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α-Relaxation in the Glass-Transition Range of Amorphous Polymers. 2. Influence of Physical Aging on the Dielectric Relaxation

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ABSTRACT: The influence of physical aging on the dielectric α-relaxation of three amorphous polymers is investigated by means of time domain dielectric experiments. It is found that the dielectric relaxation behavior in a, “isostructural” state out-of-equilibrium can be well described by the Kohlrausch−Williams−Watts (KWW) function, the dielectric relaxation time increasing strongly with aging time but the KWW shape parameter being weakly affected by physical aging. The dependence of the relaxation time on physical aging is interpreted in terms of the Adam and Gibbs theory. The effects of physical aging on the configurational entropy obtained by applying the Adam and Gibbs equation to the dielectric relaxation times are compared with the effects on enthalpy relaxation data obtained calorimetrically. For the three polymers investigated, both quantities equilibrate in the same time scale. A phenomenological model of physical aging with parameters determined from the equilibrium supercooled melt behavior is developed. Assuming that the structural and dielectric relaxation times are proportional to each other, it is shown that the dynamical parameters obtained from equilibrium dielectric experiments can account for the time dependence of both dielectric and enthalpy relaxation in the nonlinear regime, at least at temperatures not too far below the glass transition temperature.

I. Introduction

Glassy polymers, as well as any other glassy material, are out-of-equilibrium not only with respect to the corresponding crystalline material, if it exists (for many polymeric systems it does not), but also with respect to the metastable equilibrium liquidlike state.[1,2] As a consequence, at temperatures below the glass transition, T_g, glassy polymers relax toward the supercooled melt metastable equilibrium state. In polymer science, this phenomenon is commonly referred to as physical aging,[3−6] although in the inorganic glass literature it is often termed as structural relaxation.[7] Physical aging is of practical importance because the properties of the material change during this process, the effects being more important when the working temperature is not far below T_g. This is the case for the most widely used amorphous polymers, which have relatively low values of T_g. Moreover, physical aging also affects the polymer segmental dynamics. This influence leads to changes in several dynamically controlled phenomena,[3] like the rate of chemical reactions in epoxy curing, rate of crystallization of semicrystalline polymers, and diffusivity among others. Therefore, physical aging is a dynamic process that at the same time affects the dynamics of the system. Thus, it is an intrinsically nonlinear phenomenon since the equilibration rate depends on the structural state of the material, which in fact depends on the prehistory.[8] This feature, together with the nonexponentiality of the glass-forming systems dynamics,[9,10] made the phenomenology of physical aging extremely rich and complex. Recent reviews concerning the physical aging phenomenology can be found elsewhere.[5,6,11,12] Because of the complex phenomenology of physical aging, a clear description of the actual experimental behavior is difficult. The simplest case is met when the thermal history is restricted to single, positive or negative, temperature jumps. However, most of the reported experiments involve a combination of continuous cooling (and/or heating) with annealing at several temperatures.[5,6,13] Under such conditions, one needs to model the whole prehistory, something which usually requires a large number of parameters.

Taking into account all the above mentioned features, the study of the physical aging processes by using a linear probe is desirable in order to characterize the dynamical state of the system during the equilibration process. The difficulty is that, due to the low mobility of glassy polymers, any dynamic experiment that deals with such systems is very time consuming. As a consequence, during the measuring time, structural relaxation affects to some extent the state of the observed system and, therefore, the experimental relaxation behavior is distorted. That is why most of the investigations on glassy systems close to T_g have focused on observing the time evolution of static properties like volume or enthalpy.[5,6,14,15] However, because of its practical importance, there is also quite a lot of experimental information concerning the influence of physical aging on mechanical properties.

In a recent publication[16] (part 1 of this work), we studied the dielectric relaxation behavior of three amorphous polymers in the neighborhood of the glass transition temperature. In that work we showed how, by means of time domain dielectric experiments involving partial polarization of the sample, it is possible to get dynamic information of glassy polymers in a nearly isostructural state. Thus, we had used a technique sensitive enough to extract the dynamical information with measuring times shorter than the characteristic mobility time of the system. Moreover, in those experiments we found that the dielectric relaxation below T_g can still be described by means of the Kohlrausch−Williams−Watts (KWW) equation, which is commonly

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used to describe the equilibrium dynamics. The KWW equation reads as follows:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad (1)$$

where $\Phi(t)$ is the normalized decay relaxation function, τ is a time scale characteristic of the mobility of the system, and $0 < \beta < 1$ is a shape parameter characterizing the nonexponentiality of the system dynamics. Therefore, by means of this dielectric method, and by setting the adequate experimental conditions, one can study how the dynamic parameters τ and β are influenced by physical aging. Although the use of eq 1 to fit dielectric data has been sometimes questioned because its asymptotic behavior differs from that of the Havriliak−Negami function,[17] eq 1 gives a good description of the main part of the dielectric losses in the α-relaxation of amorphous polymers by using a single shape parameter. Therefore, the effect of physical aging in the relaxation shape can be monitored in a more reliable way.

