PHYSICAL REVIEW B **73**, 104205 (2006)

Effect of thermodynamic history on secondary relaxation in glassy phenolphthalein-dimethyl-ether

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(Received 13 September 2005; revised manuscript received 29 November 2005; published 24 March 2006)

We present a study of the intermediate secondary relaxation process of phenolphthalein-dimethyl-ether. Though this process is intramolecular in nature, it reveals pronounced pressure dependence. Moreover, its relaxation frequency and intensity exhibit pronounced dependence on the thermal history followed during vitrification. These results suggest that the nonequilibrium nature of the glassy state influences this secondary relaxation principally through the dependence on the specific volume.

DOI: 10.1103/PhysRevB.73.104205 PACS number(s): 71.55.Jv, 77.22.Gm, 62.50.+p

I. INTRODUCTION

Glasses are in a nonequilibrium state, not only relative to the thermodynamic stable crystalline state, but also relative to the metastable-equilibrium liquidlike state, i.e., the glassy state with a minimum in the free energy. The nonequilibrium state of a glass originates from a kinetic event, occurring when the increasingly long relaxation time of the structure of the system prevents it from reaching its equilibrium molecular arrangement in the available time. The molecular arrangement frozen in the glass depends on its thermal history, and is reflected by the nonequilibrium values of its thermodynamic properties (enthalpy, volume, etc.). Therefore glasses at the same temperature and pressure, with different thermal and pressure histories, have different values of thermodynamic properties. In addition, dynamic processes can reflect the different molecular arrangement frozen in the glass. Different values of the relaxation times and relative intensities are observed when a glass is prepared by different procedures. This phenomenon is well-known for the structural process measured just below the glass temperature, T_g, after different cooling rates.[1]

Beside the structural (α) process, glassy systems exhibit one or more secondary relaxation processes, which contrary to the structural are active on the time scale of typical experiments (to 10^2-10^3 s) even in the glassy state. The microscopic nature of these processes is not completely clear: Recently criteria for distinguishing secondary processes originating from the noncooperative motion of the single entire molecule (Johari Goldstein, JG, process),[2,3] from those of intramolecular[4] origin were proposed.[5] How secondary processes depend on the molecular arrangement frozen in the glassy state is not yet well-known. In general, the JG process, reflecting the motion of the entire molecule, is supposed to be sensitive to the molecular arrangement frozen in the glass[6] and to the thermodynamic history followed in the vitrification process, in a manner similar to that of the structural one. This hypothesis agrees with some theories of relaxation dynamics predicting the existence of a secondary relaxation process that is connected to and is the precursor of the structural process.[7,8] Many experiments were performed testing the effect of thermodynamic history on secondary processes, and usually only a dependence of the relaxation strength of the secondary process is observed both for JG and intramolecular secondary processes.[2,3] Only recently, an effect of the thermal history on the relaxation frequency was shown in dipropylene glycol dibenzoate being considerable for the JG process present in this system and negligible for the intramolecular secondary process.[9] Moreover, thermal hysteresis of the secondary relaxation frequency were observed close to T_g for several secondary processes, also of intramolecular origin.[10,11]

We present a study of relaxation dynamics of phenolphthalein-dimethyl-ether (PDE) in the glassy state. Relaxation dynamics of glassy PDE presents three different features: an excess wing, developing from the high frequency tail of the structural process, and two secondary relaxation processes.[12–14] In this paper, we focus on the slower secondary process of the two, and we extend its study with respect to previous works by presenting measurements under pressure variations and measurements performed in the glassy states after different thermodynamic histories. We show that the slow secondary relaxation process cannot be considered of the JG type, according to a classification recently proposed[5] and in agreement with conclusions from NMR results,[14] although it presents pronounced pressure dependence and its characteristic relaxation frequency presents a strong dependence on the thermodynamic history followed for the vitrification. These results clearly show that not only the time scales of the structural and the JG secondary relaxation processes depend on the thermodynamic history of the glass, but that those of the intramolecular secondary relaxation processes do too. In other words, also intramolecular degrees of freedom can be sensitive to the nonequilibrium thermodynamic state of glassy materials. The interest for this type of research is both for the characterization of dynamic properties of secondary relaxation processes in glass formers, and also for the more general interest in proposing an extension of the thermodynamic description of the nonequilibrium states in glasses.

