

Non-Debye dielectric relaxation around the liquid-glass transition of a glass-forming polymer

A. Alegría, E. Guerrica-Echevarría, I. Tellería, and J. Colmenero

Departamento de Física de Materiales, Universidad del País Vasco, Facultad de Química, Apartado 1072, 20080 San Sebastián, Spain

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The dynamics of glass-forming liquids shows universal features like non-Debye behavior, scaling, and non-Arrhenius temperature dependence of the characteristic rates. These features have been mainly established in the time range between 10^{-9} and 10 s. It is well known that when the temperature of a glass-forming liquid is lowered and the characteristic relaxation time becomes larger than hundreds of seconds, the system falls out of equilibrium and a glass is obtained. However, whether or not the typical features of the glass-forming-liquid dynamics extend to the glass phase through the experimental liquid-glass transition, T_g is still unknown. Trying to address this question better we have performed a study of the dielectric relaxation of a glass-forming polymer, poly(bisphenol-A, 2-hydroxypropylether), around T_g . By using both frequency-domain and time-domain dielectric techniques, we have studied the dynamical processes in the range 10^{-5} – 10^5 s. We have also carried out calorimetric measurements for comparison. In the supercooled-liquid state ($T > T_g$) we have observed all the universal features expected. However, although in the glassy state ($T \lesssim T_g$) the non-Debye character is preserved the scaling is broken, i.e., we observed a relaxation shape depending on the temperature and the state of the glass. Moreover, the temperature dependence of the characteristic time scale of the dielectric relaxation below T_g is Arrhenius-like albeit the apparent activation energy is too high to be a truly activated process. All the features observed have been discussed in the framework of several theoretical approaches.

I. INTRODUCTION

The dynamics of glass-forming liquids has been extensively studied during recent years from both experimental and theoretical points of view.^{1–4} The main dynamical process occurring in glass-forming liquids is referred to as the α relaxation and is identified as a structural relaxation. In addition to this α relaxation, glassy materials display other dynamical processes which are, in general, weaker and faster. From an experimental point of view the α relaxation shows some universal features regardless of the type of glass-forming system considered^{1–3} (ionic, low molecular weight organic, inorganic, polymeric, etc.). These features can be summarized as follows.

(1) The dynamics of the α relaxation shows a clear non-Debye behavior. This is characterized by a half width of the susceptibility loss peak which is larger than 1.14 decades, which corresponds to a Debye peak. In the time domain this corresponds to a stretched, nonexponential, time decay.

(2) Generally, the α relaxation shows scaling behavior. This means that the normalized susceptibility spectrum corresponding to a given excitation is a temperature-independent function when the frequency ω is rescaled by a characteristic time scale $\tau(T)$, $\omega_r = \omega\tau(T)$ (similar behavior is found in the time domain). So, the temperature dependence of the α relaxation only enters via the characteristic time scale $\tau(T)$.

(3) The characteristic time scales $\tau(T)$ obtained from different probes follow a non-Arrhenius temperature behavior which is unusual in physics. In general, this behavior can be parametrized by means of the empirical Vogel-Fulcher law, although some deviations are noted in

the high- T range as well as close to the liquid-glass transition temperature T_g .

All of these features have mainly been established in the supercooled liquid state, i.e., on a time scale ranging from 10^{-6} to 10 s. During recent years several studies have extended these investigations to a rather microscopic time range between 10^{-7} and 10^{-11} s (mesoscopic range).^{5–7} These studies have shown that the characteristic features of the α relaxation on the macroscopic scale also apply to the mesoscopic time range.

Since the α relaxation can be considered as the main structural relaxation, it should be directly related to the liquid-glass transition. This is commonly characterized by a temperature T_g which, in fact, defines a temperature range where such a transition takes place. It is commonly accepted that this transition is associated with the fact that when T is low enough, the relaxation rates become so small that in the usual experimental conditions the system falls out of equilibrium. However, the strong T dependence of the characteristic times of the α relaxation of glass-forming liquids near T_g has led to several authors to look for a true thermodynamic transition behind the experimental one.^{4,8,9} This remains controversial despite the great effort made from both theoretical and experimental points of view.

As mentioned above, the liquid-glass transition is related to the loss of the metastable equilibrium of the supercooled liquid. Below T_g a glassy state with a very low mobility is achieved. The mobility in the glass is proved by the so-called structural recovery and physical aging processes^{10,11} that produce a density increase and modify to some extent several macroscopic properties. Such processes are expected to be controlled by the dynamical

characteristics of the glassy system. One could consider the dynamics of a glass to be directly related to the dynamics of the corresponding supercooled liquid. However, almost nothing is known about the behavior of the α relaxation across the T_g range. It is not clear whether below T_g the α relaxation is completely arrested or only slowed down. It has even been suggested that the glassy dynamics is controlled by solidlike processes, like hopping diffusion,⁴ and therefore is not straightforwardly connected with the supercooled-liquid dynamics.

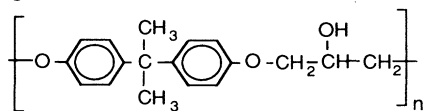
All experiments that deal with the dynamics of a glassy system near T_g are very time consuming due to the low mobility. This leads to a modification of the observed system during the measurement due to the structural recovery. Most of the investigations of the glassy dynamics close to T_g are therefore focused on observing the evolution of static properties like volume or enthalpy.^{10,11}

In this paper we report on the study of the dynamics of the glass-forming polymeric system poly(bisphenol-*A*, 2-hydroxypropylether) by means of dielectric spectroscopy. By using two different experimental setups we have been able to cover a wide scale between 10^{-5} and 10^5 s which includes the time range which is relevant for both the liquid-glass transition and the structural recovery processes in the glassy state close to T_g . In addition, we have measured the enthalpy recovery of the sample below T_g . In this way we have shown that our experimental method allows one to obtain the dielectric dynamic behavior of the glass in a state which is characterized by a constant value of the "fictive temperature." A few (see, for example, Refs. 12 and 13) dynamical studies of the α relaxation of glass-forming systems in the glassy state just below T_g have been previously reported. However, the "state" of the glass to which the behavior observed has to be assigned is not usually considered.

