PHYSICAL REVIEW E VOLUME 61, NUMBER 1 JANUARY 2000

Scaling behavior of the α relaxation in fragile glass-forming liquids under conditions of high compression

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(Received 1 June 1999)

The effect of pressure variation on dynamics of α relaxation process in poly[(phenyl glycidyl ether)-*co*-formaldehyde] has been investigated both under isothermal ($T=293\,\mathrm{K}$) and isobaric ($P=0.1$, 60, 120, 180, and 240 MPa) conditions using broad band dielectric spectroscopy (10^{-2} to $10^{6}\,\mathrm{Hz}$). The α relaxation is analyzed by means of the Havriliak-Negami relaxation function which has two shape parameters (α and γ) to characterize non-Debye behavior. As a result we found that the shape parameters of the dielectric function collected for different pressures fall on master curves constructed by plotting α and $\alpha\gamma$ against the logarithm of relaxation time. The scaling of shape parameters for different pressure stems from pressure independence of fragility. This provides strong experimental evidence supporting correlation of non-Debye behavior with non-Arrhenius relaxation under high pressure. From an analysis of the shape parameters of relaxation function, in terms of the Schonhals and Schlosser model, we drew conclusions that the molecular mobility of PPG is controlled in the same way by temperature and pressure. The relaxation times exhibit a clear non-Arrhenius behavior under isothermal and isobaric condition.

PACS number(s): 64.70.Pf, 77.22.Gm, 65.50.+m

INTRODUCTION

The vitrification process both in low molecular weight liquids and in complex systems, like polymers, is usually studied as a function of temperature at ambient pressure. Although cooling of a metastable liquid is the procedure most often applied to induce the liquid-glass transition, it does not mean that it is the only route leading to glassy state [1]. Among other ways there is also the possibility to generate glass transition by compressing liquid. The influence of pressure on the dynamics of supercooled liquids is in many respects similar to the effect of temperature [2]. In a previous paper we showed that the isothermal pressure dependence of dielectric relaxation times (or viscosity) can be described analogously to temperature dependence at atmospheric pressure [2,3]. As the glass transition is approached through compression of the liquid, the α-relaxation time τ increases in the non-Arrhenius fashion and shows a curvature analogous to the temperature dependence of τ. As a result, it was found for fragile glass-forming liquids that isothermal data $\tau(P)$ does not obey the simple volume activation model: $\tau=\tau_0\exp(PV/RT)$ [2].

A non-Arrhenius temperature (or pressure) evolution of relaxation times is not the sole characteristic feature of dynamics of supercooled liquids and glasses. It has been known for a long time that dynamics glass transition also features the non-Debye behavior of the relaxation function or equivalently nonexponential character of response function [4]. Unfortunately, only few experimental papers that analyze the influence of pressure on the shape dielectric function are available [5]. It is still unclear how the pressure variation would influence on the nonexponentiality. The exploration of this question is partially possible due to the correlation which has been established between the shape of relaxation function (nonexponentiality) and the degree to which normalized the temperature dependence of relaxation time departs from Arrhenius behavior (fragility) [6]. Analyzing the pressure effect on fragility one can come to some conclusions regarding the influence of isothermal density changes on nonexponentiality. In particular, if $\tau(T_g/T)$ dependencies obtained at different pressures constitute a master curve (fragility is pressure independent) then one would expect that temperature characteristics of nonexponentiality for various pressures will also fall onto a single scaling curve. In these considerations we have skipped, however, over a fundamental question, whether or not the correlation quoted is still preserved under the condition of high compression. Therefore, it may be of interest to explore the consequences of pressure variation on correlation between fragility and nonexponentiality.

The aim of this paper is to study the problems discussed above. Among other things we examine if the scaling behavior of α relaxation in glass-forming liquid is influenced by high pressure. To this effect we carried out the measurements of dielectric relaxation function in poly[(phenyl glycidyl ether)-*co*-formaldehyde] over a wide range of pressure, temperature, and frequency.

