Changes in dynamic crossover with temperature and pressure in glass-forming diethyl phthalate

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(Received 24 February 2003; published 12 August 2003)

Dielectric relaxation measurements have been used to study the crossover in dynamics with temperature and pressure, onset of breakdown of the Debye-Stokes-Einstein law, and the relation between the α and the β relaxations in diethyl phthalate. The measurements made over 10 decades in frequency and a broad range of temperature and pressure enable the dc conductivity and the α- and the β-relaxations to be studied altogether. The isobaric data show that the α-relaxation time τ_α has temperature dependence that crosses over from one Vogel-Fulcher-Tammann-Hesse form to another at $T_B \approx 227$ K and $\tau_\alpha \approx 10^{-2}$ s. The dc conductivity σ exhibits similar crossover at the same T_B. At temperatures above T_B, τ_α and σ have the same temperature dependence, but below T_B they become different and the Debye-Stokes-Einstein law breaks down. The breadth of the α relaxation is nearly constant for $T < T_B$, but decreases with increasing temperature for $T > T_B$. The time dependence of τ_β is Arrhenius, which when extrapolated to higher temperatures intersects τ_α at T_β nearly coincident with T_B. Isothermal measurements at various applied pressures when compared with isobaric data show that the shape of the α-relaxation depends only on τ_α, and not on the T and P combinations. At a constant temperature, while τ_α increases rapidly with pressure, the β-relaxation time τ_β is insensitive to applied pressure. This behavior is exactly the same as found in 1,1'-bis (p-methoxyphenyl) cyclohexane. The findings are discussed in the framework of the coupling model.

INTRODUCTION

Many molecular liquids can be supercooled to avoid crystallization and eventually transformed to the glassy state [1–3]. For those that possess permanent dipole moment, broadband dielectric spectroscopy can be used to probe different molecular motions over a wide range of time scales from picoseconds in the liquid to hundreds of seconds in the vicinity of glass transition [4–9]. Typical relaxation processes observed by means of this spectroscopy method are the cooperative α-relaxation and the local, noncooperative secondary β relaxation [4,5,7,10–15]. The secondary β relaxations are either of intramolecular or intermolecular in origin. The latter is best exemplified by the secondary relaxations in rigid molecules and often referred to as the Johari-Goldstein (J-G) relaxation. However, at the present time, there is no general agreement on the precise definition of a J-G relaxation. In addition, there is the dc conductivity σ, which originates from mobile ions commonly present in dipolar liquids. As dc conductivity is related to viscosity of the liquid by the combination of Nernst-Einstein and Stokes-Einstein equations, it also provides useful information about the α relaxation [4,16–23].

In recent years, the change in relaxation dynamics at a temperature T_B (about $1.2 T_g$ for fragile liquids and even higher for intermediate liquids) from a simpler one at higher temperatures to a more complex one at lower temperatures has drawn considerable interest [15,24,25]. The temperature dependence of α-relaxation time τ_α is well described by a Vogel-Fulcher-Tammann-Hesse (VFTH) equation for $T > T_B$, but conforms to another VFTH equation for $T < T_B$ [24,26]. Above T_B the temperature dependences of the self-diffusion coefficient and viscosity are the same, but below T_B they differ leading to a breakdown of the Stokes-Einstein

relation [26–28]. From extrapolation, T_B seems to be the temperature below which the secondary relaxation emerges and splits off from the α relaxation. T_B is also the temperature above which the dispersion of the α relaxation is narrow and below which the dispersion becomes broader [29,30]. Up to now, most experimental works on the dynamics of supercooled liquids are based on temperature variation at atmospheric pressure [4–6,11,12,19,20,24,25]. As an alternative to temperature change, the dynamics of the relaxation processes also can be investigated by compression of a liquid at constant temperature. The effect of pressure on the dynamics is determined by the activation volume, in analogy to activation energy in temperature variation [8,14,21–23,31–39]. Of course, our understanding of the dynamics of various processes can be improved by measurements by varying both temperature and pressure. In this paper, we present an experimental study of dynamic glass transition at different pressures and temperatures in diethyl phthalate (DEP), a low molecular liquid. This liquid has a resolved secondary relaxation at lower temperatures and Arrhenius temperature dependence for τ_β, which when extrapolated to higher temperatures seems to indicate that τ_β merges with τ_α at a temperature T_β, nearly the same as T_B. This behavior suggests that of a typical Johari Goldstein. However, the pressure dependence of τ_β indicates otherwise, as we shall see from the results to be presented.