II. EXPERIMENT

A. Sample

A polar glassy polymer, poly(bisphenol-*A*, 2-hydroxypropylether), resulting from the reaction of epichlorohydrin with bisphenol-*A*, has been investigated. Its repeating unit is



The polymer was supplied by Union Carbide (grade PHKK) and is commonly known as phenoxy. It has a density of 1.18 g cm^{-3} and number-averaged and weight-averaged molecular masses of $\bar{M}_n = 18\,000 \text{ g mol}^{-1}$ and $\bar{M}_w = 50\,700 \text{ g mol}^{-1}$, respectively.¹⁴ Its calorimetric glass transition temperature, $T_g = 370 \text{ K}$, was determined from the middle point of the differential scanning calorimetry (DSC) scan at 10 K/min heating rate.

B. Frequency domain dielectric spectroscopy

The dielectric measurements in the frequency domain were performed following standard procedures. The ex-

perimental setup uses a lock-in amplifier EG&G PAR 5208 with an internal oscillator covering the range from 5 to 10^5 Hz . The stray capacitance of the measurement cell was lower than 10^{-14} F . The sample was kept between two aluminum capacitor plates that were maintained at a fixed distance. The capacitance of the sample cell was of the order of 10^{-11} F . A standard 10-pF air capacitor was used as a reference in order to minimize errors in the dielectric loss measurements, leading to an experimental limit for the loss factor of about 10^{-4} . Frequency scans were performed for each temperature, which was decreased in steps of 2 K . The real and imaginary parts of the dielectric permittivity of the sample cell were obtained as a function of frequency at each temperature.

C. Time domain dielectric measurements

The experimental procedure followed in the time domain is based on the transient current method.¹⁵ The sample which filled a parallel plate capacitor was first heated above T_g and then cooled at constant rate (10 K/min) until a certain temperature was reached. At this temperature a constant dc voltage was applied during a given polarization time t_p , followed by a measurement of the corresponding depolarization current as a function of time by means of a Keithley 642 electrometer. When studying the change of the dielectric relaxation behavior through T_g we have used t_p values ranging from a few to several thousand s. This experimental procedure can be used in the temperature range where the characteristic time of the depolarization process of the sample is greater than the time characteristics of the electrometer response, about 0.1 s , but is low enough to provide measurable values of the depolarization current. These limitations allow one to obtain the dielectric response in the time range from 10^{-1} to 10^6 s .

The depolarization current depends on the polarization time used, not only because the final polarization depends on t_p , but also because of the fact that the resulting "glassy state," and therefore its subsequent depolarization rate, depends on the thermal history. This latter effect is related with the intrinsic structural instability of the glassy state and will be discussed extensively below.

D. Enthalpy measurements

A Perkin-Elmer DSC-4 setup was used in order to monitor the enthalpy recovery in the $T < T_g$ range. A relative configurational enthalpy δH defined as

$$\delta H(T) = \int_{T_r}^T [C_p(T') - C_{pg}] dT' \quad (1)$$

was determined by integration of the $C_p(T)$ curves as measured during a temperature scan at 10 K/min . In Eq. (1), T_r is a reference temperature above T_g and C_{pg} is the specific heat of the glass well below T_g . The enthalpy recovery during annealing was determined from the difference between two consecutive DSC scans corresponding to the annealed and nonannealed samples, respectively, and has been described elsewhere.¹⁶

III. RESULTS

A. Frequency domain ($T > T_g$)

The frequency behavior observed for the complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ at several temperatures is shown in Fig. 1. We observe that the relaxation is very different from a simple Debye relaxation process [half circle in the inset of Fig. 1(a)] but, as usually found for supercooled liquids,^{15,17,18} is much broader and markedly asymmetric [see inset of Fig. 1(a)]. In the dielectric loss curves $\epsilon''(\omega)$ [Fig. 1(b)], a clear low-frequency tail is present. This tail follows a $\epsilon''(\omega) \propto \omega^{-1}$ law [see inset of Fig. 1(b)] and can therefore be straightforwardly attributed to the dc conductivity of the sample.

To describe the experimental results we used the well-known Havriliak-Negami (HN) empirical relaxation function^{18,19} plus a conductivity term, giving the complex permittivity:

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_S - \epsilon_\infty)\Phi^*(\omega) - i\sigma_{dc}\omega^{-1}, \quad (2)$$

where ϵ_∞ and ϵ_S are, respectively, the unrelaxed and completely relaxed (static) permittivities, σ_{dc} is the conductivity, and $\Phi^*(\omega)$ is the complex HN relaxation func-

tion given by

$$\Phi^*(\omega) = \frac{1}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma}. \quad (3)$$

Here α and γ are two shape parameters in the range zero-unity ($0 < \alpha, \gamma < 1$) and τ_{HN} is a characteristic relaxation time. The HN relaxation function also accounts for the high-frequency asymptotic behavior corresponding to the Curie-von Schweidler law,²⁰ $\epsilon''(\omega) \propto \omega^{-b}$, the product $\alpha\gamma$ being equal to the von Schweidler (vS) exponent b . We have fitted the experimental data [both $\epsilon'(\omega)$ and $\epsilon''(\omega)$] by means of Eqs. (2) and (3) to obtain optimized values of the fitting parameters at each temperature. The solid lines in Fig. 1 show the fitting curves obtained.