II. EXPERIMENT

A PDE sample (for the molecular structure see Ref. 15) was synthesized in the laboratory of Professor H. Sillescu and obtained from Dr. Roland Böhmer of Johannes Gutenberg Universitat, Mainz, Germany. The glass temperature of PDE at atmospheric pressure is $T_g = 298$ K (Ref. 16) and T_g was observed to vary nearly linearly with pressure with a coefficient of about 0.26 K/MPa (up to 200 MPa).[13] We present dielectric relaxation dynamics in the glassy state over eight frequency decades, studied by varying both temperature and pressure. Dielectric measurements were performed with an Alpha analyzer from Novocontrol. For isobaric measurements at atmospheric pressure the sample was placed in a parallel plate capacitor and the temperature was controlled by a Quatro Cryosystem. For measurements with varying pressure, the sample was placed again in a parallel plate capacitor that, properly insulated from the external environment, was placed in a pressure chamber, where the pressure was generated through silicon oil pumped by a manual pump. A thermostat connected to a jacket around the pressure chamber allowed control of temperature in the interval 353–233 K. Repeatability of the measurements in the supercooled liquid state was checked to assure that the sample was not contaminated by the pressure transmitting oil, after that the sample was held at high pressure.

III. RESULTS AND DISCUSSION

Previously, PDE was studied by means of several techniques, but most of the attention was focused on the structural dynamics and on the excess wing.[12–17] Only recently, Kahle and co-workers[14] showed the presence at atmospheric pressure of two distinct secondary relaxation peaks, one smaller in amplitude appearing just below T_g, and the second one, with a greater dielectric strength, appearing well below T_g. Comparing dielectric and NMR measurements they concluded that the smaller (and slower) secondary relaxation process reflects the phenyl flip motion.[14] In Fig. 1 some selected dielectric loss, ε'', spectra of glassy PDE are presented. In the upper panel measurements performed at atmospheric pressure at different temperatures are reported. The presence of a small relaxation (β) peak can be observed shifting to lower frequencies as the temperature is decreased, while the rise of the signal at higher frequencies is partially due to the other incoming secondary peak. Comparing our spectra with those reported in Fig. 4 of Ref. 14 we can conclude that the β process is the same secondary relaxation that Kahle and co-workers ascribed to the phenyl flip motion. In the lower panel of Fig. 1 measurements performed at constant temperature (275 K) by varying the pressure are reported. The increase of pressure shifts the β peak to lower frequencies. A change of P of 400 MPa causes a shift in frequency of more than one decade. The detailed analysis of the temperature and pressure dependences of the β process is outside the scope of the present paper and will be presented subsequently.

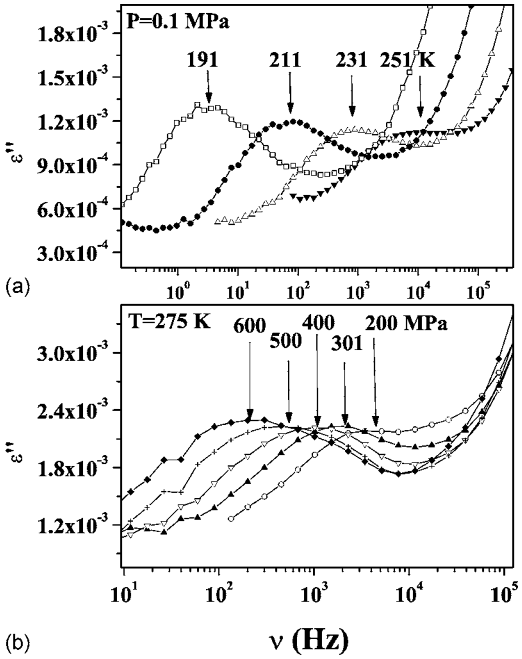

FIG. 1. Dielectric loss, ε'', spectra (symbols) as a function of frequency, ν, for glassy PDE collected (a) at P=0.1 MPa for the indicated values of temperature, and (b) at 276 K for the indicated values of pressure. The lines are guides for the eye. The peak shifting toward lower frequencies on decreasing (increasing) temperature (pressure) corresponds to the β relaxation.