EXPERIMENTAL

The molecular structure of the diethyl phthalate is displayed in inset of Fig. 2. The sample was supplied by Aldrich Chemicals. The temperature-dependent dielectric measurements were carried out using the experimental setup made by Novo-Control GmbH. This system was equipped with a
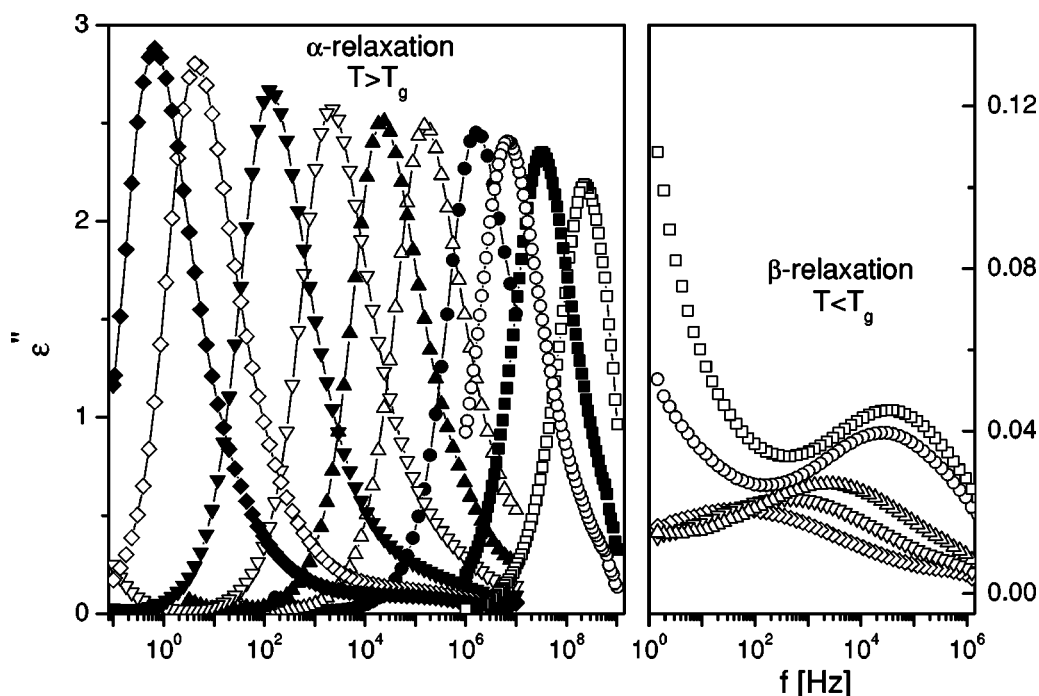
FIG. 1. The frequency dependence of the dielectric loss ε'' for DEP at different temperatures. Left part of the figure presents evolution of α relaxation for $T>T_g$. Right part presents dependence of β-relaxation process for temperatures lower than T_g.

Novo-Control GMBH Alpha dielectric spectrometer ($10^{-2}-10^7$ Hz) and Agilent 4291B impedance analyzer ($10^6-1.8\times10^9$ Hz) for measurement of the dielectric permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$. The sample was placed in a parallel plate cell (diameter 20 mm, gap 0.1 mm). The temperature was controlled using a nitrogen-gas cryostat, with temperature stabilization better than 0.1 K.

For high-pressure measurements, we used a pressure system constructed by UNIPRESS with a home-made special flat parallel capacitor. The pressure was exerted on the sample by steel piston. The tested sample was in contact only with stainless steel and Teflon. The temperature was controlled to within 0.1 K by liquid flow provided by a thermostatic bath.

RESULTS AND DISCUSSION

A. Isobaric measurements

The isothermal dielectric loss spectra of DEP are depicted in Fig. 1. The left panel shows the dominant primary α relaxation for $T>T_g$, which progressively slows down and the width becomes broader with decreasing temperature. The right panel shows data taken at temperatures below T_g. At these temperatures, the α relaxation is moved out of accessible frequency range and the weaker β-relaxation becomes the main feature in the spectra.