EXPERIMENT

Poly[(phenyl glycidyl ether)-*co*-formaldehyde] (PPG) with an average molecular weight of about 345 was purchased from Aldrich Chemicals. This compound, similarly as other epoxy systems, exhibits a permanent strong dipole moment originating from the epoxy ring [7–9]. It is noteworthy

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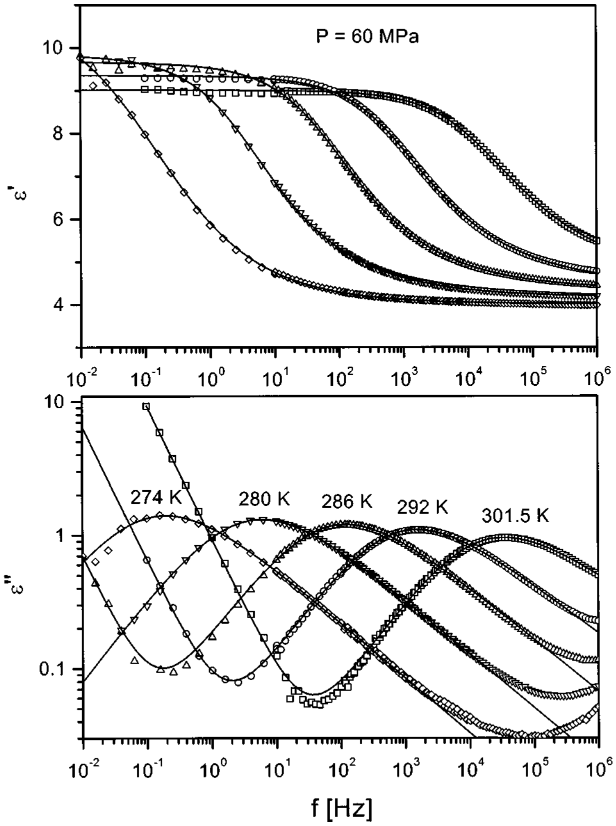

FIG. 1. Real and imaginary parts, ε' and ε'', of the dielectric permittivity of PPG versus frequency at constant pressure and different temperatures. The experimental data have been fitted by the superposition of a conductivity contribution and a relaxation function according to Havriliak-Negami.

that the glass transition temperature $T_g = 264\,\mathrm{K}$ at ambient pressure [determined from differential scanning calorimetry (DSC)] is relatively high which facilitates the high-pressure experiments.

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured in the frequency range from 10^{-2} Hz up to 10^6 Hz. In this frequency range two systems were used: a frequency response analyzer (Solartron SI-1260) and an impedance analyzer (HP-4192). The experimental setup used for high-pressure dielectric studies has been described in detail elsewhere [10]. The pressure was measured by a Nova Swiss tensometric pressure meter, with resolution ±0.1 MPa and accuracy ±0.4 MPa. The temperature was varied in interval 270–330 K and was controlled within ±0.1 K by means of a liquid flow provided by a thermostatic bath.

RESULTS

Measurements of complex dielectric permittivity have been carried out for five different isobars (0.1, 60, 120, 180, and 240 MPa) and one isotherm (293 K). Typical dielectric spectra measured in PPG for various temperatures and at constant pressure are displayed in Fig. 1. The presented spectra exhibit two different relaxation modes. The most prominent relaxation process, occurring as a maximum of loss curve, is associated with the α process whereas an upgoing trend in $\varepsilon''(\omega)$ at the lowest frequencies is identified as dc-conductivity relaxation which occurs due to the presence of charged carriers in liquid. In order to extract information about the shape of the relaxation function of the α-relaxation process, the experimental data $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ have been analyzed by an empirical relaxation function introduced by Havriliak and Negami (HN) [11]. Since loss spectra also cover dc conductivity, the appropriate term, $\sigma_0/\omega\varepsilon_0$, which accounts for such behavior has been added to the HN form. Therefore, the fit function representing the frequency dependence of the complex dielectric permittivity takes the following form:

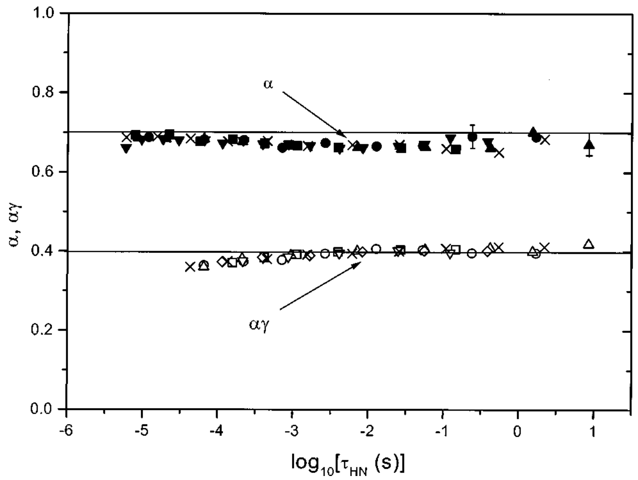

FIG. 2. Parameters α and $\alpha\gamma$ determined from isobaric and isothermal data versus log τ_{HN}. The solid straight lines are guides for the eyes. The symbols are the same as in Fig. 3.

