Pressure effects on the α and α' relaxations in polymethylphenylsiloxane

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In some polymers, in addition to the usual structural α relaxation, a slower α' relaxation is observed with a non-Arrhenius temperature dependence. In order to understand better the molecular origin of this α' relaxation in poly(methylphenylsiloxane) (PMPS) we have studied, for the first time, the pressure dependence of its relaxation time, together with the usual temperature dependence, by means of dynamic light scattering (DLS). For the same material the α relaxation was also studied by means of DLS and dielectric spectroscopy (DS) in broad temperature and pressure ranges. We find that the temperature dependence of both α and α' relaxation times, at all pressures studied, can be described by a double Vogel-Fulcher-Tammann (VFT) law. The pressure dependence of the characteristic temperatures T_g (glass transition temperature) and T_0 (Vogel temperature) as well as the activation volumes for both α and α' processes are very similar, indicating, that both relaxation processes originate from similar local molecular dynamics. Additionally, for both α and α' relaxations the combined temperature and pressure dependences of the relaxation times can be described using a parameter $\Gamma=\rho^n/T$ with the same value of the exponent n.
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INTRODUCTION

Dynamic processes observed in supercooled liquids usually consist of the structural (α) relaxation of non-Arrhenius temperature dependence and, in most cases, other faster processes whose temperature dependence is usually of Arrhenius type. The relaxation pattern in polysiloxanes is qualitatively different due to the occurrence of an additional relaxation process usually called α'.[1] This additional process was observed in dynamic light scattering (DLS) photon correlation spectroscopy (PCS) studies on monodisperse bulk poly(methylphenylsiloxane) (PMPS) of $M_w=28\,500$ g/mol, whereas it was not visible in the dielectric spectra[2] of this polymer. The relaxation times of the α' process obtained from both polarized (VV) and depolarized (VH) correlation functions were approximately equal and longer by about three orders of magnitude than those of the α relaxation. Recently,[3] an α' process was also reported in poly(propylene glycol) (PPG) by DLS. Similar additional processes were observed in the dielectric spectra of poly(propylene oxide) (PPO)[4–6] and *cis*-poly(isoprene)[7,8] and were assigned to the normal modes of the polymer chains, since in these polymers there exists a dipole component parallel to the chain contour. Consequently, the same physical origin was suggested for the slow process in PMPS.[2] The α' relaxation was also observed in PCS studies of poly(methyl-*p*-tolylsiloxane) (PM*p*TS) of $M_w=15\,000$ g/mol.[1,9]

In this work the effect of pressure, in addition to the usual temperature dependence, on the α and α' relaxations is studied. An important parameter, which can be evaluated from pressure dependent measurements of the relaxation times, is the activation volume $\Delta V^{\#}$. In light scattering the possible contributions of normal modes and segmental modes to the observed orientational correlation function and their respective volume requirements are not clear. One of the aims of this work is to find out whether the α' process observed in PCS studies in polysiloxanes can be identified with the normal modes of the polymer chain reported for other polymeric liquids in dielectric spectroscopy (DS) studies. Additionally, it is interesting to see if the combined temperature and pressure dependences of the relaxation times of both α and α' processes can be expressed in terms of a parameter $\Gamma=\rho^n/T$, where ρ is the density with the same value of the exponent n as was reported for poly(propylene glycol).[10] To gain a better insight into the physical origin and interrelations of both α and α' relaxations in polysiloxanes,

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we report herein experimental studies of the temperature and pressure dependences of the relaxation times of both processes by means of dynamic light scattering PCS in very broad temperature and pressure ranges.

EXPERIMENTAL

Materials

The poly(methylphenylsiloxane) sample was obtained by an anionic polymerization process and had a molecular weight of $M_w = 10\,500$ g/mol with a polydispersity of 1.04. Details of the synthesis can be found elsewhere.[11] A dust-free sample, suitable for light scattering, was prepared by dissolving a proper amount of polymer in toluene and filtering the solution through a 0.47 μm Teflon Millipore filter into a dust-free, round glass cell with 10 mm outer diameter. The solvent was removed afterwards by treating the sample in a vacuum oven at $T \approx 100$ °C for several days.