Figure 2 shows the dependences of the primary and the secondary relaxation times on temperature at atmospheric pressure. The results obtained from the spectra in Fig. 1 provide a complete relaxation map of both processes in the supercooled and glassy state. The most probable relaxation time τ_β of the β relaxation follows an Arrhenius temperature

behavior, while the primary relaxation time has stronger temperature dependence. On extrapolating the Arrhenius temperature dependence of τ_β to higher temperatures (dotted line in Fig. 2), τ_β intersects τ_α at $T_\beta=227$ K, the apparent merging temperature. However, because the result relies on extrapolation, an actual merging of the α and β relaxations at T_β may not necessarily take place at T_β and in the manner as indicated in Fig. 2 [11,24].

Often the temperature dependence of τ_α can only be described by more than one VFTH equation. This is conveniently brought out by the method proposed by Stickel and co-workers [11,24]. They observed that any VFTH dependence of a measured quantity x will be transformed to a linear dependence on $1/T$ when the new variable ϕ_x
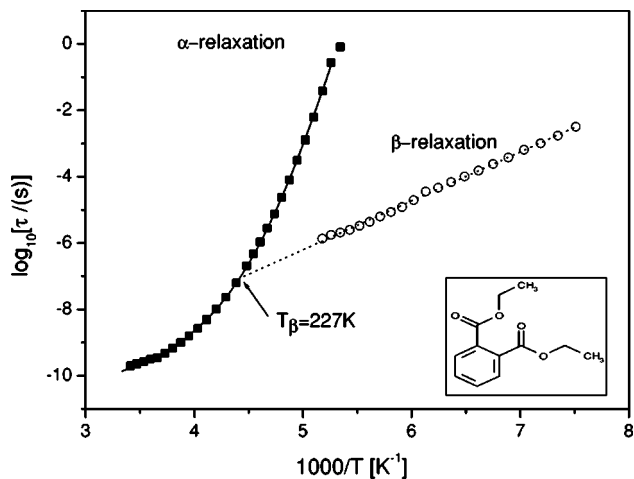

FIG. 2. A comparison of temperature dependence of α- and β-relaxation times for DEP.
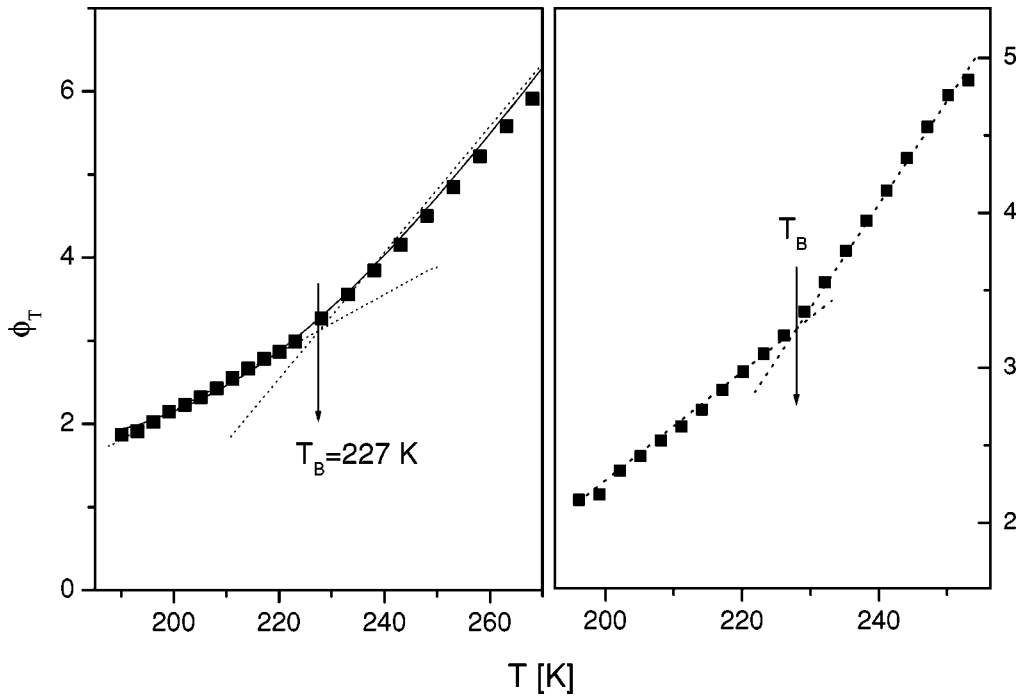
FIG. 3. In the left part of figure is presented the derivative quantity ϕ_T vs temperature as obtained from α-relaxation times data. The solid curve represents the Stickel representation of the Cohen-Grest fit data [47,48]. The right part presents the Stickel plot obtained from dc conductivity data. The dotted lines represent VFTH behaviors; the arrow indicates the crossover temperature T_B.