In this paper, we report on the influence of physical aging on the dielectric relaxation below the glass transition of the same three amorphous polymers used in part 1,[16] poly(Bisphenol A, 2-hydroxypropyl ether), poly(vinyl acetate), and poly(vinyl methyl ether). In the present study, time domain dielectric measurements in the time range 1 to 10^6 s were performed. The influence of the physical aging on the dielectric relaxation time is interpreted in the framework of the Adam and Gibbs theory.[18,19] In this framework, the evolution of the configurational entropy during the aging process is obtained and compared with the enthalpy recovery behavior. A simple phenomenological description of the dependence on the physical aging of both the enthalpy and the dielectric relaxation is proposed. This approach allows us to account for the experimental behavior in the nonlinear regime by using parameters determined experimentally from the linear regime, i.e., in the supercooled liquidlike state.

II. Experimental and Data Analysis

Detailed information concerning the samples and the experimental techniques used was already given in the first part of this work.[16] Therefore, in this section, we will summarize only those details that are relevant to the study of physical aging.

The samples investigated, poly(Bisphenol A, 2-hydroxypropyl ether), PH, poly(vinyl acetate), PVAc, and poly(vinyl methyl ether), PVME, are commercial amorphous polymers with glass transition temperatures of 370, 320, and 247 K, respectively (for more details see Table 1 in part 1).

The enthalpy recovery was investigated by using a Perkin-Elmer DSC-4 differential scanning calorimeter. The temperature was varied at 10 K/min during both heating and cooling. The enthalpy recovery during the annealing process was determined by integration of the difference between the two consecutive scans at the same conditions on annealed and nonannealed samples (eq 1 of part 1).

Time domain dielectric experiments were based on the transient current method.[9] The particular procedure followed in the present study is summarized in Figure 1. The sample was first heated to about $T_g + 30$ K, in order to remove the effects of prior thermal history, and subsequently cooled at a constant rate (10 K/min) to the measuring temperature. At this temperature, after a certain waiting time t_w, the transient current experiment was performed with a polarization time t_p ranging from 10^2 to 10^5 s. Thus, the effective annealing time at the beginning of the depolarization process was $t_a = t_w + t_p$. Both the waiting and polarization times determine the structural state of the sample (see Figure 1) as well as the level of polarization achieved.

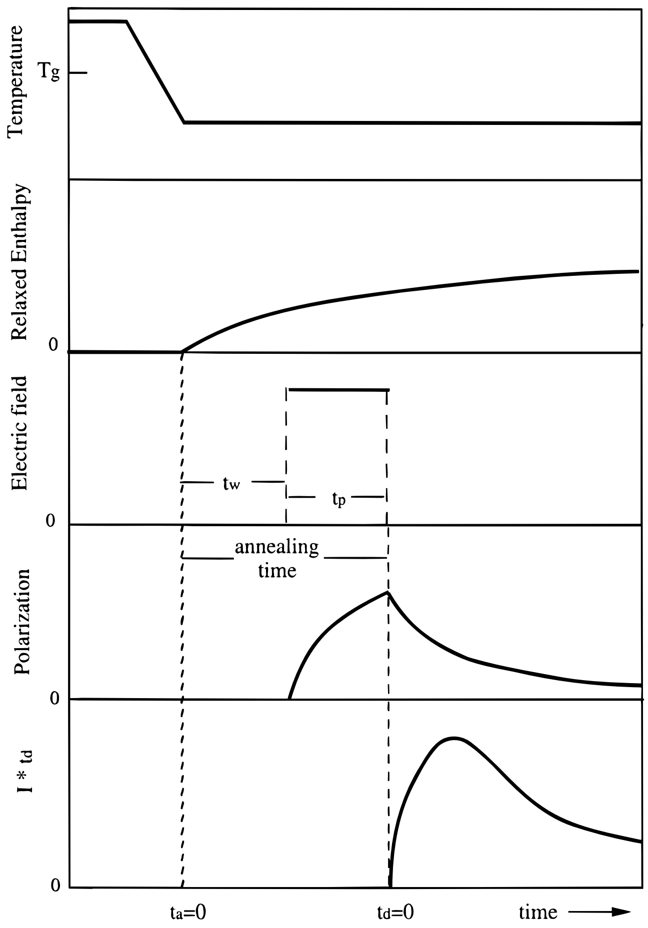

Figure 1. Schematic diagram of the time evolution of the different quantities involved in the dielectric time domain experiments.