Figure 2 shows the temperature dependence of the HN parameters characterizing the dielectric dynamical behavior of phenoxy above T_g . As usually found in polymer melts,¹⁵ the characteristic time τ_{HN} displays a clear non-Arrhenius behavior [see Fig. 2(a)] which can be well parametrized by means of the Vogel-Fulcher (VF) equation,

$$\tau(T) = \tau_0 \exp \frac{DT_0}{T - T_0}. \quad (4)$$

Here τ_0 is the reciprocal of an attempt frequency, T_0 is a temperature below the experimental range at which the

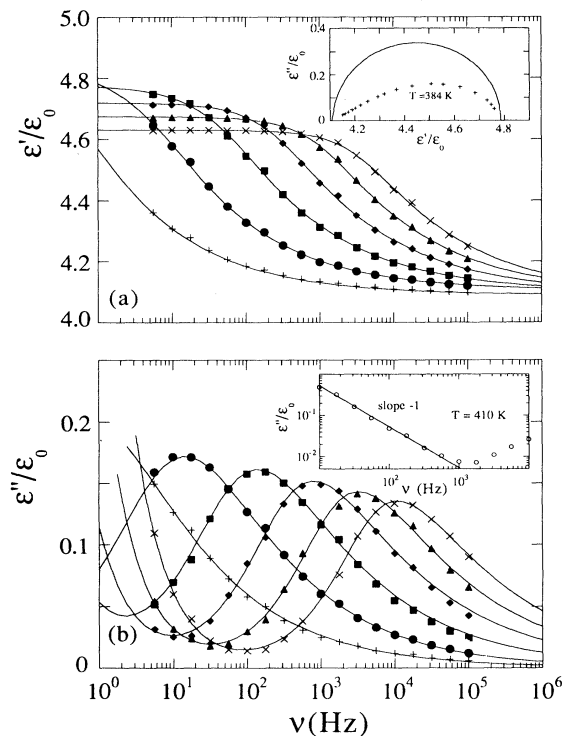


FIG. 1. (a) Frequency dependence of the real part of the dielectric permittivity in the α -relaxation range of phenoxy [(+) 376 K, (●) 380 K, (■) 384 K, (◆) 388 K, (▲) 392 K, and (×) 394 K]. The inset shows a Cole-Cole plot of the isotherm of 384 K and the half circle corresponding to a Debye-like process. (b) Frequency dependence of the imaginary part of the dielectric permittivity in the α -relaxation range of phenoxy (same symbols than above). The inset shows the conductivity contribution tail.

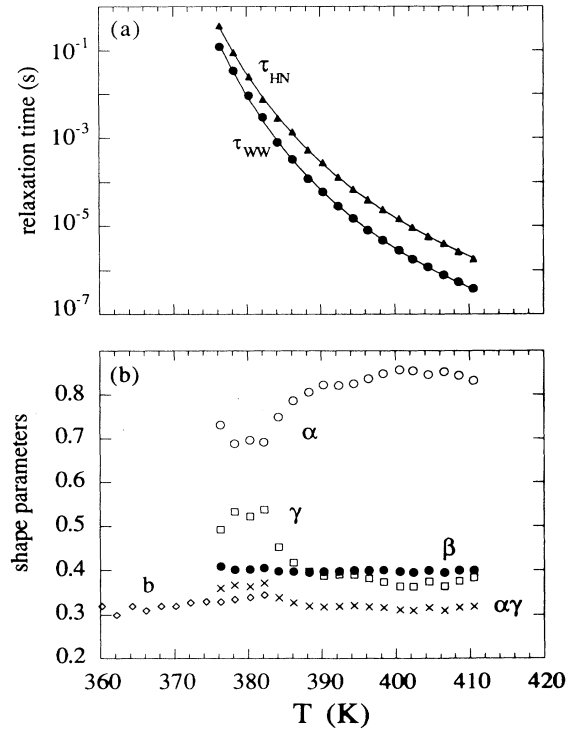


FIG. 2. (a) Temperature dependence of the characteristic times of the dielectric α relaxation of phenoxy above T_g . Solid lines correspond to the VF fits [Eq. (4)] (see parameters in Table I). (b) Temperature dependence of the shape parameters characterizing the dielectric α relaxation of phenoxy above T_g .

extrapolated relaxation time diverges, and D is a parameter which can be related to the fragility concept first introduced by Angell.²¹ The values of the VF parameters obtained by fitting Eq. (4) to the $\tau_{\text{HN}}(T)$ data [solid line in Fig. 2(a)] are listed in Table I. For D , we obtain quite a low value which indicates that within the framework of the fragility scheme phenoxo should be considered as a very fragile polymeric liquid.²² The value obtained for T_0 is in the range $T_g - 30$ K in agreement with this fragile character.

Figure 2(b) shows the T dependence of the HN shape parameters α and γ . There is no systematic behavior in this T range although at the highest temperatures both α and γ appear to be nearly constant. However, the T behavior of α and γ are clearly correlated which is obvious from the fact that $\alpha\gamma$ is constant within the error bars (± 0.03) for all T [see Fig. 2(b)]. On the other hand, the value of $b = \alpha\gamma$ can be independently determined from the experimental data in the low- T range near T_g where the high-frequency tail is the only part of the response accessible for our limited frequency window. The such-determined value of b is T independent within the experimental uncertainty and takes a value of 0.33 ± 0.03 . This value is in agreement with the value of $\alpha\gamma$ deduced from the fitting of the higher-temperature data.

