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ORIGINAL CONTRIBUTION

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Dynamics of supercooled van der Waals liquid under pressure. A dynamic light scattering study

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Abstract Dynamics of 1,1'-di(*p*-methoxyphenyl)cyclohexane (BMPC) was studied in a temperature range of 253–313 K and a pressure range of 0.1–180 MPa by means of depolarized dynamic light scattering-photon correlation spectroscopy. The temperature dependence of the mean structural relaxation times measured at constant pressures was analyzed using the Vogel-Fulcher-Tamman (FVT) equation. From the FVT analysis the values of the fragility and the glass transition temperature T_g and T_0 as well as their pressure dependence dT_g/dP and dT_0/dP were obtained and compared with the corresponding quantities obtained for a chemically similar but dynamically different liquid 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC), in which two additional intramolecular relaxations were previously reported. The temperature and pressure dependence of the mean structural relaxation times was also analyzed using the Avramov model.

Keywords High pressure · Photon correlation spectroscopy · Glass transition · Fragility

List of abbreviations BMMPC: 1,1′-Di(4-methoxy-5-methylphenyl) cyclohexane · BMPC: 1,1′-Di (*p*-methoxyphenyl)cyclohexane · KWW: Kohlrausch-Williams-Watts · VFT: Vogel-Fulcher-Tamman

Introduction

Complete physical description of supercooled liquids and the liquid-glass transition, using well defined physical parameters, is important for the entire field of amorphous materials as well as for practical purposes. Usually, the glassy state is obtained by sufficiently fast cooling of a liquid performed in such a way that crystallization is avoided. A liquid can also be turned into glass by compression at constant temperature. On approaching the glass transition the structural relaxation time and viscosity of supercooled liquids increase dramatically. Most experimental studies in this field were performed by changing temperature at constant atmospheric pressure. In this case both density and thermal effects are involved. In order to separate the contributions of these two effects to the slowing down of the relaxation on approaching the glass transition both temperature and pressure dependent studies are necessary.

Substantial experimental knowledge has been accumulated concerning the dynamics of supercooled liquids and correlations between empirical parameters used for their characterization. It has been shown that fragility, which describes the deviation of the temperature dependence of the structural relaxation time from Arrhenius behavior, correlates well with non-exponentiality of the relaxation, defined as a deviation from the Debye form. It has been suggested that the fragility is related to the structure stability of supercooled liquid with regard to a temperature change. A fragile glass forming liquid is usually characterized by high fragility, high non-exponentiality and strong glass transition temperature dependence on pressure. Some exceptions from these correlations have been reported [1, 2] and explained later as due to limitations of a particular experimental method (report in preparation).

In recent temperature and pressure dependent studies it has been shown [3, 4, 5] that both fragility and non-exponentiality are changing with pressure. An interesting question is whether correlations between them observed at ambient pressure also hold at high compression. Two van der Waals glass forming liquids 1,1′-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC) and 1,1′-bis(*p*-methoxyphenyl)cyclohexane (BMPC) have very similar chemical structure, the only difference being two additional methyl groups in the former one. This chemical difference results in a dramatic difference in the relaxation processes. While in BMMPC only the α-relaxation appears, in BMPC two additional internal relaxation processes due to the phenyl flip and CH_3 group rotation can be seen [6]. Dynamics of BMMPC has been already studied as a function of temperature and pressure [4]. In this paper we report similar studies on BMPC and we investigate to what extent the presence of internal relaxations influences the temperature and pressure behavior of a van der Waals glass forming liquid.

Experimental

Depolarized dynamic light scattering-photon correlation spectroscopy measurements were performed using the experimental setup for high pressure and the experimental procedures described elsewhere [3]. This experimental setup consists of an argon-ion laser operating at $\lambda = 514.5$ nm, a high pressure light scattering cell, an avalanche diode detector and ALV5000 digital correlator. The sample was pressurized using nitrogen (0.1–180 MPa).

Both 1,1′-di(*p*-methoxyphenyl)cyclohexane (BMPC) and 1,1′-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC) were synthesized according to the procedure described in [6]. A purity of 99.2% for BMPC and 99.5% for BMMPC was achieved, as measured by HPLC analysis. The chemical structure of BMPC is shown in Fig. 1.