In part 1 of this work, it was proved that, by means of the experimental procedure described above, the first part of the depolarization process (the time range until the maximum of the *It* curves) reflects the dynamic behavior of the system in a state of nearly constant enthalpy (an isostructural state); i.e., it is possible to obtain a snapshot of the dynamic state of the sample during the evolution from the glass out-of-equilibrium to the liquidlike metastable equilibrium state (physical aging process). Moreover, it was also shown that this part of the depolarization curve can be well described by means of a KWW relaxation function. This implies that, even out-of-equilibrium, the dynamic state of the polymer can be characterized by the parameters τ and β of the KWW equation provided that the structural state remains unchanged. This type of study in our experimental setup needs a minimum annealing time of 100 s, which is about twice the time required to stabilize the temperature within ±0.1 K. Figure 2 shows, as an example, the experimental curves obtained for PVAc at 305 K for different values of the polarization and annealing times. It should be noted that the differences observed in the experimental curves are produced not only by the different annealing times involved but also due to the different polarizations achieved in each experiment. In the framework of the linear response theory, the isothermal depolarization current corresponding to the experimental conditions used can be expressed as the first derivative of the response corresponding to a block shape excitation:[17]

$$I(t) \propto -\frac{d}{dt}[\Phi(t) - \Phi(t + t_p)] \qquad (2a)$$

where $I(t)$ is the measured depolarization current, t_p is the experimental polarization time, and $\Phi(t)$ is the normalized

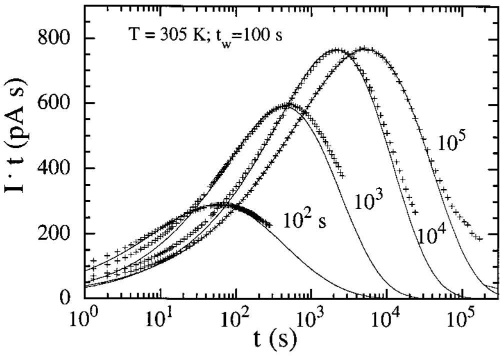

Figure 2. Experimental spectra of PVAc at 305 K for samples first annealed during 100 s at the measurement temperature and subsequently partially polarized during the polarizing times indicated. The lines through the data correspond to KWW fits according to eq 2b.

relaxation function corresponding to a fully polarized sample. Since $\Phi(t)$ is assumed to be of the KWW form, eq 2a transforms into

$$I(t) \propto -\frac{\beta}{\tau}\{t^{\beta-1}\exp[-(t/\tau)^{\beta}] - (t+t_p)^{\beta-1}\exp[(-(t+t_p)/\tau)^{\beta}]\} \tag{2b}$$

Lines in Figure 2 stand for the curves obtained by fitting eq 2b to the time range of the depolarization current around the maximum of the *It* curves. As can be observed, the description based on the KWW function is satisfactory although small discrepancies are apparent. The discrepancies in the short time tail can be attributed to the influence of the secondary relaxation tail and/or to the widely reported failure of the KWW law in describing the fast part of the α-relaxation.[20] On the other hand, at times above the maximum of the *It* curves, the effect of physical aging on the dielectric relaxation becomes relevant and the fit is not possible. Only for long annealing times, when the sample is close to equilibrium, does the KWW equation allow the fitting of the high time range.

Finally, it should be noted that experiments performed at the same temperature using different values of t_w and t_p, but involving the same annealing time ($t_w + t_p$) yield fitting parameters of eq 2b that, within the experimental uncertainties, are the same. Therefore, the relaxation parameters are mainly determined by the thermal prehistory (structural state) and not by the details of the dielectric experiment. This result shows that dielectric relaxation acts as a linear probe that is able to reflect actually the dynamic state of the sample.