Experimental setup for light scattering studies

The time photon correlation functions of scattered light were measured as a function of temperature and pressure using a homemade high pressure system, which basically consists of the optical high pressure cell which was first described by Fytas *et al.*[12] This high pressure cell works in a temperature range between −20 and 120 °C at pressures up to 2 kbars. The pressure-transmitting medium is gaseous nitrogen. This is feasible, since the diffusion coefficient of nitrogen in a liquid (and also our sample) at ambient conditions is about 10^{-5} cm^2/s and it thus takes a long time for the gas to diffuse into the optical cell filled up usually 2 cm above the laser beam level. Consequently, the measurements are safe with regard to softening of the sample with gas. The optical windows are made of a SF 57 NSK glass (Schott, Mainz), which neither scrambles nor depolarizes the incident laser beam under conditions of high pressure. Hence, it is possible to preserve the polarization of the incident and scattered beams and therefore polarization selective measurements under pressure are possible. The correlation functions were taken in the VH geometry probing orientational correlations. The scattering angle was $\theta = 135°$ and the laser wavelength was 514.5 nm (Spectra Physics model 2060). A monomode optical fiber was used to feed the scattered light into an avalanche photodiode working in the photon counting mode. The VH intensity timecorrelation function $G^{(2)}(t)$ was calculated in real time by means of an ALV 5000E digital correlator (ALV GmbH, Langen, Germany). For the homodyne case the intensity autocorrelation function $G^{(2)}(t) = \langle I(t)I(0)\rangle$ is related to the electric field $E(t)$ normalized autocorrelation function $g^{(1)}(t)$ via the Siegert relation as follows:

$$G^{(2)}(t) = \langle I\rangle^2(1 + f|g^{(1)}(t)|^2), \tag{1}$$

where f is an experimental factor and $\langle I\rangle$ is the mean intensity. To model the field autocorrelation function $g^{(1)}(t)$, we use the well-known Kohlrausch-Williams-Watts (KWW) function

$$g^{(1)}(t) = A \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\beta}\right] \quad \text{with } 0 < \beta \leqslant 1 \tag{2}$$

for each individual relaxation process. From the knowledge of τ_{KWW} and β a mean relaxation time $\langle\tau\rangle$ is obtained by

$$\langle\tau\rangle = \frac{\tau_{\mathrm{KWW}}}{\beta}\Gamma\left(\frac{1}{\beta}\right), \tag{3}$$

where Γ denotes the gamma function.

Experimental setup for dielectric relaxation measurements

The temperature dependent dielectric measurements were carried out using the experimental setup made by Novo-Control GmbH. We measured the complex permittivity: $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ over ten decades of frequency using an Alfa impedance analyzer (10^{-2}–10^6 Hz), in combination with an Agilent impedance analyzer (10^{-6}–10^9 Hz). The sample was placed in a parallel plate capacitor. The temperature was controlled by the Quatro system, employing a nitrogen-gas cryostat, with a stability better than 0.1 K.

For the high pressure studies we used a pressure system constructed by UNIPRESS (Warsaw, Poland) with an analogous sample cell as described elsewhere.[13] The capacitor, filled with tested material, was placed in the high pressure chamber. Pressure was exerted on the chamber from a pressure source (special chamber with a piston placed under hydraulic press) through silicone oil. The sample capacitor was sealed and mounted inside a Teflon ring to separate the sample from the silicone oil. Pressure was measured by the Nova Swiss tensometric pressure meter with a resolution of 1 bar. The temperature was controlled within 0.1 K by means of a liquid flow provided by a thermostatic bath. More details on the high pressure setup can be found elsewhere.[14]

RESULTS AND DISCUSSION

A typical VH correlation function measured at a temperature of 0.2 °C and a pressure of 600 bars is shown in Fig. 1. Two relaxation processes can be seen: the usual α relaxation (fast process) and an additional α' relaxation (slow process). The correlation functions were fitted with a double Kohlrausch-Williams-Watts function

$$g^{(1)}(t) = A_1 \exp\left[-\left(\frac{t}{\tau_{1,\mathrm{KWW}}}\right)^{\beta_1}\right] + A_2 \times \exp\left[-\left(\frac{t}{\tau_{2,\mathrm{KWW}}}\right)^{\beta_2}\right] \tag{4}$$

from which the amplitudes A_i, the stretching exponents $\beta_{i,\mathrm{KWW}}$ (also called nonexponentiality parameter), and the mean relaxation times $\langle\tau\rangle_i$ were obtained via Eq. (3).

