Research Article

Temperature Dependence of the Activation Volume of Secondary Relaxation in Glass Formers

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We study a nonmonotonic behavior with temperature of the activation volume ΔV_β of secondary relaxation in PPGE [Poly[(phenyl glycidyl ether)-co-formaldehyde]] and PVAc [Poly(vinyl acetate)] glass formers. Our results show that the non-monotonic behaviour of secondary relaxation does not depend on the type of the secondary relaxation. Moreover, the study of secondary relaxation under pressure at isothermal paths shows two different behaviours of ΔV_β in the glassy state (which describe two different types of glasses); for temperatures higher than the glass transition temperature (T_g), ΔV_β increases with a decrease of the temperature while at temperatures lower than T_g , ΔV_β decreases with a decrease of the temperature.

1. Introduction

The glassy state is a nonequilibrium state of materials [1]. As a consequence, the observed thermodynamic and relaxation properties slowly evolve with time because of the evolution of the molecular configuration towards a state with a lower energy [2]. Another consequence of the none-equilibrium condition of glasses is that the thermodynamic and relaxation properties show different values when measured in the glassy state at a fixed thermodynamic condition as a consequence of different vitrification histories [3–5]. For example, this was observed for the relaxation frequency of several secondary processes [3, 6] as a consequence of cooling with different rates, or after vitrification combining different sequences of cooling and compression steps [7–9]. Glass formers are characterized by a complex relaxation pattern, which evolves over several decades. Dielectric spectroscopy has proven particularly useful for studying such a scenario, as it is able to monitor the dielectric dynamics of a system over a range up to sixteen decades. It has been turned out that in such a broad dynamic range, several molecular processes take place, and most of them are usually characterized by non-exponential relaxation functions. In case that such processes depend on the local motion of hole molecule (intermolecular

process), they are usually called the Johari-Goldstein relaxation (JG relaxation) which is a type of secondary relaxation [10, 11]; otherwise they are called non-JG relaxation or intramolecular secondary relaxation. It has been suggested that the connection or the similarity of dynamic properties (dependence of relaxation time on temperature, pressure, thermodynamic history of glass formation) of the secondary relaxation with those of the structural one, can be used as a criterium to distinguish JG and non-JG relaxations [12]. However, the existence of such a connection is still questionable, and there is a debate about the validity of this criterium. A study of the pressure dependence of the JG relaxation of PPGE, along several isotherms, shows that ΔV_β in the glassy state first increases and then slightly decreases on lowering T , reaching a maximum at the T_g [13]. This kind of temperature dependence occurs in the region of the T_g at ambient pressure. A similar temperature dependence of the mean whole volume dispersion is proposed on the literature. Such an explanation supports previous work, suggesting that this process is of the JG type [14]. In this work, we present experimental studies varying pressure and temperature of secondary processes in two glass formers. Firstly, we study the temperature dependence of the activation volume of one observed secondary relaxation in PVAc and compare

FIGURE 1: Isothermal loss spectra of (a) PPGE at $T = 244$ K and (b) PVAc at $T = 263$ K, at various pressures in the glassy state. We can see the secondary peak that slightly moves with pressure.

results with JG relaxation of PPGE. We focused on the slower secondary process of PPGE (JG relaxation) and on the one observed in PVAc whose microscopic origin is not clear. We found a non-monotonic behaviour of ΔV_β in secondary relaxation in PVAc.

2. Experimental

PPGE, with average molecular weight, MW of 345 g/mol, and T_g around 258 ± 1 K [14] and PVAc with MW of 167 Kg/mol and $T_g = 310.7$ K were purchased from Sigma-Aldrich. PVAc has interesting structural variations and can be obtained

in the atactic and, thus, amorphous form, which is crucial for investigations of the glass transition. PVAc has often been chosen to test the current aspects of various theories related with glass transition phenomena. An ample dipole moment makes PVAc a good candidate for dielectric spectroscopy [15, 16]. Dielectric measurements were carried out using a dielectric spectrometer (Alpha-Novocontrol) in the frequency interval 10^{-2} – 10^7 Hz. For measurements at ambient pressure, the sample was placed in a parallel plate cell (diameter = 30 mm, gap = 0.1 mm) and the temperature control was performed with a precision better than 0.1 K by using a dry-nitrogen-stream-based system. For measurements at high pressure, the sample was placed in a parallel plate cell (diameter = 20 mm, gap = 0.05 mm) which was properly insulated from the external environment and located inside a pressure chamber. Pressure variations (0.1–600 MPa) were generated by a manual pump and transmitted to the sample through silicon oil. A liquid circulator connected to a jacket and wrapped around the pressure room allowed the control of the temperature (353–233 K) within ± 0.1 K.

3. Results

Representative isothermal dielectric loss spectra of the investigated glass formers in the glassy state are presented in Figure 1. We obtained dielectric spectra by varying the pressure from 0.1 MPa and up to the maximum value of 600 MPa. In both systems we can observe a peak corresponding to the secondary relaxation. In the case of PPGE, we observe at high frequencies a rise in the signal partly due to the presence of a faster relaxation, which, however, is never completely visible with our apparatus for the high-pressure measurements. The β -relaxation moves to lower frequencies. It is reported that the β -secondary process of PPGE is of the JG relaxation type [17]. We analyzed spectra in terms of a Cole-Cole equation (CC equation) for the secondary relaxation. As known, the CC equation is a special case of the Havriliak-Negami equation (HN equation) (1) when the symmetry parameter (β) is equal to 1

$$\epsilon(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{\left[1 + (i\omega\tau_\beta)^{1-\alpha}\right]^\beta}, \quad (1)$$

where $\epsilon^*(\omega)$ is the complex dielectric constant, $\Delta\epsilon \equiv \epsilon_s - \epsilon_\infty$: ϵ_s and ϵ_∞ are the “static” and “infinite frequency” dielectric constants, ω is the angular frequency, τ is a relaxation constant, and the parameter α is an experimentally determined correction factor. In the case of PPGE, we added a HN equation (1) for fitting the faster secondary relaxation (γ -relaxation). The shape parameters used in the HN equation for the γ -relaxation in this system were obtained from spectral fitting at very low temperature and ambient pressure where the γ -relaxation can be clearly observed. Moreover, a similar procedure was used for fitting to the tail of the structural peak when present in the spectra.