$=[d(\ln(x))/d(1000/T)]^{-1/2}$ is considered, and the need for two VFTH equations to fit the data becomes absolutely clear. We apply this method to τ_α and the dc conductivity, and the results are shown in Fig. 3. For both measured quantities, two different VFTH equations, valid respectively in two distinct temperature regimes separated by a temperature T_B, are needed to fit the data. It is striking that $T_B=227$ K is the same for ϕ_τ and ϕ_σ, and is equal to T_β. This behavior suggests a change of the dynamics of the sample on cooling past $T_B=227$ K. For $T>T_B$, molecular motions move practically in noncooperative fashion, whereas for $T<T_B$ the motions are cooperative [29].

As a further evidence of occurrence of a crossover in dynamics near T_B, we make a crossplot of $\log\sigma$ against $\log\tau_\alpha$ in Fig. 4. The Debye-Stokes-Einstein (DSE) relation [22,23]

$$\sigma\tau=\text{const.,} \qquad (1)$$

if valid, implies that the data would fall on a straight line with slope s equal to -1 in Fig. 5. This is true only at temperatures higher than T_B ($s=0.99$). Below T_B, the slope is noticeably different from -1 and the DSE law breakdowns, as was found in many systems with high viscosity on approaching the glass transition [18–20,22,23]. The fractional Debye-Stokes-Einstein (DSE) law [22,23] is

$$\sigma\tau^S=\text{const.,} \qquad (2)$$

where s is a fractional exponent less than 1, now replaces Eq. (1). For DEP, $s=0.92$ at temperatures below T_B.

In Fig. 5, the dependences of τ_α and σ on T are superimposed on the same plot. One can again observe two distinct

temperature regions (Fig. 6). For $T>T_B$, both quantities superpose well to indicate that they have the same temperature dependence, but below T_B one can see that they decouple from each other. It is remarkable that the same temperature T_B has been found for the crossover in the temperature dependences of τ_α and σ as well as the onset of the breakdown of the DSE law.

The crossover behavior is also visible in the temperature dependence of the shape parameters of the primary relaxation absorption peak, α and $\alpha\beta$, determined by Havrilak-Negami fits to the dielectric spectra:
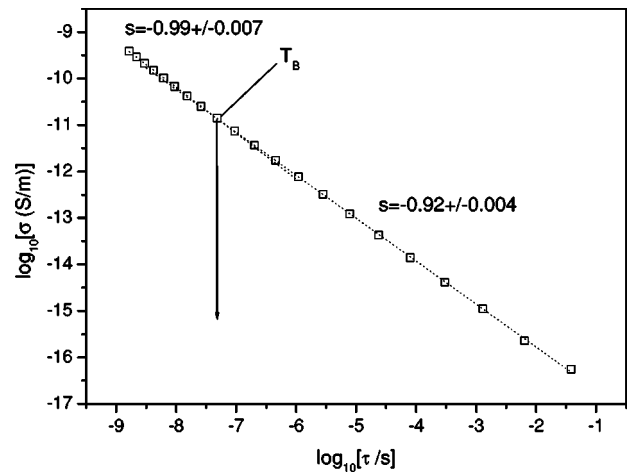