III. Results

By means of the analysis method described above, the influence of physical aging on the dynamical KWW parameters τ and β were obtained. Figure 3 shows the dependence of the dielectric characteristic time on the annealing time at two temperatures for each of the three samples investigated. The arrows in Figure 3 stand for the equilibrium values deduced from extrapolation of the liquidlike equilibrium state (see part 1). Although the extrapolation for PH gives values higher than 10^5 s at the two temperatures, it should be taken into account that for this polymer there is an important conductivity contribution to the dielectric losses that yield high uncertainties in the extrapolations.[16] In fact, the experimental behavior obtained for PH at 363 K seems to indicate that the equilibrium value of τ at this temperature is around 2×10^4 s. On the other hand, in Figure 3 it is apparent that τ increases markedly with the annealing time toward the equilibrium value. During the main part of the aging process, the values of τ follow approximately the usual power law behavior $\tau \propto t_a^{\mu}$.[3] However, when the annealing time is of the order of the equilibrium time scale, the values of τ bend toward the equilibrium value, which is eventually achieved for annealing times of about 10 times longer than the equilibrium relaxation time. The value of μ is about 0.5 (dashed line) for the samples at temperatures where the equilibrium is reached in the experimental window. However, for lower temperatures μ seems to be slightly higher. These values are in agreement with the previously reported for dependence on physical aging of the dielectric shift factor in PVAc[21] as well as of the mechanical shift factor[3] (well below T_g μ is close to 1, but near T_g the values found are systematically lower).

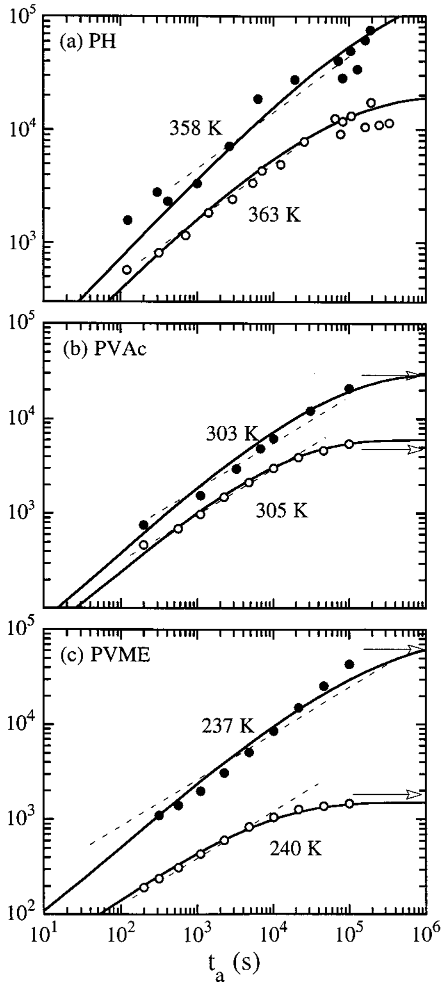

Figure 3. Dielectric relaxation time as a function of physical aging at the indicated temperatures for (a) PH, (b) PVAc, and (c) PVME. The dashed lines correspond to a $t^{0.5}$ law. Filled and empty symbols correspond to the high and low temperatures, respectively. The arrows correspond to the equilibrium values deduced from extrapolation of frequency domain experiments. The solid lines are the ones obtained from the calculation according to the model proposed in this work.

The effect of the physical aging on the shape parameter β is shown in Figure 4. For short annealing times β seems to be systematically higher than the equilibrium value (dashed line) obtained from frequency domain measurements (part 1), in agreement with previous findings.[22-24] However, as aging proceeds, β decreases and the equilibrium value is eventually reached at very long annealing times. Nevertheless, the changes of the shape parameter, although systematic, are not dramatic, being about twice the estimated uncertainty.

It is noteworthy that both the characteristic relaxation time and the shape parameter seem to reach the equilibrium value only after annealing times one decade

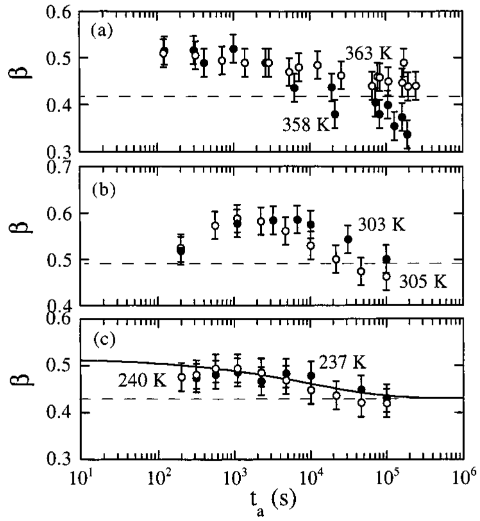

Figure 4. Nonexponentiality parameter as a function of physical aging at the indicated temperatures for (a) PH, (b) PVAc, and (c) PVME. Filled and empty symbols correspond to the high and low temperatures, respectively. The dashed lines stand for the equilibrium values deduced from extrapolation of frequency domain experiments. The solid line in Figure 4c corresponds to eq 12.

longer than the equilibrium dielectric relaxation time (see Figures 3b and 4b for $T = 305$ K and Figures 3c and 4c for $T = 240$ K).

