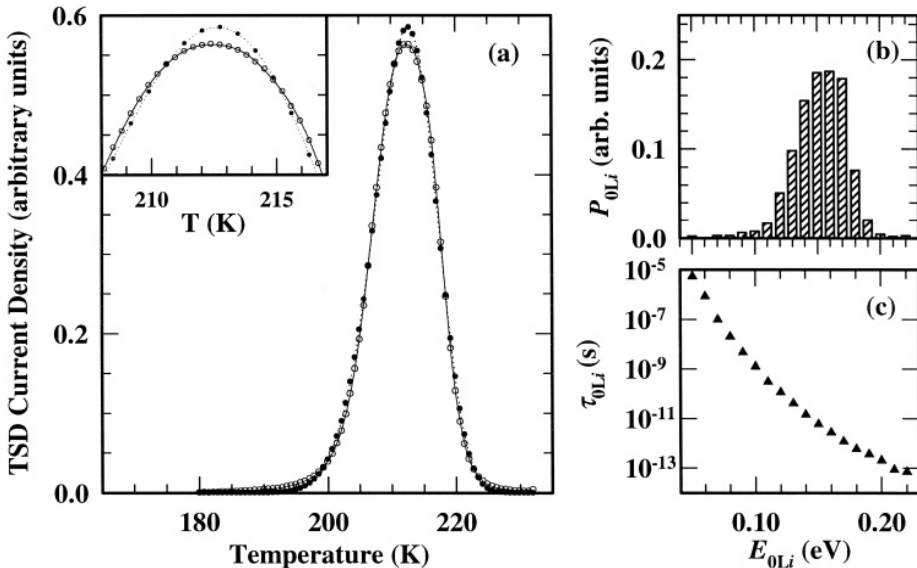

Figure 5: TSDC α-curve of poly(ε-caprolactone): (a) O experimental points; —— results of the SADSA fitting; .... M-L fitting to equation (1); ● M-L fitting to equation (2); (b) energy histogram; (c) variation of τ_{0Li} with the energy bin value. The inset shows the detail of the different fittings around the maximum.

out by calculating it with the VTF parameters, using $f = \alpha(T_m - T_0)$ with the thermal expansion coefficient $\alpha = k/E$. Marchal's parameters would yield an overestimated value of 12%, while Alegría *et al*.'s and SADSA would give 2.9% and 3.3%, respectively, which seems more reasonable and in agreement with reported values (15).

Conclusions

The analysis of computer generated curves with two different current densities derivations both assuming KWW decay functions for the stored charge(10, 11), is performed by using the SADSA procedure in order to find the distribution of relaxation times. Different results are obtained as *ß* increases; Alegría *et al*.'s expression leading to a broadening of the curve without significant temperature shifts, and Marchal's expression steeply shifting the curve to higher temperatures and broadening it as *ß* grows. The SADSA method shows that the two sets of curves can be adjusted by a single Debye peak whose relaxation parameters are different from those used in the curve generation. However, the overall relaxation times measured by TSDC are within the same order of magnitude. The fittings to both expressions of the α-peak in poly(ε-caprolactone) are in worst agreement than the SADSA procedure, and both of them give the same adjusted trace. However the energy values in the case of equation (1) seem to be much too low and they lead to an estimate of a too large fractional free volume.

Acknowledgments

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