Results

The time correlation functions $g^{(1)}(t)$ of the depolarized component of scattered light measured in a photon correlation experiment were analyzed using the empirical Kohlrausch-Williams-Watts (KWW) formula [7]:

$$g^{(1)}(t) = A \exp\left[-(t/\tau_{KWW})^{\beta_{KWW}}\right] \quad (1)$$

Typical photon autocorrelation functions together with fits using the KWW formula are shown in Fig. 1. From this analysis the values of the structural relaxation time τ_{KWW} and the non-exponentiality parameter β_{KWW} at various temperatures and pressures were obtained. The behavior of the structural relaxation time is most commonly discussed in terms of the average KWW relaxation time $<\tau_{\mathrm{KWW}}>$, defined as

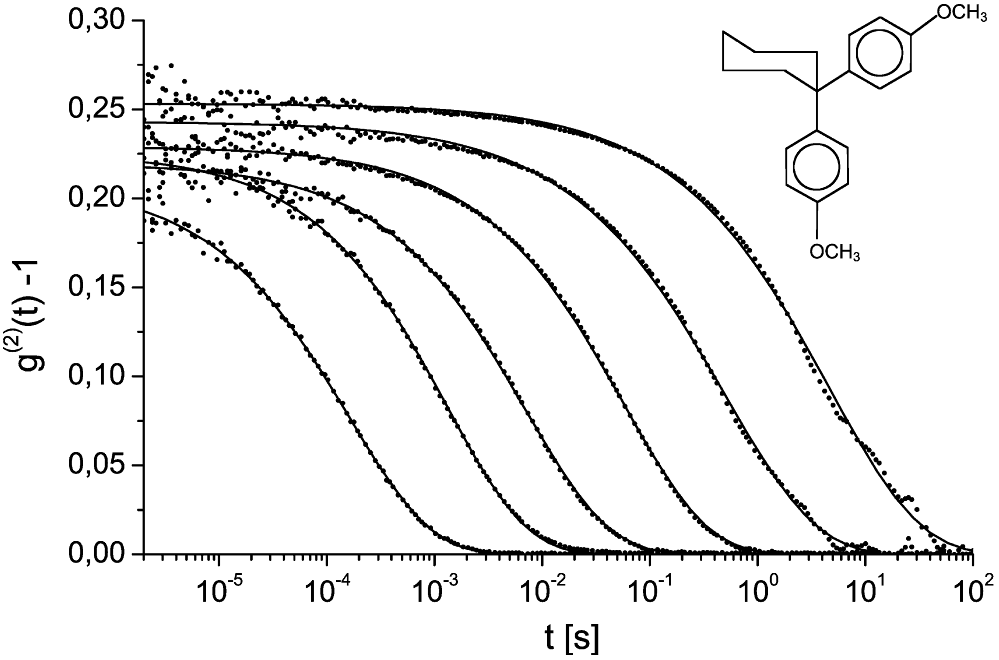
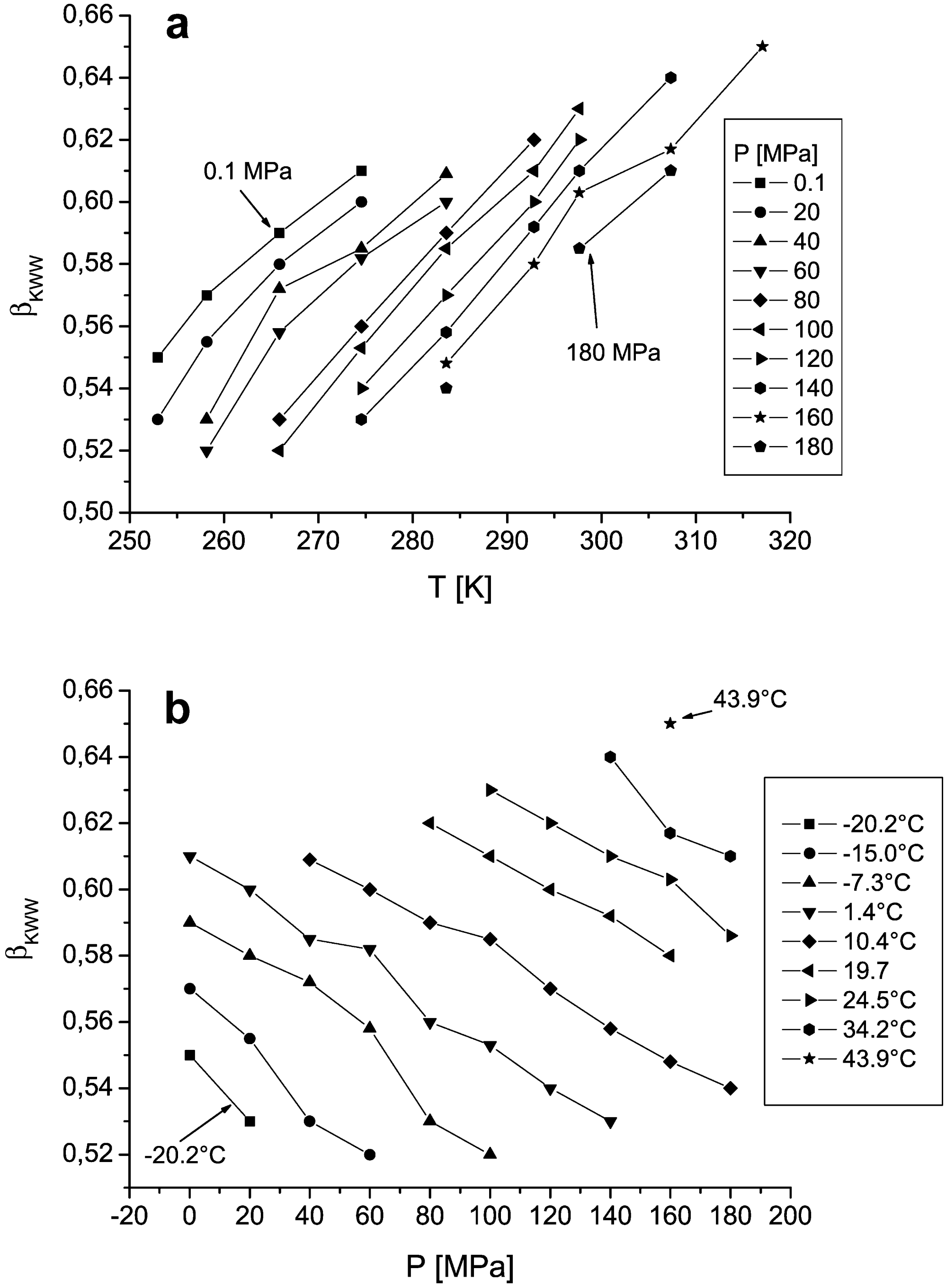