It is commonly believed that JG processes should be sensitive to pressure changes. In fact, the secondary relaxation in the 17.2 mol % mixture of chlorobenzene in decalin, which is a JG process,[2,18] is pressure dependent. Of course, not only JG secondary relaxation are supposed to feel pressure variations, but, to the knowledge of the authors up until now, all secondary relaxations presenting appreciable pressure dependence are of JG type.[5,9,12,19,20] The frequency shift of the β peak of PDE at 275 K is about a factor of 10 for a pressure variation of 400 MPa and it is of the same order of magnitude than what was shown by some JG processes.[5] The β process in PDE seems to be of intramolecular origin but it shares properties usually found for the intermolecular JG processes. A quantitative criterion for distinguishing JG from intramolecular secondary processes is provided by a recent extension of the coupling model (CM).[8,21] The CM predicts that the characteristic relaxation frequency, ν_0, of its primitive relaxation is related to the characteristic frequency, ν_α, of the structural process by[8]

$$\nu_0 = (2\pi t_c)^{-n}(\nu_\alpha)^{1-n} \tag{1}$$

where t_c is a temperature independent constant (2 ps for glass formers) and n is related to the stretching parameter of the Kohlrausch function fitting to the structural peak.[8] It has been proposed, and experimentally verified,[5,21] that the primitive and the JG relaxation process should have similar dynamic characteristics, so that $\nu_0 \approx \nu_{\mathrm{JG}}$. Equation (1) provides a tool to predict the relaxation frequency of the JG process, once the parameters n and ν_α are known. In Fig. 2 two spectra of PDE are shown: one of the supercooled liquid at $P=0.1$ MPa and $T=303$ K, the other of the glass at $P=0.1$ MPa and $T=233$ K. From the analysis of the spectrum

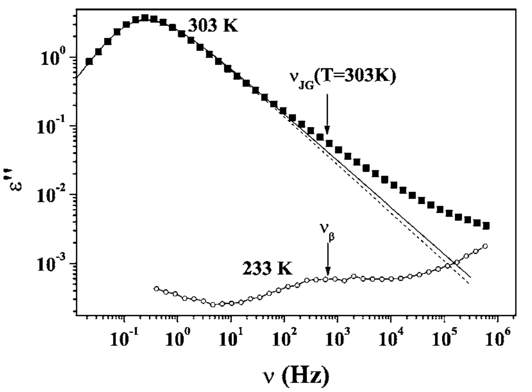

FIG. 2. Dielectric loss spectra representing the structural process at 303 K (closed squares) and the β process at 233 K (open circles connected by line). The continuous and dashed lines represent a Fourier transform Kohlrausch function with stretching parameters 0.68 and 0.7, respectively. The vertical arrows indicate the value of ν_{JG} at 303 K [Eq. (1)], and the estimated value of ν_β at 233 K.

measured above T_g we can estimate that $n=0.30\pm0.05$ and $\nu_\alpha=0.24\pm0.04$ Hz (Fig. 2), which substituted in Eq. (1) yields $\nu_{JG}\approx\nu_0=690$ Hz. Unfortunately, the β relaxation is not visible at 303 K, so that the value of ν_{JG} predicted by Eq. (1) for $T=303$ K cannot be directly compared to the experimental value of ν_β. However, the relaxation frequency of the β process reaches 690 Hz at about 233 K (Fig. 2), i.e., 70 K below the temperature at which it is predicted by Eq. (1). It can be concluded that at 303 K the relaxation frequency of the β process is much higher than that predicted by Eq. (1). Similar results have been obtained by the analysis of spectra measured varying pressure. The use of Eq. (1) as a criterion for identifying the JG relaxation led to the conclusion that the β process in PDE is of intramolecular origin, in agreement with the conclusion drawn by NMR measurements.[14] It is worth noting that in the frequency region where the CM predicts the JG process at 303 K, an excess wing is visible as a deviation from the Kohlrausch fit of the PDE spectrum (Fig. 2). The existence of an excess wing in PDE is well documented.[12,22] Then our spectra support the hypothesis that the excess wing in PDE is nothing else than a hidden secondary relaxation (in this case of the JG type), in accordance with the conclusion drawn for many other systems.[5,19,20]