FIG. 4. dc conductivity vs α-relaxation times on a log-log scale, obtained from isobaric data in DEP. The arrow indicates the temperature of transition from DSE to FDSE law. Error bars for all data points are smaller than the used symbol size.
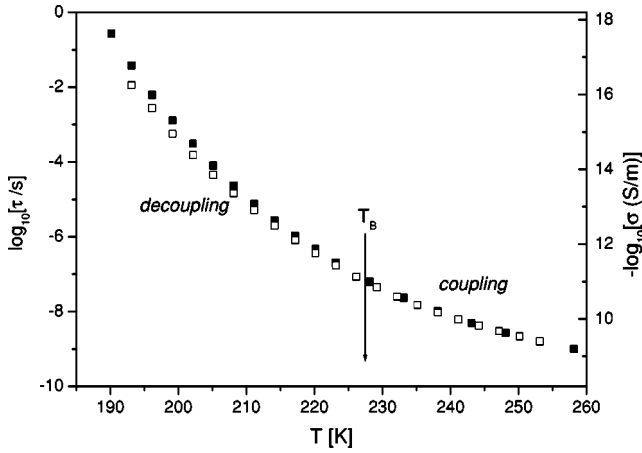
FIG. 5. Temperature dependence of the α-relaxation times and the rescaled dc conductivity superimposed on one curve. The arrow points out the temperature T_B, at which decoupling takes place.

$$\varepsilon^*(\omega) = i\frac{\sigma}{\omega\varepsilon_0} + \varepsilon_\infty + (\varepsilon_S - \varepsilon_\infty)[1 + (i\omega\tau_{HN})^\alpha]^{-\beta}, \quad (3)$$

where σ and ε_0 denote dc conductivity and permittivity of free space, respectively, ε_∞ represents the asymptotic value of the permittivity at high frequencies, ε_s is the value of the opposite limit, τ_{HN} is the characteristic relaxation time, and α and β are parameters in the range between 0 and 1 [40]. The parameter α, which describes shape of the low-frequency flank of the peak, is almost constant and close to unity. The other shape parameter $\alpha\beta$ describing the slope of the high frequency wing is constant at temperatures below 220 K. Above 220 K, $\alpha\beta$ increases monotonically with increasing temperature. This means that it is only in the temperature range below T_B that time-temperature superposition is fulfilled [41]. Above T_B, the loss peak narrows with increasing temperature and becomes almost a Debye process at the higher measurement temperatures.

B. Isothermal measurements

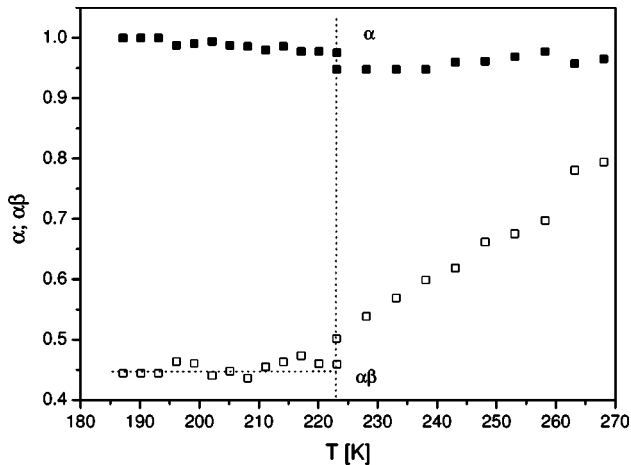By comparing isobaric data with isothermal data, important conclusions can be drawn. In Fig. 7, we present shape

FIG. 7. Shape parameters α, $\alpha\beta$ vs the α-relaxation times for $T < T_B$. In all presented temperature and pressure ranges time-temperature-pressure-superposition law is fulfilled.

parameters α and $\alpha\beta$ as functions of the primary relaxation time τ_α, obtained from isobaric (at constant $P = 0.1$ MPa) and isothermal (at constant $T = 293$ K) measurements. The data from both isobaric and isothermal measurements superimpose almost on top of each other. Hence, over the whole time range of about eight decades, isochronal temperature-pressure superposition holds for the α relaxation. (Note that the above behavior is valid below the crossover temperature only.) However, the entire spectrum, including both the α and β relaxations, does not obey isochronal temperature-pressure superpositioning. This is shown in Fig. 8 for two combinations of T and P which have exactly the same shape and location in the α-relaxation loss peak, but not in the β relaxation. The τ_β of the two cases differs by more than an order of magnitude. This lack of correspondence between the α and β relaxations of DEP is to be contrasted with that found in sorbitol at lower pressure range [37]. In sorbitol, τ_β is the same for two different P and T combinations that have the same τ_α. This difference between DEP and sorbitol in