The pressure dependence of secondary relaxation for the different materials with different origins is represented in

FIGURE 2: Logarithm of the maximum frequency of the dielectric loss peak of secondary relaxation as a function of pressure at different temperatures (as indicated in the figure) for (a) PPGE, (b) PVAc.

Figure 2. The maximum frequency was calculated by $\nu_m = (1/2\pi\tau_{cc})$, where τ_{cc} is the parameter from fitting with CC function, that is, relaxation time of the τ_β , ($\beta = 1$) at (1).

The logarithm of the maximum frequency decreases linearly with increasing pressure for both systems. This dependence can be described by the pressure counterpart of the temperature Arrhenius law, $[\nu_{\max}^\beta = \nu_{P=0} \exp[-P\Delta V_\beta / (K_b T)]]$. From the analysis of the pressure dependence of the relaxation frequency, we obtained the values of ΔV_β (reported in Table 1).

4. Discussion

The experimental procedure followed for studying the temperature dependence of ΔV_β in PVAc is represented in Figure 3. A similar procedure was used for PPGE as well. In

FIGURE 3: Schematic representations of the thermodynamic paths chosen for the investigation of the temperature dependence of ΔV_β in PVAc. Square points show $T_g(P)$ line [14], and AC and DE are isothermal paths.

TABLE 1: Parameters describing the pressure dependence of secondary processes.

	$T(K)$	$d\log(\nu_{\max})/dP$ (1/MPa)	ΔV_β (mL/mol)	$\log(\nu_{\max})_{P=0}$
PPGE	293	$(26.1 \pm 1)10^{-4}$	14.7 ± 0.5	4.92 ± 0.09
	283	$(29.6 \pm 1)10^{-4}$	16.1 ± 0.5	4.61 ± 0.07
	268	$(352 \pm 2)10^{-5}$	18.2 ± 0.1	4.31 ± 0.02
	263	$(365 \pm 2)10^{-5}$	18.5 ± 0.1	4.07 ± 0.03
	253	$(369 \pm 2)10^{-5}$	18.0 ± 0.1	3.84 ± 0.02
	243	$(369 \pm 2)10^{-5}$	17.4 ± 0.1	3.5 ± 0.05
PVAc	342	$(174 \pm 3)10^{-5}$	12.3 ± 0.2	6.71 ± 0.01
	323	$(218 \pm 4)10^{-5}$	14.6 ± 0.2	6.5 ± 0.01
	302	$(32.8 \pm 1)10^{-4}$	20.6 ± 0.6	6.6 ± 0.04
	282	$(31.4 \pm 1)10^{-4}$	19.6 ± 0.6	6.4 ± 0.04
	263	$(339 \pm 6)10^{-5}$	18.5 ± 0.3	5.3 ± 0.02
	244	$(353 \pm 6)10^{-5}$	17.8 ± 0.3	4.8 ± 0.02

all the cases, the β -relaxation was investigated in the glassy state; however, in region A the glass was formed by increasing P from the temperature at which the system at ambient pressure is in the liquid state (e.g., line A-C in Figure 3). Instead, in region B, the system is already in the glassy state at ambient pressure (e.g., line D-E in Figure 3).

Figure 4 presents the values of ΔV_β as a function of temperature for PPGE and PVAc (values in Table 1). The activation volume in region A increases with decreasing temperature for both systems. Most studies about activation volume of α -relaxation, ΔV_α , in the liquid and supercooled liquid state evidence that also ΔV_α increases with decreasing temperature [18]. So, the activation volumes of the secondary relaxation in the region A have a behaviour similar to that of the α -relaxation. Instead, in region B, the activation volume of secondary relaxation is constant or slightly

FIGURE 4: Activation volume of secondary relaxation (ΔV_β) in the glassy state as a function of temperature for (a) PPGE and (b) PVAc.

decreases with temperature. This result is contrasting with the intuition that decreasing the temperature leads to the reduction of the free volume and consequently to the energy barrier to be overcome and that activation volume should increase. Finally, glass under pressure and temperature has two different regions.

The study on the relation between alpha and secondary relaxation near glass transition has shown that at T_g JG relaxation has the same position after different thermodynamic paths (different pressures and temperatures at T_g) and effect of thermodynamic paths comes after the glass transition temperature and pressure inside the glass [19, 20]. We know,

free volume inside the glass is showing a peak at T_g and this behaviour is similar to the maximum of activation volume at T_g [13]. So, our results show that the non-monotonic behaviour of secondary relaxation inside the glass does not depend on the type of secondary relaxation, but it depends on the free volume inside the glass.

5. Conclusions

We investigated the temperature dependence of the activation volume in PPGE and PVAc, exploring the region where the glass was formed either by compression (region A) or by cooling (region B). In both cases, the temperature dependence is non-monotonic since in region A the activation volume increases with a decrease of the temperature, but in region B, it decreases with a decrease of the temperature; thus, it seems that we can prepare two different regions. This behaviour does not depend on the type of relaxation.

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