It is beforehand not obvious that the fast relaxation component is related to the α process. To prove that, DS measurements were also performed. Boese *et al.*[2] have shown that in the case of PMPS no α' process is visible, employing the DS technique. The same result was found for our sample which is documented in Fig. 2, where the dielectric loss ε'' as a function of frequency is shown for different temperatures.

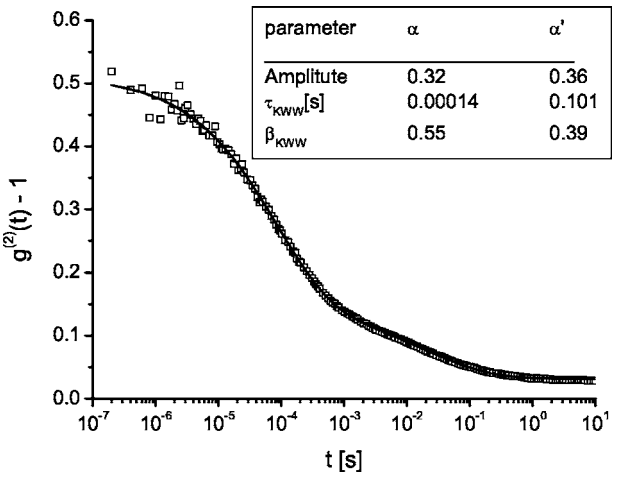

FIG. 1. Time autocorrelation function of the depolarized component of scattered light measured at a temperature of 0.2 °C and a pressure of 600 bars. The full line is a fit of Eq. (4) to the data. The table in the inset shows the parameters of a double KWW fit. Both the "regular" α process and the slow (α') component contribute equally to this correlation function.

A single intense loss peak, corresponding to the usual structural (segmental) α relaxation, is seen. However, at lower temperatures another weak relaxation process exists at higher frequencies (β process) with a distinctly different T dependence. In this analysis, for all DS spectra we have used the empirical equation of Havriliak and Negami (HN):[15]

$$\frac{\varepsilon^*(T,P,\omega)-\varepsilon_\infty(T,P)}{\Delta\varepsilon(T,P)}=\frac{1}{\{1+[i\omega\tau_{\mathrm{HN}}(T,P)]^\alpha\}^\gamma}, \tag{5}$$

where $\tau_{\mathrm{HN}}(T,P)$ is the characteristic relaxation time. In this equation $\Delta\varepsilon(T,P)=\varepsilon_s(T,P)-\varepsilon_\infty(T,P)$ is the relaxation strength of the process under investigation, and α and γ describe the symmetrical and asymmetrical broadenings of the distribution of relaxation times, respectively $(0<\alpha,\gamma\leqslant 1)$. In the fitting procedure we used the ε'' spectra, and only in some cases, the ε' data were also used for consistency check. The linear rise of the ε'' at lower frequency is caused by the conductivity $\varepsilon''\propto(\sigma_0/\varepsilon_0)\omega^{-1}$, where σ_0 is the dc conductivity

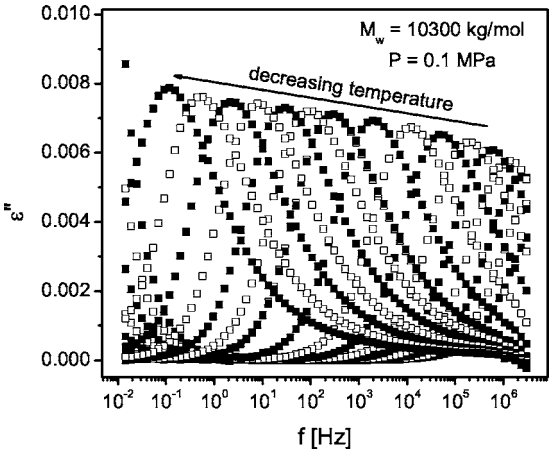

FIG. 2. The series of dielectric spectra obtained at ambient pressure for different temperatures from 242 to 289 K. A single component model fits the data around the peaks satisfactorily. The mean time and calculated β_{KWW} exponent correspond well to the parameters of the faster (α) process in the PCS correlation function.

