Effect of glass structure on the dynamics of the secondary relaxation in diisobutyl and diisoctyl phthalates

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The β relaxation is a principal source of information about the dynamics in the glassy state; however, the nature of this process remains a controversial issue. In this paper, we show that properties of the β relaxation measured below T_g are sensitive to the structure of the glass; that is, the thermodynamic path from the equilibrium liquid strongly affects the β relaxation times, their distribution, and the activation energy quantifying their temperature dependence. These results support the idea that the Johari-Goldstein β process is the precursor to the structural relaxation transpiring at longer times. We discuss the experimental findings in light of the heterogeneous and homogeneous scenarios for the β process.

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INTRODUCTION

The usual method of forming a glass is by cooling at a rate sufficient to avoid crystallization. This technique has been practiced for thousands of years, with glasses having found many applications, both technological and mundane, throughout our daily life. Nevertheless, many aspects of the glassy state remain shrouded in mystery, even though knowledge about the local structure and dynamics of glasses would seem essential to their full utilization.^{1–3} The liquid-glass transition remains one of the more significant unresolved problems in condensed matter physics.

Studies of the dynamical properties of low molecular glasses usually focus on two universal processes: the structural (α) relaxation and the Johari-Goldstein (JG) β relaxation.⁴ The former is identified with rearrangements of the local liquid structure, which become kinetically frozen at the glass temperature, T_g . The JG β process is believed to arise from small amplitude, noncooperative motions of molecules. It possesses two characteristic features in the glassy state, a broad (non-Debye) symmetrical relaxation function and an Arrhenius dependence of its relaxation time, τ_{β} .

The β relaxation is faster than the α process and its relaxation time changes more slowly with temperature, which allows it to be monitored in the glassy state over a wide range of temperatures. In contrast, structural relaxation is too slow and τ_{α} increases too markedly to be probed below $T_{\rm g}$. Thus, the β process is a unique source of information on the dynamics in the glassy state, and its properties can be considered as fundamental characteristics of the glass. A principal aim of this paper is to observe how changes in the structure of the glass for a given material affect the β process. Since it precedes in time structural relaxation, yet has various relationships to the latter, the β relaxation serves as the precursor to the glass transition, and thus can yield information about $T_{\rm g}$.^{5,6}

Two mechanisms for the β process have been proposed. Johari put forth the idea that in regions of lower density ("islands of mobility") molecules can partially reorient, giving rise to the β process.⁷ These islands of mobility are isolated regions of loosely packed molecules within the glassy matrix. Only molecules within such regions possess enough configurational freedom to undergo the rapid and independent motion underlying the β process. According to Johari, the β relaxation is an inhomogenous process, originating only from molecules within the islands of mobility.^{8,9} A somewhat related description is due to Tanaka,¹⁰ according to which, in the nonArrhenius regime ($\geq T_g$), the β mode is strongly modulated by the α process, so that it has the properties of the latter. However, in the Arrhenius region ($< T_g$), where α and β modes are decoupled, the β process reflects "metastable islands" and becomes pressure insensitive. The Tanaka model also envisions the secondary relaxation as a heterogeneous process.

A completely different interpretation was put forth by Williams and Watts.¹¹ They ascribed the β process to fast, small-angle reorientations of all molecules. This motion is restricted to smaller amplitudes than the primary α process.¹² While defects in the glassy matrix are an inevitable consequence of the freezing in of local density fluctuations during the vitrification, in this scenario they do not govern the β dynamics. If essentially all molecules are involved, the JG process has a homogeneous character, in contrast to Johari's concept.

These competing interpretations of the β relaxation are currently debated, with much effort devoted to understanding this basic aspect of the process.^{13–23} Clearly, progress in this area can benefit greatly from extending experimental studies beyond a single thermodynamical variable (i.e., the usual temperature measurements at ambient pressure). As various recent works have shown, high-pressure measurements can provide new insights into the relaxation dynamics of glassforming liquids.⁶

In this paper we adopt a strategy to investigate the β relaxation in two molecular liquids, diisobutyl phthalate (DIBP) and dioctyl phthalate (DIOP), by characterizing the dynamics in glassy states attained via different thermodynamical pathways. We show that the mean β -relaxation times and their distribution, as well as the activation energy,



FIG. 1. Schematic plot presenting typical behavior of the temperature evolution of α - and β -relaxation times at ambient and elevated pressure.

depend strongly on the structure of the glass. These findings are discussed within the framework of existing theories.