In two previous papers²³ some of us have shown that the HN relaxation function $\Phi^*(\omega)$ corresponds to a time decay function $\phi(t)$ which, for certain values of α and γ , is well described by means of the Kohlrausch-Williams-Watts (KWW) law:²⁴

$$\phi(t) \cong \psi(t) = \exp \left[- \left(\frac{t}{\tau_{\text{WW}}} \right)^\beta \right], \quad (5)$$

where β is the parameter characterizing the non-Debye character of the time decay, and τ_{WW} is a characteristic relaxation time. In the above-mentioned papers, the range of values of the HN parameters for which this correspondence is applicable and the relationships between the HN and KWW parameters has been established. The values of the HN parameters for phenoxo shown in Fig. 2 are in the range where the correspondence between the two descriptions is expected to be very good. Therefore, we have deduced the values of the KWW parameters. A nearly constant value of β as well as a VF-like behavior for $\tau_{\text{WW}}(T)$ were obtained (also shown in Fig. 2). The values of the VF parameters obtained by fitting Eq. (4) to the τ_{WW} values were similar to those obtained by fitting $\tau_{\text{HN}}(T)$ (see Table I). Since τ_{WW} and τ_{HN} are both characterizing the same dielectric response, this fact is consistent with a T -independent shape of the α relaxation of phenoxo.

TABLE I. Vogel-Fulcher fitting parameters of conductivity and dielectric relaxation times above T_g for phenoxo.

	Prefactor	D	T_0 (K)
τ_{HN} (s)	4.39×10^{-11}	1.997	346.0
τ_{WW} (s)	8.36×10^{-12}	1.932	347.8
σ_{dc} ($\Omega^{-1} \text{s}^{-1}$)	1.42×10^{-8}	0.945	353.8

The fitting procedure described above also yields the low- and high-frequency limits of the dielectric permittivity as well as the dc conductivity. The temperature behavior of these quantities is shown in Fig. 3. Figure 3(a) shows that ϵ_∞ is nearly constant, while ϵ_s decreases with temperature but much faster than one would expect from the Onsager law ($\epsilon_s \propto 1/T$).¹⁸ The deviation from the Onsager law can be interpreted as a consequence of the presence of some kind of interaction between dipoles, not considered in the Onsager approximation.

The T behavior of σ_{dc} is shown in Fig. 3(b) and is clearly non-Arrhenius like. This result can be well described again by a VF-like equation, i.e.,

$$\sigma(T) = \sigma_0 \exp \frac{-DT}{T - T_0}. \quad (6)$$

The values of the fitting parameters D , T_0 , and σ_0 are included in Table I. The observed T behavior is very different from the T behavior observed for thermally activated conduction mechanisms (Arrhenius behavior) and can be a result of conduction mechanisms controlled by the free volume in the sample.²⁵

B. Time domain ($T < T_g$)

Figure 4 shows an example of the relaxation behavior obtained in the time domain. This behavior strongly

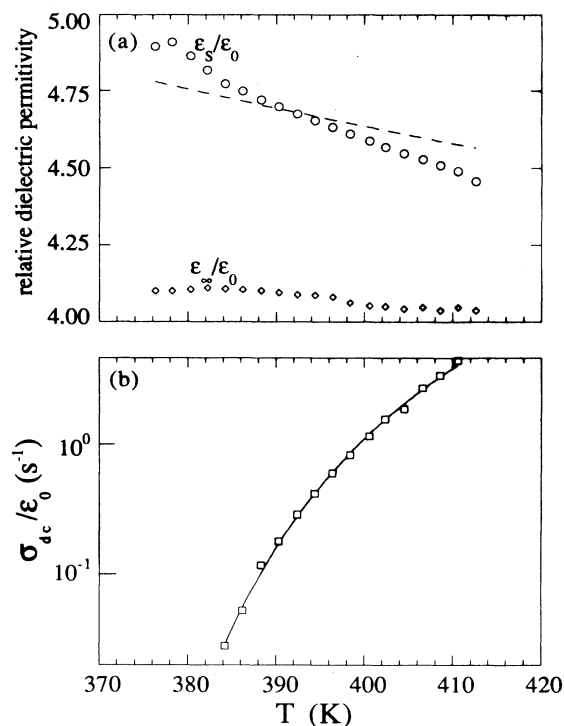


FIG. 3. (a) Temperature dependence of the low- (ϵ_s) and high- (ϵ_∞) frequency limits of the dielectric permittivity in the α -relaxation range of phenoxo. The dashed line corresponds to the best Onsager law fitting the data. (b) Temperature dependence of the dc conductivity of phenoxo. The solid line corresponds to the VF fit [Eq. (6)] (see parameters in Table I).

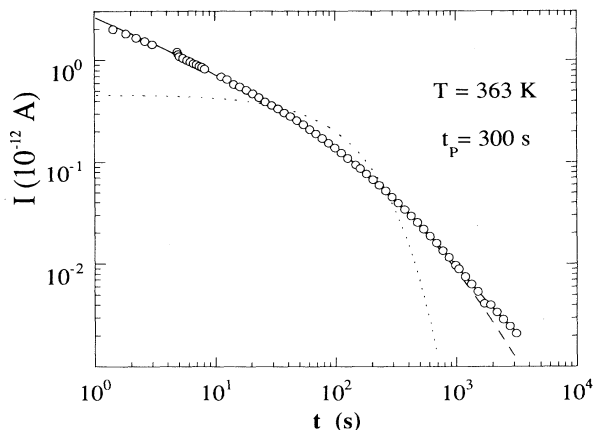


FIG. 4. Typical isothermal depolarization current as function of time. The solid line is the best fit obtained by means of Eqs. (7) and (8). The dashed line represents the pure dipolar contribution. The dotted line corresponds to the isothermal depolarization current resulting from a single exponential time decay function.

differs again from a Debye decay (dotted line). The short-time regime of the response follows a fractional power law (Curie–von Schweidler law), $I(t) \propto t^{b-1}$. However, this regime is only clear some degrees below T_g becoming hardly accessible in the experimental time window at higher T . Then, the values of b can only be calculated below T_g [see Fig. 5(a)].