Fig. 1 Experimental photon correlation functions measured at T = −7.3 °C and pressures of 0.1, 20, 40, 60, 80, 100 MPa. KWW fits are shown as *solid lines*. In the *inset* the chemical structure of BMPC is shown

Fig. 2a,b The dependence of the non-exponential parameter β_{KWW} on: **a** temperature at the pressures of 0.1, 20, 40, ..., 180 MPa; **b** pressure at indicated temperatures



$$\langle\tau_{KWW}\rangle = \frac{\tau_{KWW}}{\beta_{KWW}}\Gamma\left(\beta_{KWW}^{-1}\right) \qquad (2)$$

where $\Gamma(x)$ is the Gamma function.

The non-exponentiality parameter β_{KWW} of the KWW functions depends on both temperature and pressure in the usual way. This dependence is shown in Fig. 2a,b.

The temperature and pressure dependence of the mean structural relaxation time $<\tau_{KWW}>$ was first analyzed using the Vogel-Fulcher-Tamman equation:

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

According to the results of our previous studies [3, 4, 8, 9] as well as the suggestion of Casalini et al. [10] the D_T parameter was assumed to be pressure independent in our VFT analysis. In Fig. 3 we show the results of VFT common fit to all the measured isobars. Such procedure reduces the errors in estimating the values of all the parameters, as was already shown in our previous reports [3, 4, 8, 9]. In this relatively narrow temperature range a single VFT function satisfactorily fitted the experimental data for each isobar.

From the VFT analysis we have obtained the values of $\tau_0(P)$ and $T_0(P)$ at all pressures measured and pressure independent $D_T = 11.6 \pm 1.4$. The value of the parameter $\tau_0(P)$ was increasing with pressure from 4.5×10^{-18} s (at 0.1 MPa) to 2.7×10^{-16} s (at 180 MPa) as usually observed. The pressure dependent values of $T_0(P)$ are shown in Fig. 4 together with the corresponding values of $T_g(P)$ obtained by extrapolating the experimental data shown in Fig. 3 to $< \tau_{KWW} > = 100$ s. From the experimental pressure dependence of both characteristic temperatures the parameters $dT_0/dP = 0.126$ K/MPa and $dT_g/dP = 0.182$ K/MPa were obtained. As usually observed in the fragile van der Waals glass forming liquids [5] $dT_0/dP < dT_g/dP$. This relationship will be discussed in more detail later in this paper.