RESULT AND DISCUSSION

The approach herein is a natural consequence of experimental observations made recently for a number of glass formers. These are schematically depicted in Fig. 1, which shows the temperature evolution of the α - and β -relaxation times at ambient and elevated pressure. The relaxation map for high pressure is shifted toward higher temperatures, so that for a given temperature, the relaxation times have different values (vertical dotted line)—an obvious consequence of their pressure dependences. However, within the glassy state, it is usually observed that β -relaxation times are insensitive to pressure.⁶ Consequently, compression of the sample in the glassy state at some reference temperature $(T_{ref}$ in Fig. 1) up to the pressure P_{ref} should not bring about any significant change in the value of τ_{β} . Thus, the same conditions of T and P, but obtained by different routes, are expected to yield different τ_{β} . The question arises whether such a difference can be experimentally observed.

Toward this end we carried out dielectric measurements on DIBP up to very high pressures (1.8 GPa). Figure 2 shows the variation in the glass transition temperature with pressure. These values of T_g correspond to the temperature at which τ_{α} equals 100 s. Glass transition temperatures determined in this way have the same pressure dependence as T_g obtained from the volume (PVT) or from heat capacity (DSC) experiments.⁶ The solid line in Fig. 2 is the fit of the empirical Andersson-Andersson equation²⁴

$$T_{\rm g} = c \left(1 + \frac{b}{a} P \right)^{1/b},\tag{1}$$

which has the same form as the equation for the melting point of simple crystals.²⁵ To achieve the common point **M** (T=253 K, P=1.8 GPa) in the glassy state, the three paths depicted in Fig. 2 were utilized: path (a), representing iso-



FIG. 2. Pressure dependence of the glass transition temperature for DIBP, along with the different thermodynamical paths, (a), (b), and (c), used to obtain point M (T=253 K, P=1.8 GPa) within the glass. The solid line represents the fit according to Eq. (1) with the following set of parameters: a=1438 MPa, b=2.06, and c=191 K.

thermal compression of the liquid at T=253 K; path (b), in which the liquid was first compressed isothermally (T=293 K) to 1.8 GPa, followed by cooling to 253 K at constant pressure; and path (c), whereby the liquid was first pressurized at constant temperature (T=333 K) to 1.8 GPa and then cooled to 253 K. The significant difference between these routes to point *M* is the particular value of *T* (and *P*) at which the DIBP vitrified.

In Fig. 3 are the dielectric loss curves of the secondary relaxation measured for the DIBP at point M. It is readily apparent that the various pathways yield very different frequencies for the maximum in the β dispersion. A higher pressure at which the liquid-glass transition is induced corresponds to a lower frequency of the β peak. These results



FIG. 3. Loss spectra of the β relaxation in DIBP measured for the same thermodynamical end condition (point *M*) but attained using different routes (*a*), (*b*), and (*c*). Note that the magnitude of the loss curves is only approximate due to variations in the sample gap.



FIG. 4. β -relaxation times for DIOP in the glassy state, formed by the application of high pressure (\bigcirc) at 343 K followed by cooling, and (\blacktriangle) directly at 258 K. The inset shows the β dispersion in the dielectric loss for the two conditions, using the same symbols as in the main figure. The frequencies measured on the sample compressed at lower temperature (\bigstar) were multiplied by 0.09 to bring the peak positions into coincidence. Note that the magnitude of the loss curves is only approximate due to variations in the sample gap.

show unequivocally that the secondary relaxation time measured in the glassy state depends on the structure of the glass, notwithstanding its "local" noncooperative character.

To further investigate this effect, we carried out dielectric measurements of the β process in DIOP. The material has a T_g at ambient pressure equal to 188 K (which is 3° lower than that T_g of DIBP). Liquid DIOP was vitrified in two ways: (a) compression to P=1.7 GPa and at T=343 K, followed by cooling, and (b) cooling at ambient pressure to 258 K ($< T_g$), with the pressure then increased to 1.7 GPa. The τ_β for the glass formed by these two paths are shown in Fig. 4. The β -relaxation times differ by as much as one decade; that is, the same material at identical conditions of T and P exhibits very different dynamics. This reflects the influence of the structure of the glass.

The effect of the glass structure is also manifested in the activation energy for the β relaxation. E_A is substantially larger, 45.4 ± 0.5 kJ/mol, for DIOP compressed at 343 K, in comparison to compression at 258 K which yields $E_A = 27.2\pm0.8$ kJ/mol. Such behavior is characteristic not only for the DIOP; for DIBP we observe a similar increase of E_A when the liquid is compressed at a higher temperature. As discussed below, the more dense packing consequent to forming the glass at higher pressure increases both τ_β and E_A .