FIG. 6. Shape parameters α, $\alpha\beta$ vs temperature. Vertical dotted line indicates temperature at which decoupling takes place.
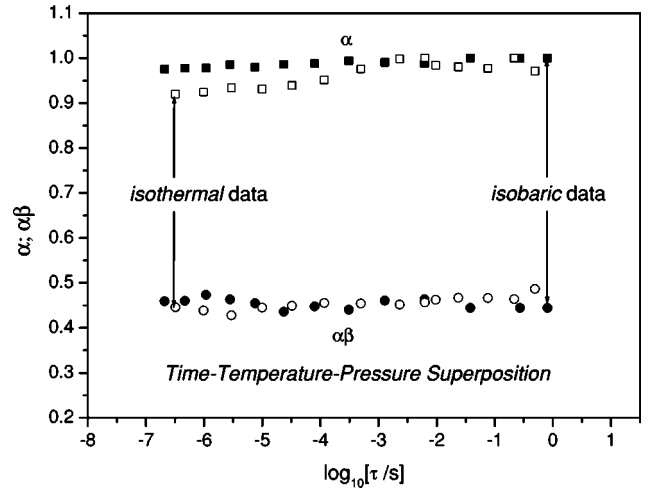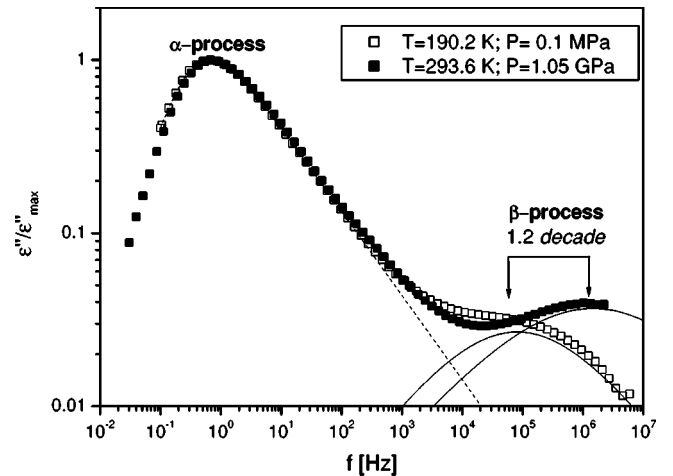

FIG. 8. A comparison of the dielectric loss spectra obtained from isothermal and isobaric measurements for DEP.
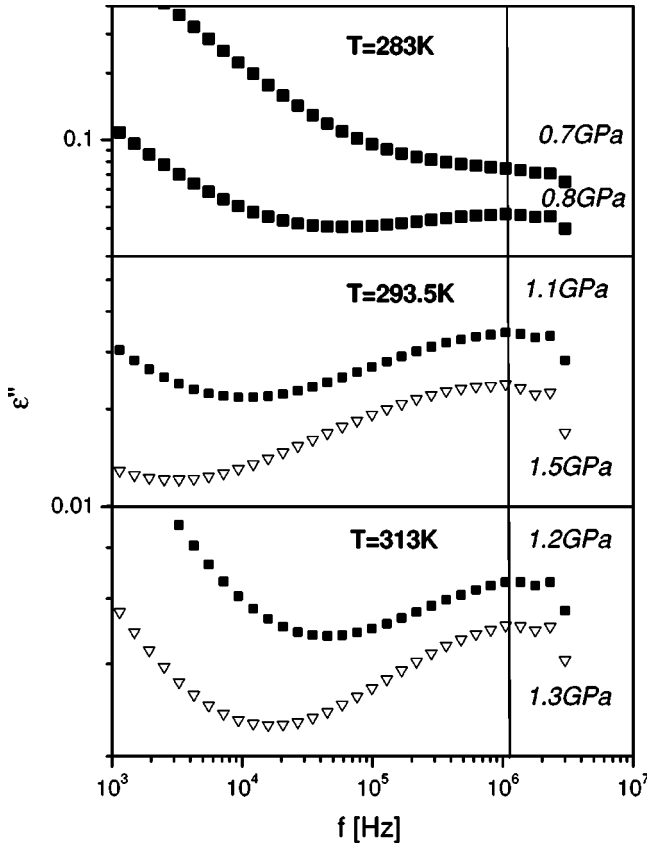
FIG. 9. A comparison of the pressure evolution of the β-relaxation loss spectra for three isotherms. The vertical dotted line points out maximum of the β-relaxation peaks.