$$\varepsilon^*_{HN}(\omega) = i\frac{\sigma_0}{\omega\varepsilon_0} + \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)[1 + (i\omega\tau_{HN})^\alpha]^{-\gamma}, \quad (1)$$

where σ_0 and ε_0 denote dc electrical conductivity and permittivity of free space, ε_∞ represents the asymptotic value of the permittivity at high frequency, ε_s is the value of the opposite limit, τ_{HN} is the characteristic relaxation time, and α and γ are parameters ranging between 0 and 1.

Equation (1) yields satisfactory fits (solid line) to data given in Fig. 1. At very high frequencies, deviations from assumed behavior were only observed. These deviations could be attributed to the second relaxation process, the maximum of which is situated beyond our measurement frequency range (the peak of the secondary process was not seen even in the lowest temperatures studied here). Since it has been assumed that its influence on the result of our analysis can be neglected, therefore, this additional relaxation process was excluded from the fitting procedure. The fits by means of Eq. (1) were not made simultaneously for the real and imaginary parts of complex permittivity. However, the similar values of parameters in Eq. (1) have been obtained in both cases. Finally, we used parameters resulting from fits of the imaginary parts of the dielectric permittivity for further analysis. An independent analysis of dispersion and absorption spectra should lead to the same result due to the fact that $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are related by Kramers-Kroning relations [12].

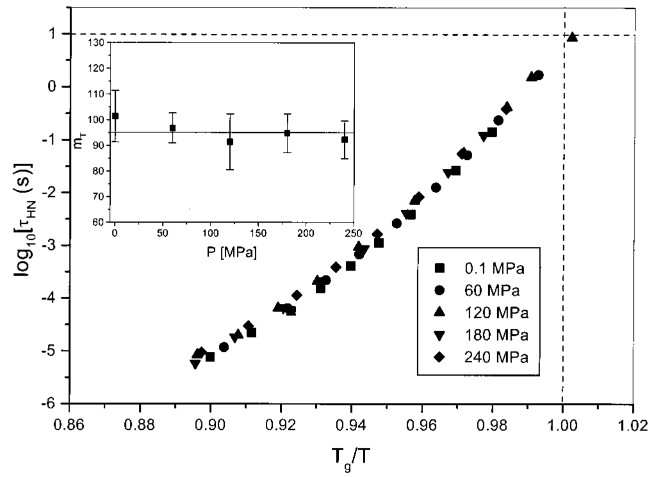

FIG. 3. (a) Isobaric and (b) isothermal data of relaxation times. Solid lines indicate the quality of the fit according to Eqs. (3a) and (3b), respectively. The dashed line represents the Arrhenius law.

DISCUSSION

The main results of our study are presented in Figs. 2–4. The parameters α and $\alpha\gamma$, determined from isobaric and isothermal measurements, are shown in Fig. 2 as a function of dielectric relaxation time. It is evident that values of parameters that characterize the shape of the relaxation function (α and $\alpha\gamma$), collapse onto two masterplots, respectively. The only region of small discrepancies in the scaling of shape parameter α is at the longest relaxation times, where the relaxation peak is at very low frequencies. These apparent discrepancies result from limited frequency range (the low-frequency part of the dielectric response is truncated). It leads to an increase in size of the error bars of the α parameter for $\log \tau > -1$. On the contrary, error bars are no larger than the size of symbols for $\log \tau < -1$. Figure 2 also shows that value α slightly decreases with the rise of $\log \tau_{\mathrm{HN}}$ whereas the second parameter $\alpha\gamma$ seems to attain a constant value of 0.4. A slight drop in the value of $\alpha\gamma$ for shorter relaxation times is probably caused by the second relaxation process, which gives a contribution to high-frequency tails of the primary process in the high range of temperatures. It is well established that the majority of low molecular weight glass-forming liquids follow the behavior with $\alpha \approx 1$ whereas the behavior with $\alpha < 1$ features mainly polymers. In the tested system $\alpha < 0.7$ is observed in whole range of $\log \tau$.