Additionally, using the parameters of the VFT fits the fragility m_T defined as

$$m_T = \left. \frac{\partial \log < \tau >}{\partial (T_g/T)} \right|_{T=T_g} = \frac{1}{\ln 10} \frac{D_T T_0 T_g}{(T_0 - T_g)^2} \tag{4}$$

was calculated. The value of fragility m_T is decreasing with increasing pressure (Fig. 5) as usually observed for fragile van der Waals glass forming liquids [5].

The BMPC has all the features of a fragile glass forming liquid: high fragility m_T, high non-exponentiality of the correlation function (low β_{KWW}), and strong dependence of the characteristic glass transition temperatures T_g and T_0 on pressure.

It has been shown previously [1] that the non-exponentiality parameter β_{KWW} and fragility m_T for glass forming liquids are related by an empirical formula:

$$m_T = 250 \pm 30 - 320\beta_{KWW} \tag{5}$$

This dependence is also fulfilled in the case of BMPC. This can be seen in Fig. 6, where the fragility $m_T(P)$ is plotted vs $\beta_{KWW}(P,T_g)$ extrapolated to T_g. In the inset the dependence of the extrapolated value of $\beta_{KWW}(P,T_g)$ on pressure is shown explicitly. As one can see the change of $\beta_{KWW}(P,T_g)$ with pressure is small as could be expected from the corresponding change of $m_T(P)$ and Eq. (5).

In our previous paper [5] we have shown, that within the framework of the VFT model, the characteristic temperatures T_0 and T_g as well as their pressure dependence are related in the following way:

$$T_0 = C \cdot T_g \tag{6}$$

and

$$\frac{dT_0}{dP} = C\frac{dT_g}{dP} + T_g \frac{dC}{dP} \tag{7}$$

where $C = \frac{1}{2}\left(2 + \frac{D'}{m_T}\right) - \frac{1}{2}\left[\frac{D'}{m_T}\left(\frac{D'}{m_T} + 4\right)\right]^{1/2}$ and $D' = D/\ln 10$.

Also, in the case of BMPC, this relationship is fulfilled taking $dm_T/dP = -0.06$ according to the data shown in Fig. 5 ($dC/dP \cong -6 \times 10^{-5}$ MPa^{-1}).

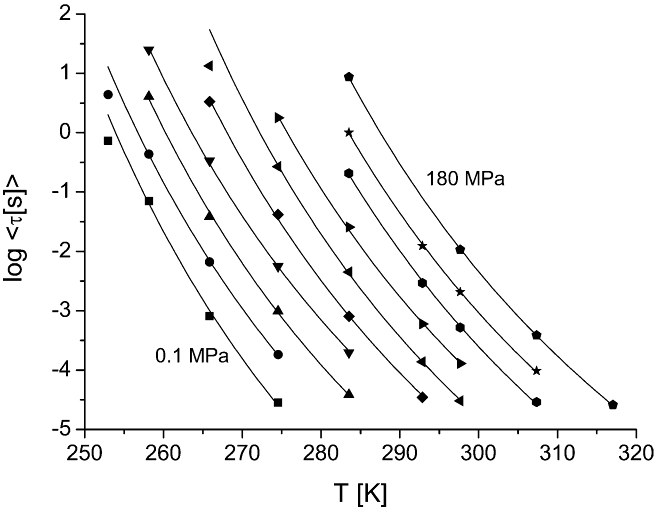


Fig. 3 Mean relaxation times $< \tau_{\mathrm{KWW}} >$ of BMPC as a function of temperature and pressure with the VFT fits. Parameter D_T was assumed pressure independent and common fit to all isobars was made to find the values of $\tau_0(P)$ and $T_0(P)$

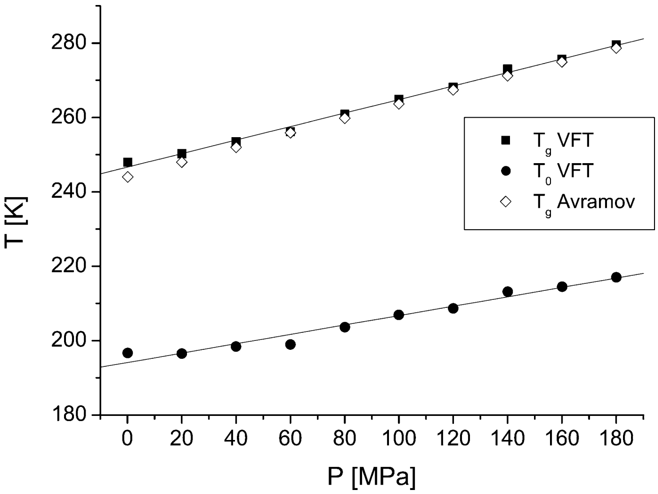


Fig. 4 Pressure dependence of the characteristic temperatures $T_0(P)$ and $T_g(P)$ At 0.1 Mpa $T_g = 246.6$K and $T_0 = 194$K