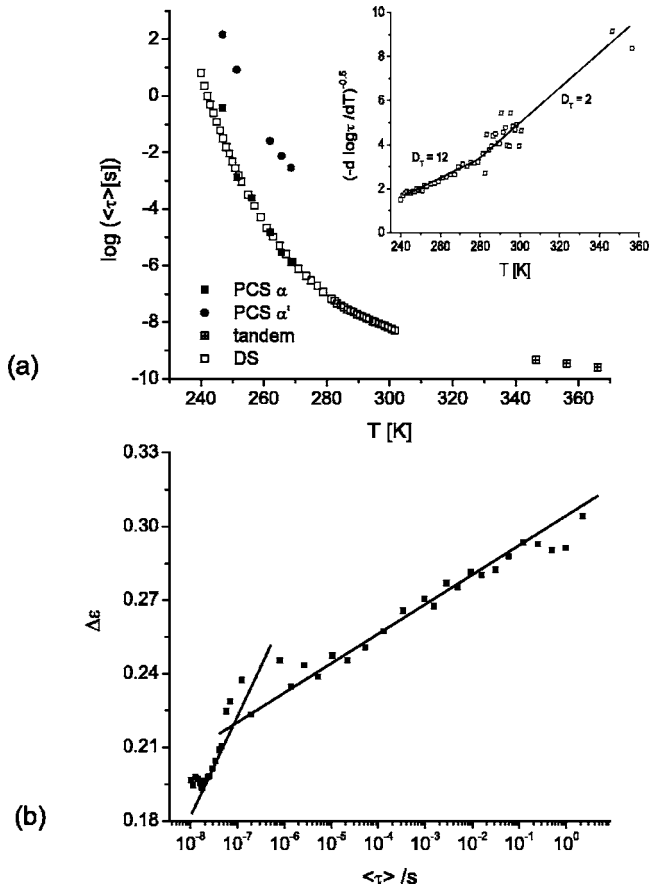

FIG. 3. (a) Logarithm of mean relaxation times of the structural α relaxation measured at ambient pressure with different techniques at different temperatures. For PCS also the times of α' relaxation are shown. In the inset we present the "Stickel plot" (Ref. 16) of the α process with a clear transition from one VFT to another at about 280 K. (b) Dependence of the relaxation strength $\Delta\varepsilon$ on the mean dielectric relaxation time $\langle\tau\rangle$ of PMPS.

and ε_0 is the permittivity of vacuum, which was included in the fitting procedure.

The loss spectra, as shown in Fig. 2, are well described by Eq. (5) in a frequency range ±2.5 decades around their maxima. The additional high frequency contribution is not accounted for, since it is well separated from the α peak. Using a procedure similar to that described by Boese *et al.*, from a Fourier transform of the simulated HN function with parameters obtained from the fit, a time dependent quantity, the dipole-dipole reorientational correlation function $\phi(t)$, can be obtained. This $\phi(t)$ is fitted by a single KWW function via Eq. (2).

The mean KWW relaxation times obtained in this way agree well with those from light scattering for the fast process of the orientational correlation function. This result is shown in Fig. 3(a). Also shown in this figure are the times for the slower (α') process observed by light scattering, which are typically about three orders of magnitude longer than the α relaxation times at a given temperature for PMPS of this molecular weight. Comparably large differences between τ_α and τ'_α have been reported for polyisoprene (PI) and PPG[10] using DS and for PMpTS[9] using dynamic light scattering.

Also included in Fig. 3(a) are three data points at high T

(around 355 K), which were obtained by Fabry-Pérot interferometry using a tandem interferometer. This setup and data treatment procedures will be described elsewhere.[17] The measured spectra $I(\omega)$ have been fitted by a Cole-Davidson function to obtain the reorientation times τ, which are plotted in the figure.

Another indication of the crossover occurring at 280 °C is the shape of the dielectric relaxation strength $\Delta\varepsilon$, which is dependent on the mean relaxation time $\langle\tau\rangle$.[18] This plot, shown in Fig. 3(b), also changes its slope at the $\langle\tau\rangle$ value corresponding to 280 °C.