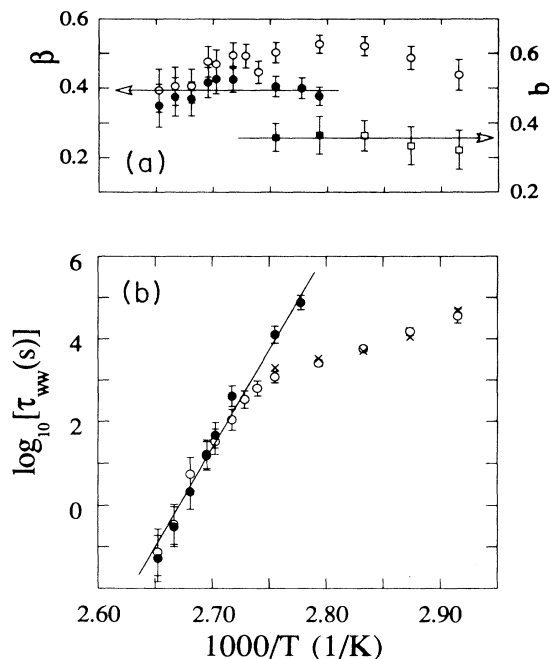


FIG. 5. (a) Temperature dependence of the shape parameters at equilibrium (solid symbols) and out of equilibrium (open symbols). (b) Temperature dependence of the characteristic time of the KWW law at equilibrium (solid symbols) and out of equilibrium (open symbols). (x) Annealing times that produce a constant fictive temperature of 365 K (enthalpy recovery of 0.3 cal g⁻¹).

A fractional power law for $I(t)$ is expected on the basis of several theoretical approximations including those that lead to a KWW law [Eq. (5)] for the polarization time decay. Therefore, taking into account the results obtained above T_g , we have also assumed a KWW function for the decay function associated with the α relaxation below T_g . In addition to this KWW behavior, a single exponential decay has been considered in order to take into account the extra current appearing at the largest times (see Fig. 4).

For our experimental conditions, the isothermal depolarization current is given by the first derivative of the response corresponding to a block shape excitation:¹⁸

$$I(t) \propto -\frac{d}{dt}[F_p(t) - F_p(t + t_p)], \quad (7)$$

where $F_p(t)$ is the time decay (step response) function that, with the assumptions outlined above, can be written as

$$F_p(t) = F_D \psi(t) + F_C \exp(-Kt), \quad (8)$$

where F_D and F_C are two constants and K is a relaxation rate. The solid line in Fig. 4 is a fit to the experimental curve using Eqs. (7) and (8). From this fitting procedure we directly obtain the values of τ_{ww} and β characterizing the dynamics of the dielectric α relaxation.

The T behavior of τ_{ww} and β obtained is shown in Fig. 5. By means of the time domain technique we cover the τ_{ww} range from 0.1 to 10⁵ s. Values of the parameters corresponding to experiments in which the sample was allowed to stabilize at the measurement temperature (before the experiment starts) a period of time large enough to obtain a depolarization behavior independent of the thermal history are plotted as solid points. Open points correspond to experiments in which the sample was cooled from above T_g at a constant rate of 10 K/min and measured immediately. Below T_g the values obtained in this way correspond to the sample out of equilibrium. In this range the thermal history strongly affects the T dependence of both τ_{ww} and β as has been reported for other polymers.^{12,13} However, we found that b is not affected by the thermal history of the sample [see Fig. 5(a)].

Concerning $\tau_{\text{ww}}(T)$, we observe that equilibrated samples show an Arrhenius-like behavior with a very high apparent activation energy (8.8 eV). This activation energy is too high to correspond to a true activated process, so its interpretation is not clear. In fact, similar results have been found in many glass-forming liquids.¹³ On the other hand, the $\tau_{\text{ww}}(T)$ behavior of nonannealed samples also exhibits an Arrhenius-like behavior. Although the apparent activation energy is lower in this case (2 eV), again it is too high to correspond to a true activated process. Similar behavior has been reported for the dielectric relaxation times of several amorphous polymers^{12,13} and for other quantities characteristic of the molecular transport in both polymeric and nonpolymeric glass-forming systems.²⁶ With respect to this, molecular-dynamics studies²⁷ suggest that some degree of mobility similar in nature to the one existing in the supercooled

liquid is still present several degrees below T_g .

The main problem arising when one tries to measure glassy properties near T_g is the structural recovery of any glassy material towards the supercooled-liquid state. This implies that measurements at different conditions correspond to different structural states of the glass under observation. Generally this is not taken into account when experiments are performed below, but near, T_g . As a consequence, it is not well established yet whether the behavior observed below T_g is associated with the glassy dynamics or is an artifact due to the fact that measurements at different temperatures actually correspond to different glassy structural states. In our experiments the sample evolves towards the metastable equilibrium state corresponding to the supercooled liquid during the measuring time (including polarization and depolarization times). The annealing time involved in a given experiment can be evaluated to be of the order of $t_p + \tau_{\text{WW}}$ (τ_{WW} when $t_p \ll \tau_{\text{WW}}$). So the state of the glassy sample to which the obtained values of β and τ_{WW} are associated depends on the experimental conditions. In order to clarify this problem, we have studied the enthalpy recovery of the sample at the same temperatures below T_g investigated dielectrically. In this way we establish the actual state of the sample for which applies the values of β and τ_{WW} obtained.