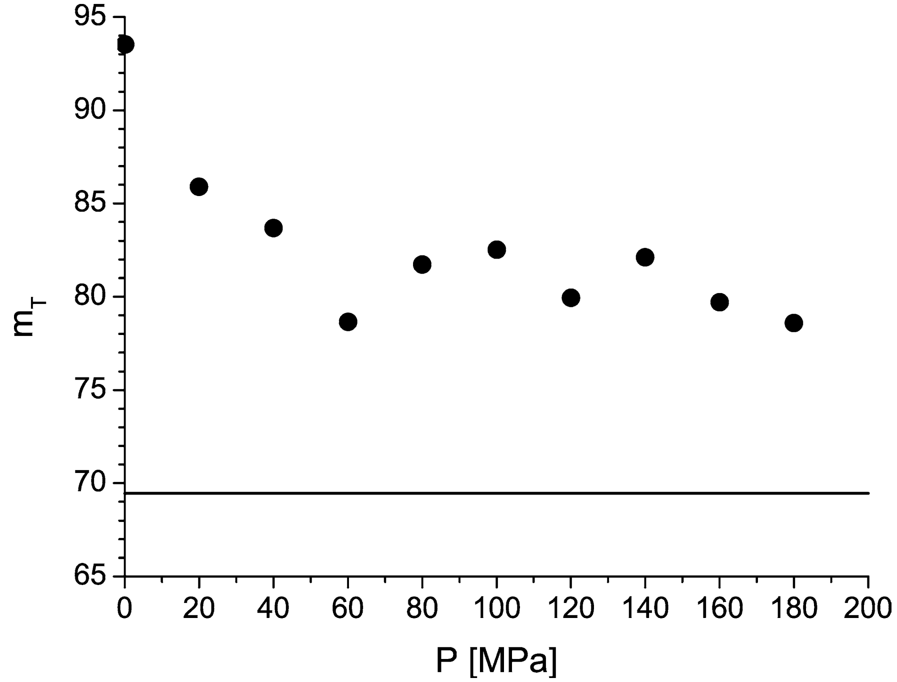


Fig. 5 The pressure dependence of the fragility m_T. Symbols: m_T calculated from VFT model; line: m_T calculated from the Avramov model

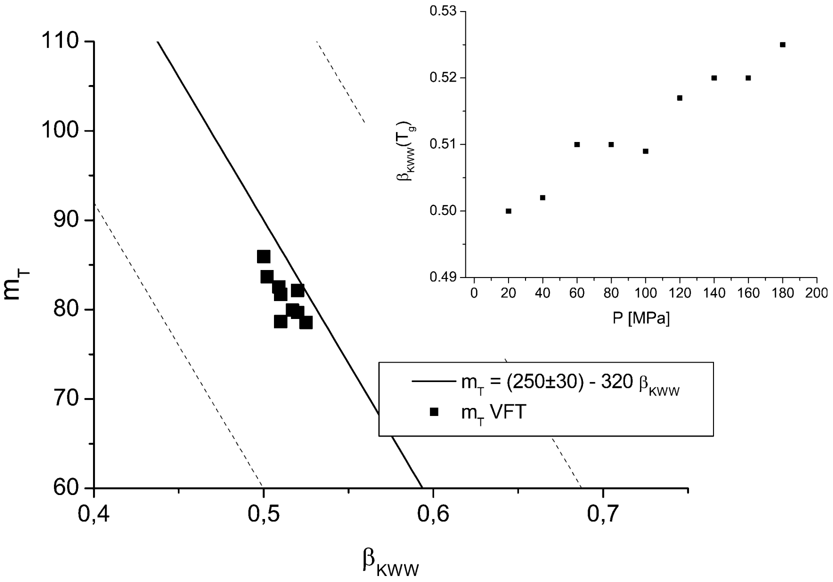


Fig. 6 Plot of the dependence of fragility $m_T(P)$ on the non-exponential parameter $\beta_{KWW}(P)$ extrapolated to T_g