The low- and high-frequency tails of the primary relaxation peak follow the simple power-law relations:

$$\varepsilon''(\omega) \sim \omega^{m}, \quad \omega \ll \omega_p \tag{2a}$$

$$\varepsilon''(\omega) \sim \omega^{-n}, \quad \omega \gg \omega_p \tag{2b}$$

where $m = \alpha$, $n = \alpha\gamma$. Therefore, the values of α and $\alpha\gamma$ determine the asymptotic behavior of permittivity at frequencies lower and higher than the maximum dielectric loss frequency. Such behavior agrees with the theoretical models, which have been developed to explain the shape of the dielectric relaxation function at the glass transition of polymers [13,14]. The model proposed by Schönhals and Schlosser [14], which is based on the idea that the molecular mobility at the glass transition is controlled by intramolecular and intermolecular interactions, provides interpretation for shape parameters in polymeric systems. According to this model, the parameter n describes the local chain dynamics of amorphous polymers whereas the other parameter m is related to the intermolecular correlation of segments of different chains. Applying this scheme to our data we can find that molecular mobility at the glass transition is controlled in the same way by both thermodynamic variables: P and T. It is also worth noting that simple scaling couples of isobaric and isothermal dielectric spectra have also been observed in another epoxy system, namely EPON 828 [11]. In view of the above results one can expect an adequate scaling behavior also for relaxation times.

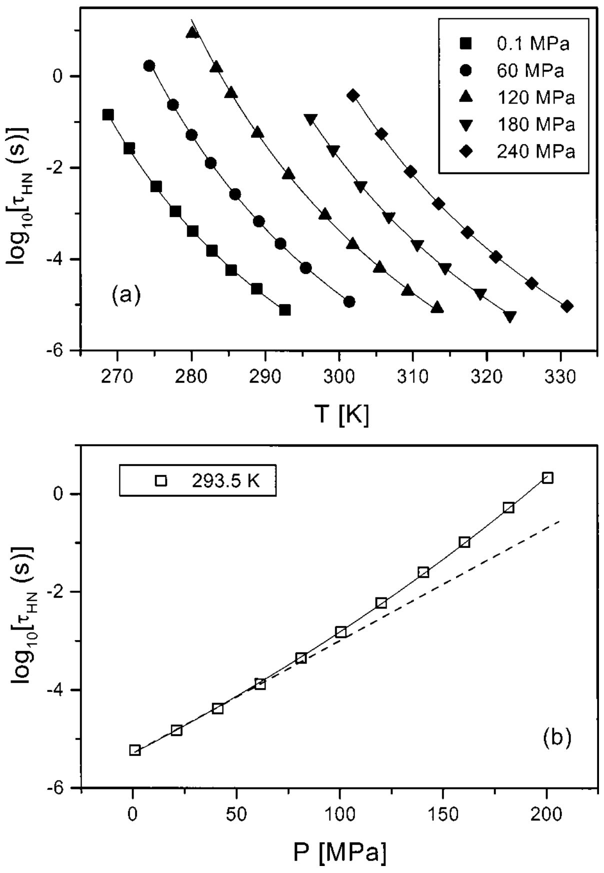

FIG. 4. Data of Fig. 3 after normalizing temperature T_g at which dielectric relaxation time equals 10 s. The inset shows that the steepness index (fragility) of PPG is pressure independent within experimental error.

The temperature and pressure dependence of the relaxation time is shown in Fig. 3. It has been observed that both isothermal and isobaric relaxation times systematically deviate from the Arrhenius behavior on approaching the glass transition. They can be very well reproduced by the temperature Vogel-Fulcher-Tammann (VFT) law [Eq. (3a)] [15] and its pressure counterpart (3b) [16]

$$\tau = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right), \tag{3a}$$

$$\tau = \tau_{0P} \exp\left(\frac{D_P P}{P_0 - P}\right), \tag{3b}$$

where τ_0 is a characteristic time constant of the order of magnitude 10^{-13}, τ_{0P} is the relaxation time at atmospheric pressure, T_0 and P_0 are the temperature and pressure of an ideal glass transition, D_T and D_P are dimensionless parameters.

The displacement of isobar $\tau(T)$ in Fig. 3 with increasing pressure along the temperature axis reflects the fact that the glass transition temperature T_g of PPG is strongly dependent on pressure. In such cases, T_g normalized Arrhenius plots become the common method for comparison of temperature dependencies of primary processes at different pressures [17–20]. Such an approach is frequently applied for the comparison of segmental relaxation of polymers with a different molecular weight [17,21]. To find out whether relaxation times superimpose we reanalyzed the isobaric data from Fig. 3(a) in terms of the reduced temperature T/T_g. From Fig. 4 it can be seen that the temperature dependence of relaxation times for different pressures collapses onto a single scaling curve. Thus, a T/T_g normalized scheme provides evidence for the pressure independence of fragility of PPG.