C. Enthalpy recovery

Figure 6 shows the enthalpy recovery behavior at different temperatures. We have plotted the dependence on the annealing time of $\Delta H = \delta H(T_a) - \delta H_a(T_a)$, where $\delta H(T_a)$ and $\delta H_a(T_a)$ [calculated by means of Eq. (1)] are the relative enthalpies at the annealing temperature T_a corresponding, respectively, to the nonannealed sample (cooled down at 10 K/min) and to the annealed sample.

From the data of Fig. 6, the out-of-equilibrium “structural” state of glassy phenoxy can be characterized in a first approximation by means of an order parameter like the fictive temperature T_f . This was first introduced by Tool and Eichlin²⁸ as a measure of the structural state of a glass and was defined as the temperature at which

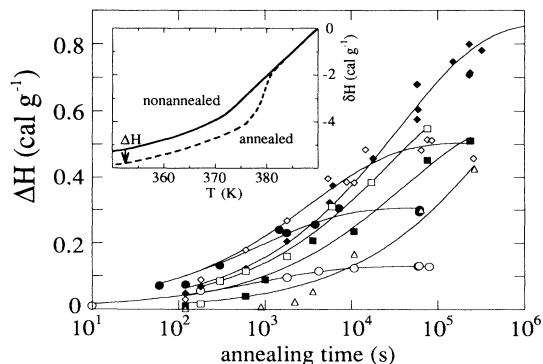


FIG. 6. Enthalpy recovery behavior of phenoxy [(○) 368 K, (●) 365 K, (◇) 363 K, (◆) 358 K, (□) 353 K, (■) 348 K, and (△) 343 K]. Solid lines are only a guide for the eye. The inset shows how the enthalpy recovery is measured.

the value of an intensive property (enthalpy in our case) in the supercooled liquid is the one corresponding to the glass. If the annealing time at each temperature is known, the resulting “structural” state can then be characterized by the corresponding T_f value obtained from the data of Fig. 6. From Figs. 5(b) and 6 we can deduce that the resulting T_f values corresponding to the sample in the time domain experiments are close to 365 K for all the experiments performed in the $T < 365$ -K range. From Fig. 6 we can also evaluate the annealing time that at each temperature yields a constant value of $T_f = 365$ K. These values, which have been included in Fig. 5(b), compare very well with the dielectric $\tau_{\text{WW}}(T)$ behavior. This clearly shows that the KWW parameters that we have obtained out of equilibrium actually correspond to a glassy state characterized by $T_f \cong 365$ K (5° below the calorimetric T_g). This is in agreement with the fact that in Fig. 5(b) only below this T the difference between annealed and nonannealed samples is apparent. Therefore, the change in the T behavior of τ_{WW} around T_g , obtained following the experimental procedure used by us, is characteristic of the glassy dynamics in an isostructural state and not an experimental artifact.

IV. DISCUSSION

The main purpose of this work was to study the dynamics of the dielectric α relaxation through T_g . As we have characterized this dynamics by means of the time scale τ_{WW} and two different exponents characterizing the relaxation shape, in this section we will mainly discuss the change of the temperature behavior of both τ_{WW} and the shape of the relaxation as temperature varies through T_g .

A. Temperature dependence of τ_{WW}

In Fig. 7, we show the T dependence of the characteristic time, $\tau_{\text{WW}}(T)$ of the α relaxation in the range investi-

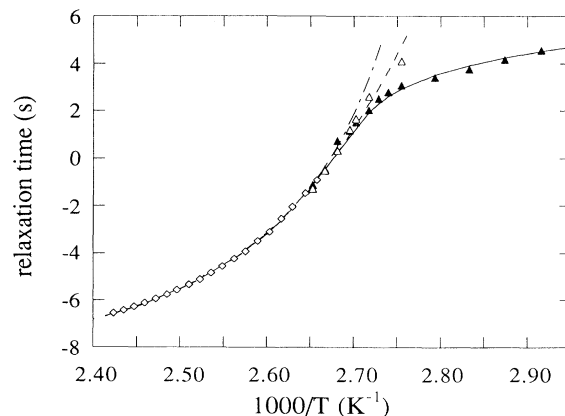


FIG. 7. Temperature dependence of the KWW characteristic time through the liquid-glass transition. (◇) values obtained from the frequency domain measurements. Supercooled-liquid (△) and glassy state (▲) values obtained from the time domain measurements. Different fittings are also shown: VF (---); CG (-.-.); the model proposed in this paper (—).

gated. It is possible to define three different regions: region I, $T > T_g$, where a VF behavior is observed; region II, $T \simeq T_g$, where deviation from the VF behavior is observed in the supercooled liquid state; and region III, $T < T_g$, where the sample is out of equilibrium and a clear Arrhenius-like behavior is obtained.

Regions I and II correspond to the supercooled-liquid state. The T behavior found has usually been observed for the relaxation times of polymer melts¹⁵ as well as for the viscosity of both polymeric and low molecular weight glass-forming systems. Such a temperature dependence is, in fact, expected on the basis of several theoretical approaches to the liquid-glass transition.^{4,29}

Mode-coupling (MC) theories⁴ predict a dynamical instability at a temperature $T_c > T_g$. Above T_c the system is ergodic, below T_c each particle has a limited spatial range available and the system becomes nonergodic. At the moment there are no theoretical predictions of MC theories for $\tau_{\text{WW}}(T)$ below T_c . Moreover, from our results there is no indication about the existence of such T_c . Therefore, it is clear that MC theories cannot be applied to describe the dynamics of the α relaxation in the T_g range, where our interest is focused.