The same pressure and temperature dependent mean relaxation times were also analyzed by means of the Avramov model [11]:

$$\log\tau = \log\tau_\infty + \left(T_g/T\right)^a (1 + P/\Pi)^b \log\left(\tau_g/\tau_\infty\right) \quad (8)$$

where Π denotes the pressure at which the thermal expansion coefficient κ decreases to half of its initial value and the original equation of Avramov was reorganized to express the relaxation time τ in terms of T_g and τ_g. The latter was set to 100 s, as commonly accepted for the glass transition conditions of low molecular weight glass forming liquids. Good fits were obtained (Fig. 7), which is not very surprising in this narrow temperature and pressure range. Since in Avramov model pressure is an explicit parameter, we performed a similar fitting procedure for the same data plotted as isotherms (Fig. 8). The results of fitting procedures for Avramov model are summarized in Table 1. Note that in this model the fragility parameter by definition is pressure independent ($m_T = \alpha\log(\tau_g/\tau_\infty)$).

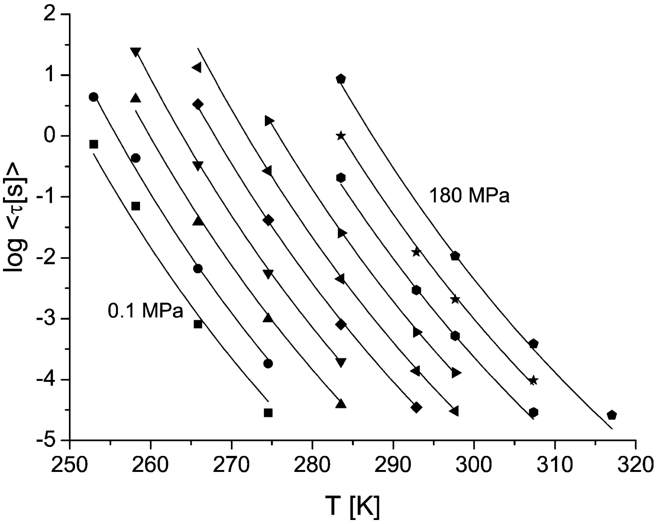


Fig. 7 Temperature dependence of the mean structural relaxation times $<\tau_{\mathrm{KWW}}>$ (*symbols*) fitted with the Avramov equation (Eq. 8—*solid lines*)

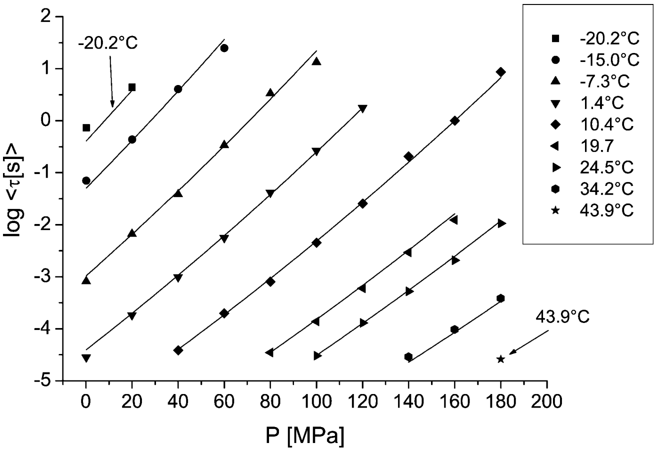


Fig. 8 Pressure dependence of the mean structural relaxation times $<\tau_{\mathrm{KWW}}>$ (*symbols*) fitted with the Avramov equation (Eq. 8—*solid lines*)

In order to verify some experimentally available assumptions of Avramov model, we utilized the PVT data reported for BMPC in [12]. Parameter Π in the Avramov model is defined as the pressure value at which the thermal expansion coefficient κ reduces to half of its initial value with the assumption that its pressure dependence is given by

$$\kappa(P) = \kappa_0 \frac{\Pi}{\Pi + P} \tag{9}$$

Using the definition of κ

$$\kappa(P) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{10}$$

Table 1 Results of Avramov common fit to all isobars and isotherms

Method	$\log \tau_\infty$ [s]	Π [MPa]	a	b	T_g [K]	m_T
Isobars	−13.5	750	4.5 ± 0.6	2.8 ± 0.4	244.0 ± 0.5	70
Isotherms	−14.7	750	4.0 ± 0.5	2.5 ± 0.1	250.0 ± 0.2	67

and the Tait equation with the parameters given in [12] we calculated the true dependence of κ on pressure. In Fig. 9 we present the results of these calculations including the best fit of Eq. (9). As one can see, κ depends on pressure in a way which is different from the Avramov model.