The temperature dependence of the mean relaxation time is usually described by a Vogel-Fulcher-Tammann (VFT) equation as follows:

$$\langle\tau\rangle = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right), \tag{6}$$

where τ_0 is a prefactor of the order of 10^{-14} s, T_0 is the Vogel temperature, and D_T is a measure of the fragility of the system. D_T is related to a kind of activation energy and is assumed to be pressure independent, as was shown for other related systems.[19] However, it is well known that the temperature dependence of $\langle\tau\rangle$ is complicated: It was found that the whole T range, corresponding to $\langle\tau\rangle$ values spanning from about 100 s at T_g to $\sim 10^{-10}$ s at the melting point, cannot be described by Eq. (6) with one set of D_T, T_0, and τ_0 parameters. To show that, Stickel *et al.*[16] proposed a representation, named Stickel plot, in which $[-d\log\langle\tau\rangle/dT]^{-1/2}$ vs T is plotted, highlighting the respective regions where single VFT functions hold. This plot is shown as an inset in Fig. 3(a) and demonstrates that the low T data of $\langle\tau\rangle$ vs T is in accordance with $D_T=12$ up to about 280 °C and then a crossover to $D_T=2.1$ for higher T is observed. There the tandem data points are very useful, since from the data around 300 K alone, this slope could not have been deduced properly.

In order to characterize the α and α' processes more extensively, we have analyzed, besides the temperature dependence, also the pressure dependence. As evidenced from Fig. 3(a), the separation in $\langle\tau\rangle$ between the α and α' processes is about three orders of magnitude at ambient pressure. This finding also holds for higher pressures and consequently it was possible to extract the pressure and temperature dependent values of the relaxation times $\langle\tau_\alpha\rangle$ and $\langle\tau'_\alpha\rangle$ and β_α and β'_α, respectively. In Fig. 4 we thus show $\langle\tau_\alpha\rangle$ as a function of T for various pressures, whereas in Fig. 5 we show the corresponding data for the α' process. The solid lines in the figures denote fits of Eq. (6) to the data. From the rather "parallel" shift of the lines it can be concluded that D_T is not pressure dependent, as was already found in other systems[19] for the α process. Here, we find the same to be valid also for the α' process. The value of the D_T parameter of the α process is $D_T=12\pm3$ and the respective parameter for the α' process is $D_T=12\pm5$. The fit parameters for the VFT fits to the isobaric data shown in Figs. 4 and 5 are given in Table I. As can be seen, the temperature dependences of the relaxation times for the α and α' processes can be expressed by a VFT law with the same D_T values. The τ_0 values are practically pressure independent for both processes. The values of T_0 are very similar for the α and α' processes at a given pressure. Using a commonly accepted definition of T_g, as the temperature at which $\langle\tau\rangle=100$ s, we calculated also the pressure dependence of T_g (Table I). The pressure dependences of T_g and T_0 for both processes are given in Fig. 6.

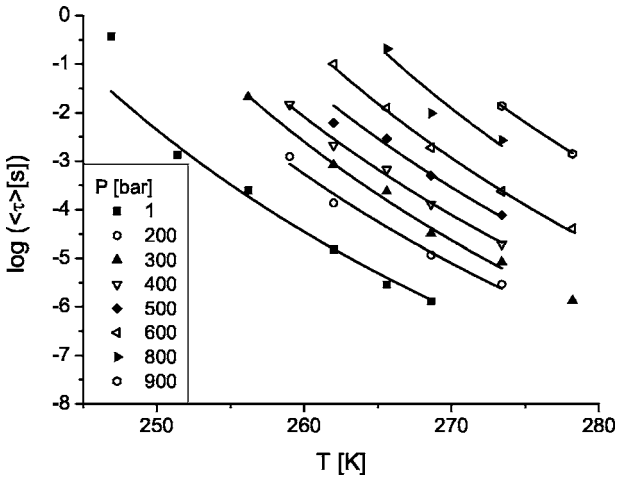

FIG. 4. Logarithm of mean relaxation times of the α relaxation measured with PCS for the whole range of temperatures and pressures studied. The lines are fits of Eq. (6) to the data.