To extract the value of the fragility parameter $m(P)$ from the dielectric data shown in Fig. 3 the standard procedure has been applied. The starting point is the definition of fragility for relaxation data introduced by Angell and co-workers [6]

$$m=\left.\frac{d\log\tau}{dT_g/T}\right|_{T=T_g}. \qquad (4)$$

As the VFT expression reproduced the experimental data very well we calculated the steepness index by means of a VFT relation [Eq. 3(a)] with the use of the above definition

$$m=\frac{D_T T_0 T_g}{(T_g-T_0)^2}, \qquad (5)$$

where T_g is determined and identified as the temperature at which $\tau=10\,\mathrm{s}$. We have chosen a 10 s time scale in defining T_g due to the fact (i) the dielectric data are available only over a limited range of frequencies and (ii) the glass transition temperature, $T_g=263.3\,\mathrm{K}$, determined from dielectric data at ambient pressure agrees with the data from DSC ($T_g=264\,\mathrm{K}$). The values of the steepness index (fragility) calculated for each isobar are presented (as a function of pressure) in the inset in Fig. 4. These data confirm the previous result that fragility is pressure independent within experimental error. Due to the large value of the steepness index and the strong non-Debye character of relaxation function PPG can be classified as a fragile system.

The question that arises immediately is whether or not the results obtained for PPG are in quantitative agreement with correlation $m(\beta)$ from Ref. [6]. In order to bring to effect such comparison, at first, we have to determine the stretching exponent $-\beta$. Therefore, the frequency-dependent dielectric spectra have been transformed by means of inverse Fourier transform to time domain and subsequently fitted by a Kohlrausch-Williams-Watts (KWW) relaxation function: $\Theta(t)\sim\exp[-(t/\tau)^{\beta}]$. From KWW fits $\beta=0.39$ is found which correspond to fragility parameter $m=116$. This result is in accord with the correlation cited above and agrees perfectly well with narrower correlation for polymer systems (see Fig. 4 in Ref. [6]). It should be stressed that the value of fragility parameter $m=116$ has been calculated applying the same definition T_g as in [6], i.e., the glass point T_g was defined as temperature at which the relaxation time equals 100 s.

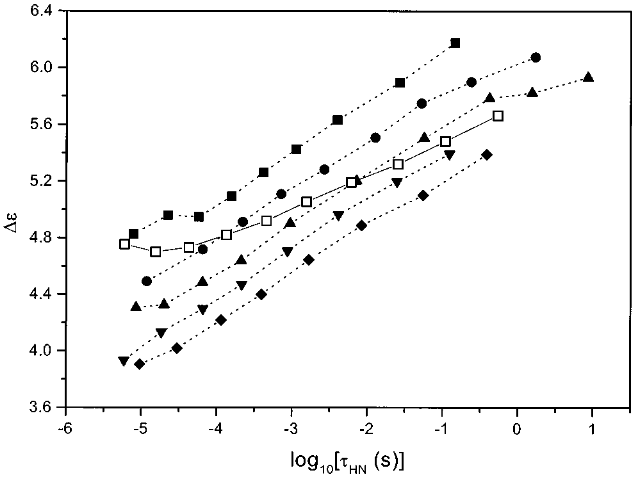

FIG. 5. $\Delta\varepsilon$ versus log τ_{HN} for both isothermal and isobaric data. The symbols are the same as in Fig. 3.

Within the framework of this work it is instructive to demonstrate the effect of pressure and temperature on the intensity of the α-relaxation process. The information about the relaxation strength is comprised in $\Delta\varepsilon=\varepsilon_s-\varepsilon_\infty$. As can be seen from the plot given in Fig. 5, temperature and pressure variables when scaled on the same relaxation time do not give identical results. The change of $\Delta\varepsilon$ with the relaxation time is stronger for isobaric than isothermal data. From data given in Fig. 5 we can infer that pressure suppresses the strength of the primary relaxation process. Comparing changes in relaxation strength brought about by T and P one should take into account that pressure affects only the density whereas the temperature alters the volume as well as the thermal energy.