Dielectric relaxation spectra at ambient pressure are presented in Figs. 3(a) and 3(b) for two different values of $T<T_g$, namely 213 and 193 K. The sample was carried to each final temperature according to two different thermal histories: first the sample was cooled from above T_g with an average rate of about 0.05 K/min (closed symbols in Fig. 3) and in a second run it was quenched from above T_g with an average rate of 20 K/min (open symbols in Fig. 3). After the rapid quench the β peak is more intense and it is located at a higher frequency than the peak observed after the slow cooling. From a rough estimation, the peak frequencies were found to differ for a factor of 2. This difference is much greater than the hysteresis effect observed in previous works for other non-JG processes,[9–11] and can be considered much greater than any experimental errors. As shown in the early study by Johari and Goldstein,[2,3] the intensity of the JG relaxation peak depends on the thermal history followed to vitrify the liquid. Also the relaxation frequency is supposed to be influenced, but only rarely such an effect was reported.[9–11] The β relaxation in PDE, which is non-JG, is sensitive to the nonequilibrium thermodynamic state of the sample. The observed dependence of the structural relaxation frequency on the cooling rate is usually explained considering that glasses formed through different routes have different values of density. Moreover, Johari proposed that also the JG process should be affected in a similar way by the density, and then by the thermodynamic history.[6] For the non-JG secondary relaxation process of PDE we found similar results to those reported for JG processes. Consequently, we can assume that different densities of the final glassy state can originate from these results: after a fast temperature jump the glassy state is less dense and the β relaxation is faster, after a slow cooling the system is more dense and the relaxation process is slower.

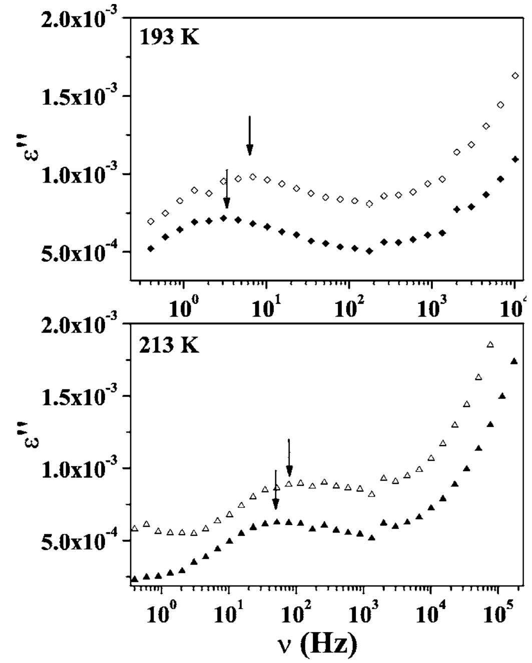

FIG. 3. Dielectric loss spectra measured at 193 and 213 K after different thermal histories: a cooling at 0.05 K/min (closed symbols) and a cooling at 20 K/min (open symbols). The arrows indicate the estimated values of ν_β.