In Fig. 7 we show the logarithm of mean relaxation times for the α and α' processes measured at different pressures and plotted as a function of $[T-T_{g,\alpha}(P)]$. As can be seen from the figure, for both processes master curves are formed, which means that the pressure dependence of the α' process is practically identical to that of the α process.

The width parameter β for the α process is a function of T and P. The variation is shown in Fig. 8.

The value of β_{KWW} of the α process varies linearly with T for a given P (Fig. 8): it increases from 0.46 to 0.60 as T increases from 247 to 278 K. This variation is in a fair agreement with the findings of Boese *et al.*,[2] who found β

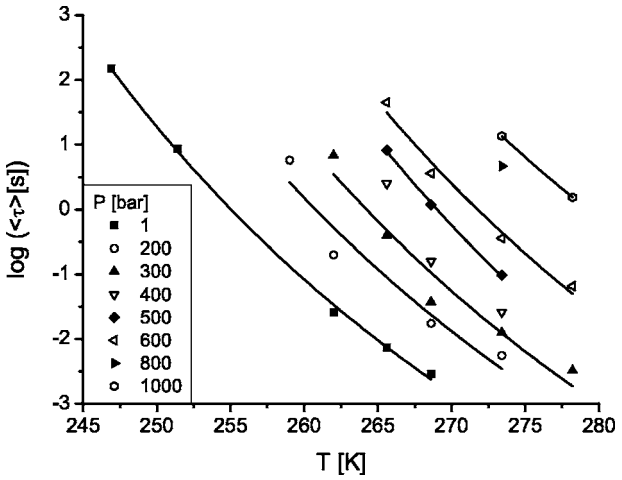

FIG. 5. Logarithm of mean relaxation times of the α' relaxation measured with PCS for the whole range of temperatures and pressures studied. The lines are fits of Eq. (6) to the data.

TABLE I. Fit parameters of the VFT equation obtained for the (a) α and (b) α' relaxation times and calculated on this basis values of T_g (100 s) and fragility m_T.

	Pressure (bar)	D_T	$\log(\tau_0/\mathrm{s})$	T_0 (K)	T_g (K)	m_T
(a)	1	11.69	−17.59	187.5	236.1	95.2
	200	11.69	−17.59	192	241.8	95.2
	300	11.69	−17.83	195	244.9	97.3
	400	11.69	−17.28	194.9	246.2	92.5
	500	11.69	−17.25	197	249.0	92.2
	600	11.69	−17.48	200.1	252.2	94.2
	800	11.69	−17.62	204	256.8	95.4
	900	11.69	−16.85	204.2	259.2	88.8
(b)	1	11.69	−15.05	190.7	247.5	74.3
	200	11.69	−15.17	195.3	253.0	75.2
	300	11.69	−15.47	198.9	256.7	77.6
	500	11.69	−16.11	204.5	261.8	82.7
	600	11.69	−15.11	203.4	263.8	74.8
	900	11.69	−13.62	203.4	269.5	63.7

values ranging from 0.46 to 0.52 in the temperature range between 253 and 273 K for PMPS of molecular weight of 28 500 kg/mol.

The pressure variation causes a parallel (within the experimental accuracy) shift of the activation curves. The extraction of the respective β_{KWW} parameters for the α' process is a bit more complicated, since the base line of the correlation function may have a considerable error for correlation times >100 s, which in turn renders the analysis ambiguous. For that reason we had to chose a fixed value for the width parameter (β=0.39) for the description of the α' process.

Using the data presented in Fig. 6 we calculated the slopes of $T_0(P)$ and $T_g(P)$ for both α and α' processes. The numbers are listed in the figure. For the α relaxation $dT_0/dP < dT_g/dP$, as usually observed, for example, in fragile van der Waals liquids.[20] This relation does not hold for the α' process.