The effect of pressure on the glass transition temperature in PPG is shown in Fig. 6. The change in T_g with pressure can be attributed to an increase of molecular packing induced by squeezing. The results for glass transition temperature show that T_g is strongly dependent on compression. It can be

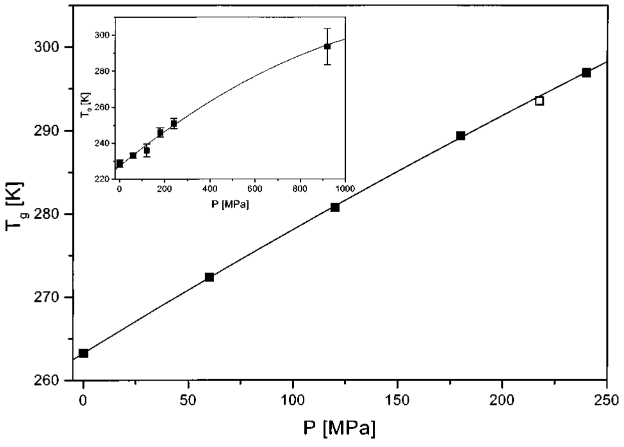

FIG. 6. Pressure dependence of Tg (main plot) and T_0 (inset). The solid lines represent a second-order polynomial fit to the experimental point. The open symbol denotes data from isothermal measurements.

also noted that changes in T_g brought about by changing pressure have a nonlinear character. Such behavior is often experimentally observed in many glass-forming liquids [18,22–24]. By fitting the second-order polynomial to $T_g(P)$ dependence we could estimate the value of the rate $(dT_g/dP)_{P=0.1\ \mathrm{MPa}}=0.154\ \mathrm{K/MPa}\pm 0.004$ for the tested material. A similar value of $(dT_g/dP)_{P=0.1\ \mathrm{MPa}}=0.156\ \mathrm{K/MPa}$ ± 0.001 has been reported by us for another epoxy system, namely poly(bisphenol *A*-co-epichlorohydrin), glycidyl endcapped [20].

According to arguments presented in a recent paper by Richert and Angell [25] the ideal glass transition temperature T_0, which for the theoretical approach is a more fundamental quantity than T_g, appears to be close to the Kauzman temperature T_K. However, the results of analysis of $T_0(P)$ dependence become far less precise than of $T_g(P)$ data owing to a large extrapolation, which is required to determine T_0. The character of pressure dependence of T_0 seems to be very similar to $T_g(P)$ dependence (see the inset in Fig. 6). The value of $(dT_0/dP)_{P=0.1\ \mathrm{MPa}}=0.1\ \mathrm{K/MPa}$ and thus is nearly the same as for $T_g(P)$ dependence.

CONCLUSION

Introducing pressure as an additional thermodynamic variable to study a liquid-glass transition valuable information about the effect of molecular packing on dynamics of α relaxation in poly[phenyl(glycidyl ether)-*co*-formaldehyde] has been obtained. It has been shown that the shape parameters of the dielectric function collected for different pressures fall on master curves constructed by plotting α and $\alpha\gamma$ against log τ. The scaling of shape parameters for different pressure stems from the pressure independence of fragility. This finding provides strong experimental evidence that the correlation between fragility and the shape of the relaxation function at atmospheric pressure may be also preserved under high pressures. Furthermore, the shape parameters of the relaxation function have been analyzed in terms of the Schonhals and Schlosser model. From this analysis we draw the conclusion that the molecular mobility of PPG is controlled in the same way by temperature and pressure.

A non-Arrhenius behavior of relaxation times is a common feature of both isothermal and isobaric data. This result shows the isomorphism of the dielectric relaxation times behavior when approaching the glass transition along the pressure and temperature path. Similar to our previous result in other glass formers we also find nonlinear character pressure dependence of glass transition temperature.

In order to provide a comprehensive description of the behavior of dynamics of the primary process under high pressures further studies are required. First of all the studies should focus on the materials that exhibit a strong pressure dependence of the steepness index (fragility). In such systems, the change of fragility with pressure should be reflected by a lack of the scaling pattern for shape parameters. In agreement with the correlation between fragility and non-exponentiality, one can expect that an increase of fragility with pressure should result in an increase of non-exponentiality. On the other hand, the drop of fragility should correspond to a decrease of non-exponentiality. A good candidate for such studies seems to be glycerol. However, due to the very small value of dT_g/dP, a much higher-pressure range (up to a few GPa) has to be used in such an experiment to obtain meaningful results.

ACKNOWLEDGMENTS

We would like to thank Professor T. Pakula and Dr. Toemsak Srikhirin for helpful discussion. The research was partially supported by the State Committee for Scientific Research (KBN, Poland) under Project No. 2 P03B 043 15 and Project No. 2 P03B 030 12.

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