On the other hand, from the data of Figure 3 it is apparent that the experimental values of τ change by more than one decade during the physical aging process. A reason for this strong influence of physical aging on the time scale of the dielectric α-relaxation can be found in the framework of the theories that relate the relaxation time to structural parameters, for instance, the free volume[8,25–27] or the configurational entropy[18,19,28] models. In part 1, this latter approach was used to account for the temperature dependence of τ through the T_g range. The Adam and Gibbs (AG) theory relates the reorientational time of a given unit to the configurational entropy of the sample in the following way:

$$\tau = \tau_0 \exp\left(\frac{N_A s_C{}^* \Delta\mu}{k_B T S_C}\right) \tag{3}$$

where N_A is Avogadro's number, $s_C{}^*$ is the entropy of the minimum number of particles able to rearrange cooperatively, $\Delta\mu$ is the elementary activation energy, and τ_0 is the reciprocal of an attempt frequency. Since the parameters τ_0, $\Delta\mu$, and $s_C{}^*$ were already obtained to describe the dielectric behavior at equilibrium (see Tables 1 and 2 in ref 16), on the basis of this approach one can obtain the values of the configurational entropy S_C from the experimental values of τ by means of eq 3.[16]

The time dependence of the so obtained excess entropy, $S_C(t) - S_C(\infty)$, is shown in Figure 5. In order to check whether this behavior reflects the actual structural relaxation, it was compared with the enthalpy relaxation behavior (see Figure 5) obtained from DSC measurements at the same temperatures (see part 1). As can be observed in Figure 5, both quantities evolve in a similar way and reach the equilibrium value in the same time range. This shows that the AG formulation actually allows one to obtain information about the structural relaxation from the dielectric relaxation experiments.

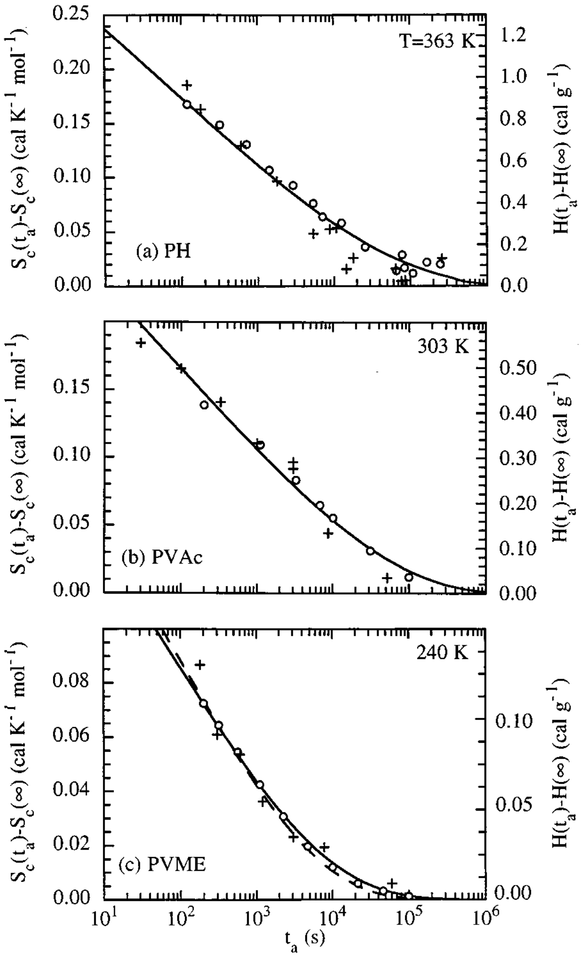

Figure 5. Time evolution of the excess configurational entropy (circles) deduced from the dielectric relaxation time using eq 3 and excess enthalpy (crosses) obtained from DSC measurements: (a) PH, (b) PVAc, and (c) PVME. The solid lines correspond to the solution of eq 9 with the values shown in Table 1. In Figure 5c, the dashed line was obtained with $\beta = 0.53$.

IV. Phenomenological Description of Physical Aging

The enthalpy relaxation during physical aging has been often described in the literature by means of the KWW law without including nonlinear effects.[29] However, the nonlinearity inherent to the physical aging makes the so obtained parameters unphysical.[30] In fact, one should take into account that the structural relaxation is not characterized by a set of τ and β parameters because, as shown by means of the dielectric experiments, both depend on the thermal history. However, by taking into account that the effect of the physical aging on the β parameter is small, as a first approximation, it could be assumed to be constant. In this case, the usual way to account for the nonlinearity of the glassy dynamics is to use the reduced time formalism.[5,6,11,31] The reduced time is an empirical concept that transforms the KWW equation in the following way:

$$\varphi(t) = \exp\left\{-\left[\int_0^t \frac{dt'}{\tau_S(t')}\right]^\beta\right\} \tag{4}$$