the relation between the α and β relaxations indicates that the β relaxations in them are of different kinds, even though both β relaxations when extrapolated seem to merge with the α relaxation. There is also another difference between the β relaxation in DEP and sorbitol in relation to an interpretation of the coupling model (CM) [42,43]. A key concept of the CM is the independent relaxation. According to the CM, its relaxation time τ_0 is related to the α-relaxation time τ_α by

$$\tau_0 = t_c^n \tau_a^{1-n}, \tag{4}$$

where $t_c (\sim 2 \text{ ps})$ is a temperature-independent constant and $(1-n)$ is the Kohlrausch-Williams-Watts fractional exponential function $\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]$ used to fit the dielectric loss peak by the one sided Fourier transform,

$$\varepsilon''(\omega) = \Delta\varepsilon \int_0^\infty dt \sin(\omega t)(-d\phi/dt). \tag{5}$$

It was found that for many glass formers, certain β relaxation is closely akin to the independent relaxation in CM [42,43]. Such a β relaxation has its most probable relaxation time τ_β located near the independent relaxation time τ_0 of the CM at T_g [42] and temperatures above [43], e.g.,
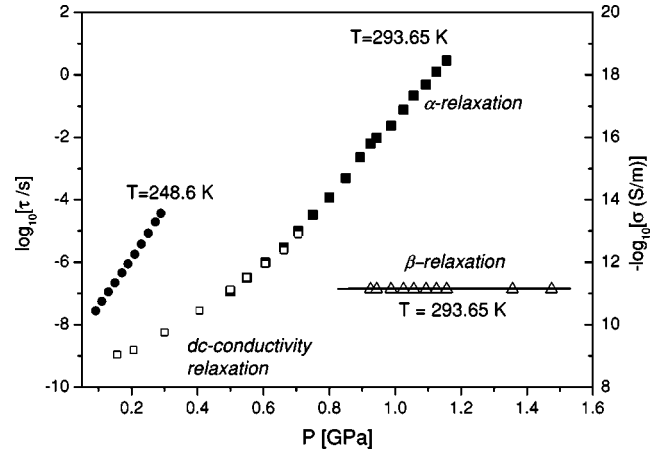
$$\tau_\beta \approx t_0. \tag{6}$$

FIG. 10. A comparison of pressure dependence of α- and β-relaxation times for DEP. The open squares represent dependence of dc conductivity relaxation superimposes (after rescaling) on the α-relaxation data for isotherm 293.65 K.

τ_0 calculated by Eq. (4) from dielectric relaxation data of sorbitol taken at ambient pressure [42,43] and at high pressures [37] is consistent with Eq. (6) for the location of τ_β of the secondary relaxation in the spectrum. This agreement does not hold for DEP. The best KWW fit to the α peak in Fig. 8 gives $n = 0.36$ and it follows from Eq. (4) that $\ln(f_0 \equiv (1/2\pi\tau_0)) = 3.85$. This value is about one decade and two decades lower than the apparent peak frequency of the observed β relaxation at $T = 190.2$ K, $P = 0.1$ MPa and $T = 293.6$ K, $P = 1.05$ GPa, respectively. This difference suggests that the β relaxation in DEP is of different kind than that in sorbitol and other glass formers, which have τ_β nearly the same as τ_0. In some glass formers, two secondary relaxations were observed [25,44]. At the glass transition temperature, one secondary relaxation is located at a frequency much higher than that calculated via Eq. (4), while there is good agreement for the other secondary relaxation [45].