On the other hand, free-volume theories²⁹ could be considered in order to understand the observed behavior. The free-volume concept was first proposed by Fox and Flory³⁰ and formally established later by Cohen and Grest (CG).²⁹ The free-volume model is a simple picture which has been useful in describing the temperature behavior of the viscosity and the different relaxation rates of glass-forming liquids. The central result of the free-volume picture is the Doolittle equation establishing a relationship between the characteristic time scale and the fractional free volume v_f ,

$$\tau = \tau_0 \exp \left[\frac{\Gamma}{v_f} \right], \quad (9)$$

where τ_0 is a preexponential factor, which in the CG approach depends weakly on T , v_f is the fractional free volume defined as the ratio between the average free volume and a volume characteristic of the molecular segment involved in the melt dynamics, and Γ is a geometrical factor of the order of unity. If a linear temperature dependence of v_f is assumed. Eq. (9) leads to the VF one [Eq. (4)]. However, in the CG approach the following equation is proposed for the temperature dependence of the fractional free volume:²⁹

$$v_f = (1/2B) \{ T - T_0 + [(T - T_0)^2 + AT]^{1/2} \}, \quad (10)$$

where A , B , and T_0 are parameters to be determined on a best-fit basis. It is noteworthy that v_f only vanishes at $T=0$. At high temperature the VF law is recuperated due to the linear dependence of v_f in this range. Cohen and Grest analyzed data from several sources and found that the value of τ_0 in the Doolittle equation should be of the order of 10^{-10} s. We have calculated the $v_f(T)$ behavior from our dielectric $\tau_{\text{WW}}(T)$ data in the following way:

$$v_f(T) = 1 / \ln[\tau_{\text{WW}}(T)/\tau_0], \quad (11)$$

where $\tau_0 = 10^{-10}$ s was assumed. Figure 8 shows the $v_f(T)$ behavior obtained. It is clear that the $v_f(T)$ behavior obtained from the dielectric relaxation time resembles the one corresponding to the volume expansion through T_g (see inset of Fig. 8). As can be seen in Fig. 8, Eq. (10) allows us to fit quite well all the values of $v_f(T)$ in the supercooled liquid (dashed line), including those that in Fig. 7 deviate from the VF law. The values of the parameters corresponding to the fitting curve are

$$T_0 = 369.77 \text{ K}, \quad B = 375.71 \text{ K}, \quad A = 2.175 \text{ K}^{-1}.$$

Therefore, this picture allows us to obtain a very good fitting of $\tau_{\text{WW}}(T)$ in regions I and II (see Fig. 7) which strongly support the free-volume scheme.

Concerning the nonequilibrium $\tau(T)$ behavior, region III, the situation is less clear. Although, as mentioned above, region III has been widely described in the literature, most of the theories fail in this region because of the lack of equilibrium. However, several empirical models which take the lack of equilibrium into account by the freezing of some "order parameter," like fictive temperature or free volume, allow a good description of the observed relaxation behavior around T_g .^{31,32} However, in general, these models have a great number of parameters to be fitted in each experiment and they do not have a clear connection with the supercooled-liquid behavior.

The free-volume approach for describing experiments out of equilibrium was introduced by Kovacs for the study of the volume recovery of glasses below T_g .¹⁰ This model was further applied by some of us for the dielectric relaxation as observed by thermally stimulated depolarization experiments.^{33,34} This approach is based on the following assumptions. First, out of equilibrium a glassy material has an excess fractional free volume δ , so $v_f = v_{f\infty} + \delta$, where $v_{f\infty}$ is the equilibrium value which is given by Eq. (10). Second, the isothermal decay of δ is given by a first-order equation:

$$\frac{d\delta}{dt} = -\frac{\delta}{\tau} \Rightarrow \frac{dv_f}{dt} = \frac{v_{f\infty} - v_f}{\tau}. \quad (12)$$

Third, even out of equilibrium τ is given by the Doolittle

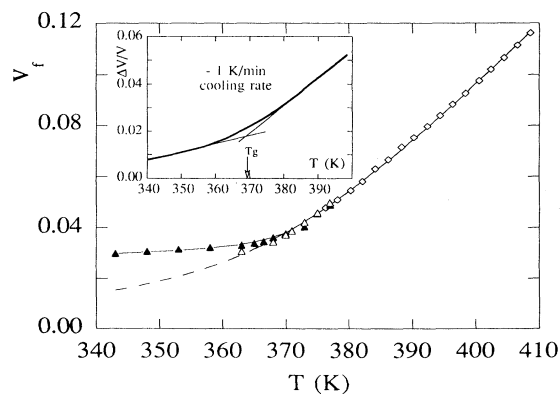


FIG. 8. Temperature dependence of the free volume deduced for $\tau_{\text{WW}}(T)$ by using Eq. (11). Symbols as in Fig. 7. The inset shows a thermal expansion curve obtained at -1 -K/min cooling rate.

equation,³⁵ i.e., $\tau = \tau_0 \exp[1/v_f(t)]$, in which τ is now considered not only a function of temperature but also of time. Fourth, the characteristic time for recovery τ and the dielectric characteristic time τ_{WW} are equal to or, at least proportional to, each other. Following these assumptions $v_f(T)$ is given by the solution of the following nonlinear equation:

$$\frac{dv_f}{dT} = \alpha_g + \frac{v_{f\infty} - v_f}{q\tau_0 \exp(1/v_f)}, \quad (13)$$

where α_g is the expansion coefficient of the free volume in the glassy state, $q = dT/dt$ is the rate of temperature variation, and τ_0 and $v_{f\infty}$ are taken from the supercooled-liquid behavior. Figure 8 shows (solid line) the $v_f(T)$ behavior calculated from Eq. (13) with $q = -1$ K/min and $\alpha_g = 8 \times 10^{-5}$ K⁻¹. As expected, α_g is much lower than the expansion coefficient of glassy phenoxy (3×10^{-4} K⁻¹). From the $v_f(T)$ behavior and through Eq. (9) we have calculated $\tau_{\text{WW}}(T)$ in the whole temperature range assuming an effective cooling rate of -1 K/min. As can be observed in Fig. 7, the calculated curve and the experimental data are in good agreement, especially if we take into account the simplicity of the model which has only one extra parameter, α_g , to describe the loss of equilibrium in the $\tau_{\text{WW}}(T)$ behavior.