Here $\varphi(t)$ is a normalized structural relaxation function and the integral in the exponent is what is defined as reduced time. The reduced time takes into account the fact that the structural relaxation time τ_s depends on the previous history. This empirical formulation has succeeded in describing many of the typical features of the glassy dynamics. However, there is no theory from which eq 4 can be deduced. Moreover, it has been reported that the reduced time formalism fails to describe accurately the structural relaxation, mainly close to equilibrium.[5,32] A more general method to introduce the nonlinearity of nonequilibrium dynamics is to specify the structural state of the glassy polymer by means of an order parameter. This way is consistent with the Adam and Gibbs formulation (eq 3) where the order parameter would be the configurational entropy. In this work we have used this latter method by making the following assumptions: (i) The structural relaxation close to equilibrium (linear regime) is described by the KWW law. (ii) The nonlinearity of the structural relaxation arises from the dependence of the structural relaxation time τ_s on S_C (AG equation), S_C being time dependent out-of-equilibrium.

According to these assumptions the structural relaxation would be driven by the following first-order differential equation:

$$-\frac{d\varphi}{dt} = \frac{\beta}{[\tau_S(S_C)]^{\beta}} t^{\beta-1}\varphi \qquad (5)$$

which close to equilibrium ($S_C \approx$ constant) yields the KWW law as a solution. However, during aging, τ_s will change because it is a function of S_C. This equation also accounts for the KWW behavior observed in an isostructural state, where S_C also remains constant.

From eq 3 one finds

$$\frac{\tau_s}{\tau_{seq}} = \exp\left(\frac{\mathrm{N_A} s_C{}^*\Delta\mu}{k_B T}\,\frac{S_C - S_{ceq}}{S_C S_{ceq}}\right) \approx \exp\left(\frac{N_A s_C{}^*\Delta\mu}{k_B T}\,\frac{\Delta S_C\,\varphi}{S_{ceq}{}^2}\right) = \left[\exp\left(\frac{N_A s_C{}^*\Delta\mu}{k_B T}\,\frac{\Delta S_C}{S_{ceq}{}^2}\right)\right]^{\varphi} \qquad (6)$$

where the subscript eq refers to equilibrium values and ΔS_C and φ refer respectively to the initial configurational entropy excess [$\Delta S_C = S_C(0) - S_{ceq}$] and the normalized configurational entropy relaxation function [$\varphi = (S_C - S_{ceq})/\Delta S_C$]. For short times, $\tau_s(t \rightarrow 0) = \tau_{si}$ and $\varphi = 1$, eq 6 transforms to

$$\frac{\tau_{si}}{\tau_{seq}} \approx \exp\left(\frac{N_A s_C{}^*\Delta\mu}{k_B T}\,\frac{\Delta S_C}{S_{ceq}{}^2}\right) \qquad (7)$$

From eqs 7a and 7b one finds

$$\tau_s \approx \tau_{seq}\left(\frac{\tau_{si}}{\tau_{seq}}\right)^{\varphi} \qquad (8)$$

In this way eq 5 transforms into a nonlinear first-order differential equation:

$$-\frac{d\varphi}{dt} = \frac{\beta}{\tau_{seq}{}^{\beta}\left(\frac{\tau_{si}}{\tau_{seq}}\right)^{\varphi\beta}}\, t^{\beta-1}\varphi \qquad (9)$$

which can be solved numerically provided the values of τ_{si}, τ_{seq}, and β are known. For the experiments performed in this work, τ_{si} has been estimated to be of the order of the reciprocal of the cooling rate used in the experiments ($\tau_{si} \approx 10$ s). The β value has been fixed to be the equilibrium one obtained from dielectric measurements at equilibrium (see Table 1), which has been reported[21] to be consistent with the structural relaxation behavior of PVAc. Thus, τ_{seq} was the single free parameter for the calculation. As can be seen in Figure 5, the solutions of eq 9 obtained in this way (solid lines) give a very good description of the experimental behavior for the three polymers. The values used for τ_{seq} are depicted in Table 1. In order to check the sensitivity of this description to the choice of the β parameter used, in Figure 5c we have included the curve corresponding to $\beta = 0.53$ (0.1 higher than the value used before), keeping τ_{seq} and τ_{si} the same (dashed line). It can be seen that the so resulting curve is not very different from that obtained before; i.e., the solution of eq 9 is weakly affected by the uncertainties in the determination of the β value.