By varying both the temperature and the pressure additional variations in the final structural state of glasses can be obtained. In Fig. 4 two spectra measured in the glassy state at $P=500$ MPa and $T=276$ K are reported, collected after two different thermodynamic paths (see inset in Fig. 4). In the first case (open squares in Fig. 4) the sample was vitrified by cooling to 276 K at ambient pressure and then the glass was isothermally compressed up to 500 MPa. In the second case (closed squares) the supercooled liquid was isothermally compressed at 353 K up to 500 MPa, entering the glassy regime at about 230–250 MPa,[13] and then the glass was cooled to 276 K. The secondary relaxation peak in the first case is more intense and located at higher frequency than in

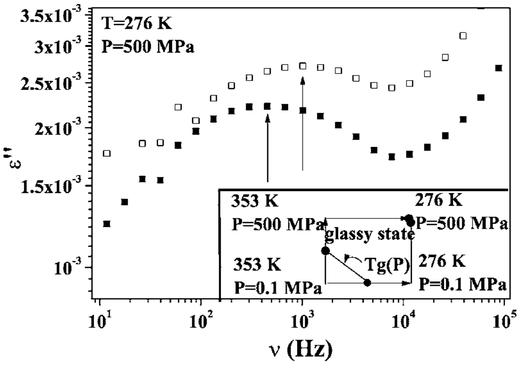

FIG. 4. Dielectric loss spectra at 276 K and 500 MPa measured after two thermodynamic paths (see the inset): in the first (open squares) the sample was vitrified by cooling at 0.1 MPa until 276 K and then it was compressed to 500 MPa. In the second one (closed squares), the sample was isothermally (353 K) compressed at 500 MPa and then cooled in isobaric condition to 276 K.

the second one (Fig. 4). In analogy to the experiment where only temperature is used, we can suppose that the first path to the vitrification produces a less dense glass with a faster secondary process than the second path.

By varying the pressure at constant temperature [Fig. 1(b)] it has been seen that the β relaxation of glassy PDE is also a function of the density. Measurements reporting the influence of the cooling rate on secondary relaxation frequency have been published for the β relaxations of dipropylene glycol dibenzoate,[9] sorbitol,[10] and pyridine-toluene solution.[11] These are all JG relaxations that are sensitive to the pressure, i.e., density. Moreover, a smaller effect is evidenced in the case of the non-JG relaxation processes of oligomers of propylene glycol[10,11] and dipropylene glycol dibenzoate,[9] which are weakly pressure sensitive. A smaller pressure dependence is accompanied by a weaker dependence of the secondary process on the thermodynamic history. The secondary process in bis(methoxyphenyl)cyclohexane, a molecular system similar to PDE, has a weaker pressure dependence and does not show any noticeable dependence on the thermodynamic history for pressures up to 500 MPa. These results suggest that in the glassy state the nonequilibrium thermodynamic state affects the secondary dynamics through a density effect, which is ineffective for non-JG secondary processes that do not feel pressure variations. To understand the behavior of PDE, it is noteworthy that a connection between the free volume, the thermal expansion coefficient, and the flip-flop motion of the phenyl ring has been previously reported for polycarbonate.[23] Consequently, a density dependence of the secondary process reflecting the flip-flop motion of the phenyl ring in PDE could be expected. Finally, it is worth noting that similarly to the results reported herein, the influence of thermodynamic history on the structural dynamics of glass forming systems is well documented and the faster the rate of cooling used to achieve the glassy state the faster is the structural relaxation time.[24–27] Since usually this result for structural relaxation was explained in terms of different densities of the obtained glasses, we propose the same explanation for the secondary relaxations. Then the same microscopic mechanism could be at the origin of the dependence on the thermodynamic history of the structural relaxation time and the secondary loss mechanisms in glasses.

IV. SUMMARY

In summary, we have shown that the β relaxation in PDE is sensitive to pressure to an extent typical of some JG process, even though it is not a JG process. Its relaxation frequency is affected by the thermodynamic history followed to vitrify the liquid system, in a manner similar to that shown by structural and JG processes. A connection seems to emerge between the pressure sensitivity of relaxation frequency of secondary processes and their sensitivity to the thermodynamic history used to form the glass, so that density seems to govern the nonequilibrium state of such processes.

ACKNOWLEDGMENTS

The support of the Polish State Committee for Scientific Research (Project No. 1PO3B 075 28) is gratefully acknowledged. M.P. also acknowledges the support of the Galileo Galilei Ph.D School in Pisa. The authors are deeply grateful to Donald J. Plazek of University of Pittsburgh for helpful discussions and valuable comments.

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