While isothermal data show that τ_α changes rapidly with pressure, the opposite is observed in τ_β. The secondary re-
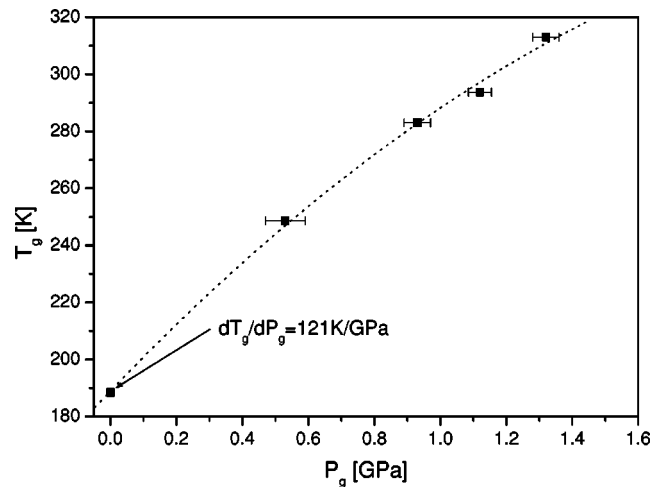

FIG. 11. Pressure dependence of the glass-transition temperature. $T_g(P)$ data were fitted by the second-order polynomial.

TABLE I. The effect of pressure on the glass-transition temperature in the examined material and some other substances.

Material	$(dT_g/dP)_{P=0.1\,\text{MPa}}$ (K/GPa)
Diethyl phthalate	121
Poly(bisphenol A-co-epichlorohydrin), glicydyl end capped [51]	141
Cresolphthalein-dimethylether [8]	300
BMMPC [50]	250
Polymethylphenylsiloxane [33]	280
Poly(propylene glycol) 400 [38]	140
Poly(propylene glycol) 4000 [38]	192

laxation turns out to be insensitive to pressure. To show this, we depict in Fig. 9 six spectra, two spectra at different pressures per isotherm at $T=283$, 293.5, and 313 K. The striking feature is that, for all the different combinations of pressure and temperature, the loss peak attributed to the β relaxation does not seem to move. The pressure dependences of the primary and the secondary relaxation times for two isotherms $T=248.6$ and 293.65 K are shown in Fig. 10. Since at 293.65 K the DSE relation is valid, we can superimpose on one curve τ_α and σ [4]. The most remarkable feature in the relaxation map is the independence of τ_β on pressure, in contrast to its strong dependence on temperature (see Fig. 2). Thus, the β relaxation process in DEP can be considered as thermally activated [46]. In contrast, $\tau_\beta s$ of the β relaxation in sorbitol [37] and in 17.2 mol % of chlorobenzene in cis +trans decalin [47] show some pressure dependence.

Finally, we examine the effect of pressure on the glass-transition temperature. Herein we define T_g as a temperature at which the relaxation time of the primary process is equal to 10s. The results, presented in Fig. 11, show that T_g of DEP is strongly dependent on compression [49,50]. To parametrize the pressure dependence of T_g, we employed a quadratic function fit to the data, and from which we estimate that the rate of change $(dT_g/dP)_{P=0.1\,\text{MPa}}$ is equal to 121 K/GPa for DEP [33]. For a comparison with the presented result, data for some other materials are presented in Table 1.

C. Conclusion

The isobaric measurements show the crossover in dynamics of DEP at $T_B=227$ K. The crossover is exemplified by (1) the change of the temperature dependence of the α-relaxation time τ_α from one VFTH dependence to another, (2) apparent merging of the β relaxation with the α relaxation at T_B, (3) decoupling of the dc conductivity from the α relaxation at temperatures below T_B, and (4) rapid narrowing of the α-relaxation dispersion at temperatures above T_B. Isothermal measurements at various applied pressure show that the α-relaxation dispersion by itself obeys isochronal temperature-pressure superposition, but not when the α and β relaxations are taken together. This breakdown of isochronal temperature-pressure superposition is due to the sensitive dependence of τ_α to pressure but the independence of τ_β to pressure. The analogy of the pressure independence of τ_β in DEP suggests that the β relaxation in DEP is not of the same kind as in sorbitol and 17.2 mol % of chlorobenzene in cis +trans decalin, where some pressure of τ_β has been observed.

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