Table 1. Dynamical Parameters Used for Describing the Structural Relaxation Behavior during Physical Aging[a]

polymer	T/K	β	τ_{seq}/s	τ_{eq}/s
PH	363	0.40	50 000	20 000
PVAc	303	0.50	75 000	30 000
PVME	240	0.43	4 500	1 500

[a] The estimates of the equilibrium dielectric relaxation times τ_{eq} are shown for comparison.

When the values of the structural times of Table 1 are compared with the dielectric ones deduced from the long time behavior in Figure 3, it is found that the equilibrium structural relaxation time is about 2.5−3.0 times the dielectric one. This is not surprising because, when different techniques are used on the same sample, the values of the relaxation times obtained are often different, both in the linear[9,33,34] and in the nonlinear regime,[35,36] whereas the temperature dependence is nearly the same. Thus, it can be assumed that the structural and the dielectric relaxation times are proportional to each other (even out-of-equilibrium). Due to the similar ratio between the structural and the dielectric relaxation times found above, we have assumed the same proportionality constant for the three polymers investigated ($\tau = \tau_s/2.7$). With this assumption, once eq 9 is solved, eq 8 allows us to calculate how the dielectric relaxation time depends on the annealing time. The so obtained behavior is shown in Figure 3 for all the temperatures investigated. The agreement between the experimental behavior and the theoretical one is excellent for all the samples investigated, mainly for temperatures close to T_g. It is noteworthy that these curves are calculated starting from equilibrium values; i.e., the nonlinear response is deduced from the parameters describing the linear regime. It should also be mentioned that the ratios between the dielectric and the structural relaxation times found for the present polymers are similar to those found for other polymers, namely a series of polybutadienes of varying microstructure.[37]

V. Discussion

Once the structural relaxation behavior during physical aging has been accounted for, it is possible to calculate the dielectric behavior in the nonlinear regime. With the assumption of a KWW law for the normalized dielectric response function $\Phi(t)$, the equilibrium dielectric behavior of a fully polarized sample is given by

$$I \propto -\frac{d\Phi}{dt} = \frac{\beta}{\tau^{\beta}} t^{\beta-1}\Phi \qquad (10)$$

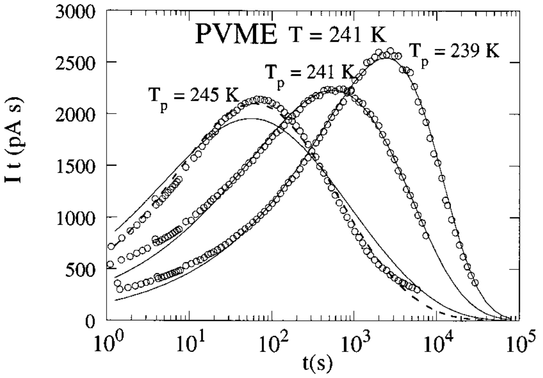

Figure 6. Depolarization spectra of PVME samples at 241 K previously equilibrated and fully polarized at the indicated temperatures T_p. Lines correspond to the description of the dielectric experimental behavior in the nonlinear regime, according to the model proposed in this work, using constant $\beta = 0.43$ (solid lines) and $\beta(t)$ given by eq 12 (dashed line), respectively.

As it was shown experimentally, out-of-equilibrium τ and β are not constant but time dependent. Moreover, dielectric relaxation being a linear probe, the time dependence of τ is not controlled by Φ but rather by the structural state of the sample (i.e., φ), as determined from the solution of eq 9. Therefore, the general out-of-equilibrium solution of eq 10 can be written as

$$\Phi(t) = \exp\left[-\int_0^t \frac{\beta(t')}{\tau(t')^{\beta(t')}}\, t'^{\beta(t')-1}\, \mathrm{d}t'\right] \qquad (11)$$

It is important to note that the time origin of eq 11 is determined by the time when the electric field is switched off whereas the time origin in eq 9 is defined by when the measurement temperature is reached (see Figure 1). If, as above, we assume β to be a constant, starting from the solution of eqs 8 and 9, and with the assumption $\tau = \tau_s/2.7$, eq 11 allows us to calculate the theoretical $\Phi(t)$ behavior at constant temperature in the nonlinear regime of a fully polarized sample.

In order to check whether these predictions agree with the experimental behavior, the depolarization spectra of PVME at 241 K, at equilibrium, and after positive (from $T = 239$ K) and negative (from $T = 245$ K) temperature jumps were measured. It should be noted that, contrary to the previous experiments used in this work, in the present experiments, equilibrium polarization was achieved at the starting temperature (the polarization temperature T_p and the starting one coincide) and the depolarization was measured immediately after the stabilization of the measurement temperature. As can be seen in Figure 6, in this way, the dramatic influence of the prior thermal history on the dielectric relaxation below T_g is clearly evidenced.