Another useful parameter used to characterize the pressure dependence of the structural relaxation time is the activation volume $\Delta V^{\#}$ defined as

$$\Delta V^{\#} = \ln 10 \log(\tau/\tau_0) RT/P \tag{11}$$

Using our experimentally obtained structural relaxation times presented in the form of isotherms (Fig. 8), temperature dependence of this activation volume was obtained and is shown in Fig. 10. The activation volume decreases with increasing temperature, as it is usually observed in fragile glass forming liquids [3, 4, 8, 9].

In order to see the influence of the internal relaxation processes on parameters characterizing the behavior of supercooled liquids the values of the glass transition temperature T_g and its pressure dependence dT_g/dP, fragility m_T and non-exponentiality parameter β_{KWW} for BMPC and BMMPC are listed in Table 2. As one can see, BMPC (with internal relaxations) is more fragile (higher m_T), has a lower glass transition temperature T_g and lower dT_g/dP than BMMPC (without internal relaxations). It would be interesting to see if similar behavior can be observed in other pairs of supercooled liquids which are chemically similar and dynamically different by the presence of internal dynamic processes.

Relative magnitudes of the temperature and volume contributions to the relaxation times can be obtained from comparison of the temperature dependence of $<\tau>$ at constant volume (isochoric activation energy):

$$E_V = R \frac{\partial \ln <\tau>}{\partial T^{-1}}\bigg|_V \tag{12}$$

and at constant pressure (isobaric activation enthalpy, more commonly referred to as the apparent activation energy) [13]:

$$E_P = R \frac{\partial \ln <\tau>}{\partial T^{-1}}\bigg|_P . \tag{13}$$

The ratio of the values of the isochoric activation energy E_V and isobaric activation energy E_P at atmospheric pressure: E_V/E_P is taken from [12] and is listed

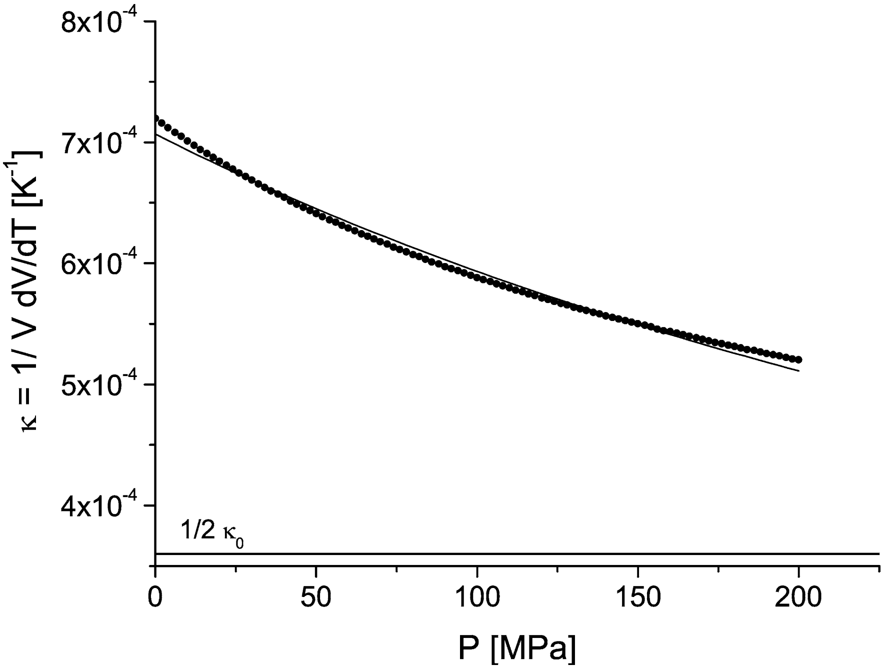


Fig. 9 Pressure dependence of the thermal expansion coefficient κ (*symbols*) measured at 303 K obtained from the PVT data taken from [12]