It is instructive to compare the two models for the β relaxation in light of the data in Figs. 3 and 4. At point *M* in the glass (Fig. 2), molecular packing, and hence the nature and extent of the putative islands of mobility, will depend on the path taken from the liquid state. Trajectory (c), for which the liquid-glass transition occurs at higher temperature and pressure $(T_g^{(c)}, P_g^{(c)})$, yields a denser glass than trajectory (a) with $T_g^{(a)}$ and $P_g^{(d)}$. According to the Johari viewpoint, below the glass transition, the defects are immersed in the disordered and rigid-glass structure. The latter being less compressible than the defects, further compression of the glass along route (a) would cause no significant change in molecular packing. Clearly, islands of mobility would be packed more densely when point M is achieved via path (c) than path (a). These differences in molecular packing lead to differences in secondary relaxation times, even though the temperature and pressure of the glass at point M are identical. Thus, if the thermodynamical state M is achieved along pathway (c), a larger value of the secondary relaxation time of glass is expected. It should be noted that physical aging, which also densifies the glassy state, has a similar effect on τ_{β} .^{18,26}

Examination of the spectra in Figs. 3 and 4 (inset) also reveals that the more compressed glasses, having longer τ_{β} , also have broader loss peaks. This is manifested mainly on the high frequency side. The implication is that less dense regions are preferentially removed by the pressurization of the liquid, which contributes to the increase in the mean relaxation time. In terms of the Johari model, the distribution of islands of mobility becomes skewed towards lower frequency.

Thus, we can state that Johari's islands of mobility model is consistent with the experimental observations herein. However, strictly speaking, our results are not at odds with the Williams-Watts homogeneous model of the β process. There is no prediction for the effect of molecular packing on the restricted rotation of all molecules within the glass. Our results reveal that the motion becomes slower, and presumably more restricted (smaller amplitude) for denser packing. The fact that the dependence of the glass transition on thermodynamic variables originates with the JG relaxation supports the idea that the latter process is the precursor to the glass transition. The JG process senses thermodynamic variables, as evidenced by the change in *T* dependence of τ_{β} at T_{g} .^{27,28}

CONCLUSIONS

Summarizing, we studied the behavior of the secondary relaxation under high pressure conditions in DIBP and DIOP. It was shown experimentally that the β -relaxation time and its activation energy depend strongly on the thermodynamic pathway from the equilibrium liquid; that is, the local, non-cooperative β relaxation senses the structure of the glass. The features of the β relaxation presented herein can be rationalized in the framework of heterogeneous models for the JG process, although the data do not allow a discrimination between competing interpretations.

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- ¹R. Zallen, *The Physics of Amorphous Solids* (John Wiley & Sons, New York, 1983).
- ²C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. 88, 3113 (2000).
- ³C. A. Angell, Science **267**, 1924 (1995).
- ⁴M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).
- ⁵K. L. Ngai and M. Paluch, J. Phys. Chem. B **107**, 6865 (2003).
- ⁶C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
- ⁷G. P. Johari and M. Goldstein, J. Phys. Chem. **53**, 2372 (1970).
- ⁸G. P. Johari, J. Phys. Chem. **58**, 1766 (1973).
- ⁹G. P. Johari, J. Non-Cryst. Solids **307-310**, 317 (2002).
- ¹⁰H. Tanaka, Phys. Rev. E **69**, 021502 (2004).
- ¹¹G. Williams and D. C. Watts, Trans. Faraday Soc. **67**, 1971 (1971).
- ¹²M. Vogel and E. Rössler, J. Phys. Chem. **115**, 10 (2001).
- ¹³A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, Europhys. Lett. **40**, 649 (1997).
- ¹⁴M. Vogel and E. Rössler, J. Phys. Chem. B **104**, 4285 (2000).
- ¹⁵J. Mattsson, R. Bergman, P. Jacobsson, and L. Börjesson, Phys. Rev. Lett. **90**, 075702 (2003).
- ¹⁶N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. E 62,

4435 (2000).

- ¹⁷J. C. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).
- ¹⁸U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).
- ¹⁹K. L. Ngai and M. Paluch, J. Phys. Chem. **120**, 857 (2004).
- ²⁰R. Casalini and C. M. Roland, Phys. Rev. Lett. **91**, 015702 (2003).
- ²¹S. Hensel-Bielowka and M. Paluch, Phys. Rev. Lett. **89**, 025704 (2002).
- ²²A. Döss, M. Paluch, H. Sillescu, and G. Hinze, Phys. Rev. Lett. 88, 095701 (2002).
- ²³A. Resier, G. Kasper, and S. Hunklinger, Phys. Rev. Lett. **92**, 125701 (2004).
- ²⁴S. P. Andersson and O. Andersson, Macromolecules **31**, 2999 (1998).
- ²⁵S. E. Babb, Rev. Mod. Phys. **35**, 400 (1963).
- ²⁶D. Prevosto, S. Capaccioli, M. Lucchesi, P. A. Rolla, and K. L. Ngai, J. Phys. Chem. **120**, 4808 (2004).
- ²⁷M. Paluch, C. M. Roland, S. Pawlusl, J. Ziolo, and K. L. Ngai, Phys. Rev. Lett. **91**, 115701 (2003).
- ²⁸T. G. Blochowicz and E. A. Rossler, Phys. Rev. Lett. **92**, 225701 (2004).