B. Temperature dependence of the relaxation shape

Two different parameters have been considered in order to describe the shape of the relaxation behavior observed, b describing the high-frequency (short-time) behavior and β describing the broadening of the main part of the relaxation process. Note that if the KWW description were perfect β and b should be equal. As can be seen in Figs. 2(b) and 5(a) we found that b values are systematically smaller than β ones. This means that the experimental high-frequency stretching of the response is slightly higher than the one corresponding to the KWW fitting. This fact was already pointed out by Fuch *et al.*³⁶ for the dielectric relaxation of ortho-terphenyl. So, the KWW description can only be considered a reasonable approximation in describing the observed relaxation. However, the fact that both b and β take nearly constant values in the supercooled-liquid state shows that the shape of the relaxation does not change appreciably with temperature in this state, at least in the range investigated.

The broadening of the α relaxation has usually been interpreted in the framework of different models which can be grouped into two major families. The first group of model assumes the presence of a very broad distribution of single (Debye) parallel relaxation processes. The second group considers the broadening of α relaxation a consequence of the correlated reorientation of the different relaxing units. Our results above T_g indicate a temperature-independent relaxation broadening which is compatible with both descriptions. Concerning the shape of the relaxation around T_g , we have observed that b is unaffected by the liquid-glass transition, which is consistent with both groups as well. Within the distribution picture, the fact that b takes the equilibrium value even

below T_g is easily understood if one takes into account that the vS law applies only for the short-time range, i.e., for times much smaller than the annealing time corresponding to the time domain experiments, of the order of τ_{WW} . Within the correlation picture,^{4,37} b is directly related to the coupling strength, so one would expect the value of b not to be affected either by the liquid-glass transition or by the structural recovery.

Concerning the $\beta(T)$ behavior around T_g , the situation is less clear. We have obtained values close to 0.4 above T_g , as well as below T_g for samples in the supercooled-liquid state. Nevertheless, we have found that β increases from 0.4 up to 0.55 around $T_g - 10$ K, when the metastable equilibrium state is lost. Below this temperature β decreases monotonically when T is decreased in the glassy state. There are no clear theoretical predictions with respect to this behavior because in this T range the material is out of equilibrium and therefore the standard theories can generally not be applied. A few other experimental results concerning the temperature dependence of β in the $T < T_g$ range of glassy polymers are available.^{12,13} These results are similar to those displayed in Fig. 5(a). Several results on nonpolymeric systems below T_g can also be found in a review article by Ngai.³⁸

Our results can be understood in the framework of a distribution picture when one considers that, while the faster processes shift towards larger times before the measurement starts, the slower processes remain frozen. A decrease of the broadening of the relaxation thus results in the range where the faster processes have characteristic times lower than t_p . Recent experimental and theoretical works, however, have shown strong evidence against the distribution picture as the main origin of the non-Debye character of the α relaxation.^{39,40,7}

In the framework of a correlation picture, the differences between the b and β behaviors around T_g could suggest that out of equilibrium the relaxation behavior deviates more from the KWW law. However, this deviation would not be significant in our experimental time range window since the fitting of the experimental behavior by assuming a KWW law is quite good. As we have shown above, on the other hand, the characteristic time of the relaxation process is affected very much by the thermal treatment leading to an expected change of the relaxation function and a modification of the KWW behavior. However, this would also imply a dependence of the relaxation rate on the structural state of the glassy material, as was assumed to account for the $\tau_{\text{WW}}(T)$ behavior around T_g . Such a nonlinear feature could lead to the observation of an apparent narrowing of the response function when the nonlinearity is disregarded in the data analysis. Work in this direction is now in progress.

V. CONCLUSIONS

We have reported on the effect of the experimental liquid-glass transition on the dielectric relaxation of an amorphous polymer. We have found that the relaxation behavior can be well described by the KWW relaxation function above T_g as well as below T_g , although below T_g

some systematic deviations have been detected. We observe that the KWW parameters characteristic of both the rate and the shape of the relaxation process are strongly affected by the liquid-glass transition. The T dependence of the characteristic time scale shows a clear crossover from a VF towards an Arrhenius behavior in the liquid-glass transition range. The characteristic time in the glassy state, which, in the range $T < 365$ K, corresponds to an isostructural state, is lower than the value corresponding to the supercooled liquid. This value is recovered when the system is allowed to stabilize and to reach the metastable equilibrium state. All of these behaviors, which extend over 10 decades in time scale, have been accounted for in the free-volume framework when a nonlinear behavior has been considered to describe the T dependence of τ_{VW} around T_g .

On the other hand, when the system falls out of equilibrium, the KWW shape parameter β appears to be

higher than the one corresponding to the supercooled liquid indicating a reduction of the broadening throughout the liquid-glass transition. However, at lower temperatures the broadening starts to increase again as the temperature is decreased in the glassy state. This behavior is not observed in the temperature dependence of the vS exponent.

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