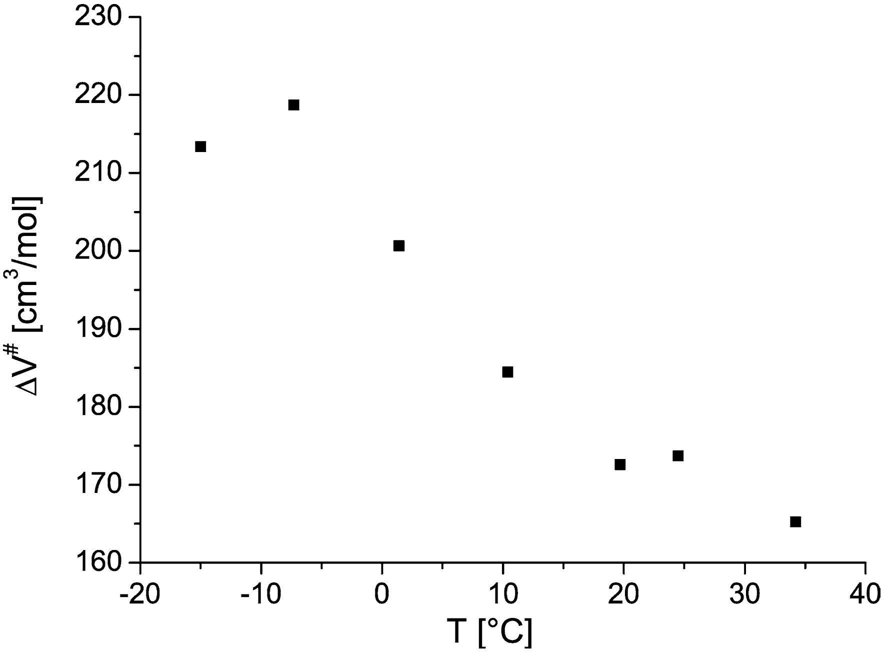


Fig. 10 Temperature dependence of the activation volume $\Delta V^{\#}$

in Table 2. Since the ratio is less than one-half, the influence of the volume on the relaxation times is greater than that of the thermal energy, but both contributions are significant.

An alternative way to estimate the relative contributions of temperature and volume is based on the ratio of the isobaric expansion coefficient, $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$, to the coefficient of isochronal expansivity, $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$, the latter evaluated at a fixed value of the relaxation time [14]. Ratios of $|\alpha_\tau|/\alpha_P$ (from [12]) listed in Table 2 are smaller than unity for both compounds. This indicates again that for BMPC and BMMPC volume is the more important control parameter than temperature [14].

Conclusions

Structural relaxation in a low molecular weight van der Waals glass forming liquid BMPC was studied in a

Table 2 Comparison of different parameters characterizing BMPC and BMMPC

Compound	T_g [K]	m_T	β_{KWW}	dT_g/dP [K/MPa]	E_v/E_p [12]	$\lvert\alpha_\tau\rvert/\alpha_P$ [12]
BMPC	247	90	0.52–0.65	0.182	0.39	0.58
BMMPC	263	60	0.53–0.62	0.227	0.41	0.72

broad temperature and pressure range by means of depolarized dynamic light scattering-photon correlation spectroscopy. Temperature dependence of the mean relaxation time (at constant pressures) was analyzed using the VFT equation. Pressure dependent values of the characteristic temperatures T_0 and T_g were obtained as well as their pressure dependence: $dT_0/dP=0.126$ K/MPa and $dT_g/dP=0.182$ K/MPa. The latter two quantities are related in the same way as previously shown.

BMPC has all the features of a fragile glass forming liquid; it is characterized by high fragility m_T, high non-exponentiality (low β_{KWW}), and strong dependence of T_0 and T_g on pressure. Both the fragility m_T, high non-exponentiality depend on pressure and the empirical relationship between them holds. The activation volume decreases with increasing temperature. Thus, BMPC behaves in a very similar way to other low molecular weight van der Waals glass forming liquids studied previously.

The main effect of internal relaxation processes (BMPC) in comparison to the sample without intramolecular relaxations (BMMPC) is that for the former material the fragility is higher while the T_g and dT_g/dP are lower. It remains to be seen if this is a general effect of internal relaxations.

Interpretation of the results obtained from the Avramov model is not unequivocal. Although the relatively narrow temperature range allows for a good fit to experimental data, the parameters of the model are strongly interrelated which leads to large errors of their estimates. The assumption concerning the functional form of $\kappa(P)$ does not precisely fit experimental PVT data leading to large uncertainty of the Π parameter. Constant, pressure independent value of the fragility parameter m_T, stays in contradiction with the results obtained from the VFT model.

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