Concerning the parameters for the calculations, the equilibrium values for the structural relaxation time and the β parameter were deduced from the fitting of the equilibrium dielectric measurement being $\tau_{seq} = 1480$ s and $\beta = 0.43$. Moreover, the equilibrium values of τ_s at the polarization (starting) temperature were used for τ_{si} ($\tau_{si} = 30$ s for down jump and $\tau_{si} = 9000$ s for up jump). Once eqs 8 and 9 were solved, the corresponding depolarization spectra were calculated by means of eq 11. The resulting depolarization curves are shown in Figure 6 as solid lines. The agreement obtained in this way is excellent for the experiment involving a positive temperature jump; however, for the negative temperature jump the calculation reproduces the peak position but fails to describe the shape of the experimental curve. In fact, the calculated curve is considerably broader than the experimental one. This is in agreement with the previous finding that in the short time range of the down-jump experiments (the ones described above), β takes values systematically higher than the equilibrium one (see Figure 4).

The results obtained in the present study concerning the influence of physical aging on β seem to be in agreement with the interpretation given in part 1 for the temperature dependence of β through the glass transition range. In that study, part of the relaxation broadening was attributed to a distribution of segmental relaxation processes that could be originated by the low molecular weight tails. In this framework, during physical aging (down jump) any distribution of independent relaxation processes should be narrow for short annealing times, since the faster processes of the distribution are able to reach equilibrium earlier.[38] Afterward, for long annealing times, the distribution should be broad and approach the equilibrium one, once the faster processes have achieved the equilibrium. Therefore, in this framework, β should not be a constant but should decrease with the annealing time, as found experimentally (see Figure 4). Although, as shown above, this feature appears not to be very important for the structural relaxation, it seems to be relevant for the dielectric one.

Taking into account that for the down-jump experiment the dielectric relaxation occurs in the time range where the difference between the equilibrium and measured values of β is high, for this case a new calculation was performed. In this calculation, β was considered to be dependent on the aging time according to the following ad-hoc equation:

$$\beta(t) = 0.43\left\{1 + 0.2\,\exp\left[-\left(\frac{t}{10000}\right)^{0.4}\right]\right\} \qquad (12)$$

which fits well the experimental behavior (see Figure 4c). As shown in Figure 6, the result of such a simulation provides a nearly perfect description of the dielectric relaxation for the down-jump experiment. This fact evidences that the effect of the annealing time on β is a relevant dynamic feature, at least for the polymers investigated in this work. This is especially true for the short times of the dielectric relaxation when down-jump experiments are concerned.

Therefore, by means of eqs 8, 9, and 11 it is possible to describe the dielectric relaxation behavior in the nonlinear regime (below T_g), at least in the experimental conditions used in the present work. However, eq 9 is too simple to account for the general structural relaxation behavior, since in eq 9 the evolution of the system is uniquely determined by the equilibrium dynamics and the initial structural state (τ_{si}). Strictly, eq 9 can only be applied for experiments involving single temperature jumps and consequently cannot account for the memory effect that usually appears when several temperature jumps and annealing processes are involved in the same experiment.[5,6] In addition, it is known[5] that both eqs 9 and 11 are inconsistent with Boltzmann superposition of multiple temperature steps. However, in the present experiments the cooling is relatively fast and therefore can be approximated by a single temperature jump, as far as aging times longer than about 100 s are concerned. One should remember that this is our experimental short time limit that is needed for the temperature equilibration. The formulation of the nonlinearity for other more complex thermal treatments and/or for systems far from equilibrium, which is now in progress, is out of the aim of this work.

VI. Conclusions

We have reported on the effects of physical aging on the dielectric relaxation parameters of three amorphous polymers. It has been shown that the dielectric relaxation spectroscopy acts as a linear probe able to extract a snapshot of the dynamical state of the system during physical aging. It has been established that physical aging strongly affects the dielectric characteristic time, which has been interpreted as a signature of its dependence on a structural parameter like the configurational entropy. On the other hand, although the shape parameter is not dramatically affected by physical aging, the changes observed seem to be of relevance for the dielectric relaxation behavior, at least for the short times.

Moreover, it has also been found that for the three polymers investigated the dielectric and the enthalpy relaxation are strongly coupled in the sense that both achieve equilibrium after similar annealing times.

The nonlinearity of the aging process has been represented by a rather simple differential equation (eq 9) that uses parameters obtained from the linear response behavior. However, it is found that, for the three polymers investigated, the structural relaxation time is about 3 times larger than the dielectric one. This approach allows us to account for both the structural recovery and the dielectric relaxation dependence on physical aging after single temperature jumps (positive or negative).

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