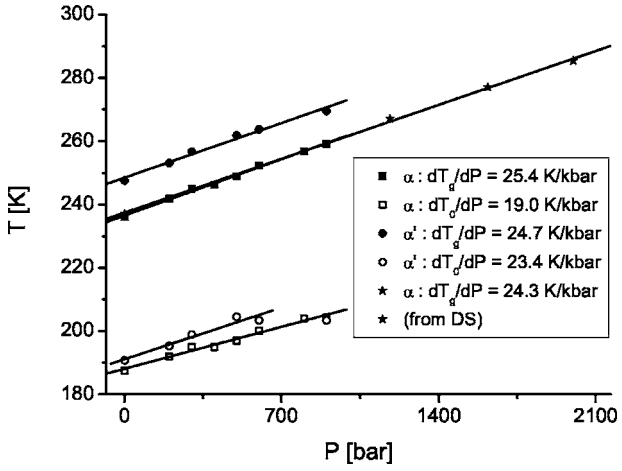

FIG. 6. The Vogel temperature T_0 and the glass transition temperature T_g calculated from the VFT fits to the isobars of the PCS results as a function of applied pressure. T_g was defined as the temperature at which the mean relaxation time reaches 100 s. Results of T_g obtained from DS data are also shown for comparison.

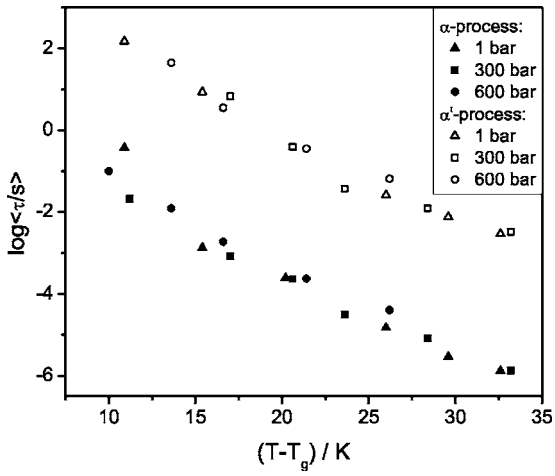

FIG. 7. Logarithm of mean relaxation times for the α (solid symbols) and α' processes (open symbols) measured at different pressures, plotted vs $T-T_{g,\alpha}(P)$.

An important parameter describing glass-forming liquids is the fragility m_T.[21] It is defined as the slope of the "Angell plot" at $T=T_g$:

$$m_T = \left.\frac{\partial \log\langle\tau\rangle}{\partial(T_g/T)}\right|_{T=T_g} = \frac{1}{\ln 10}\frac{D_T T_0 T_G}{(T_0 - T_g)^2}. \tag{7}$$

In Fig. 9 we plot m_T as a function of pressure for the α process.

Usually it is found that m_T is a weakly decreasing function of P. However, if we force fit the data of Figs. 3 and 4 with a single VFT function, thereby also taking into account values which were obtained with the tandem interferometer, then a very steep P dependence of m_T is obtained, as shown in Fig. 9. This finding contradicts the combined results of the PCS data and the DS results we have obtained for 1 bar and 2 kbars. The weak P dependence of m_T is in agreement with other findings[19] and seems to be correct; moreover, it is indirectly evidenced by the Stickel plot [see inset of Fig. 3(a)], where the use of one set of VFT parameters for the whole T range at a given P was shown to be incorrect. In Fig. 10 we

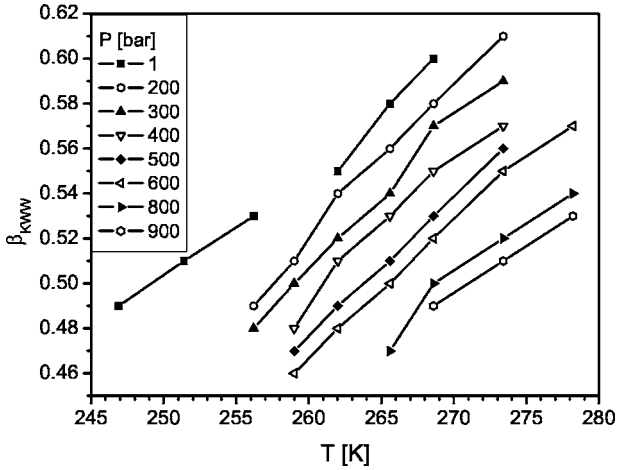

FIG. 8. β exponent of the KWW function, corresponding to the α relaxation, as a function of temperature and pressure. PCS results. The lines are guides to the eye.

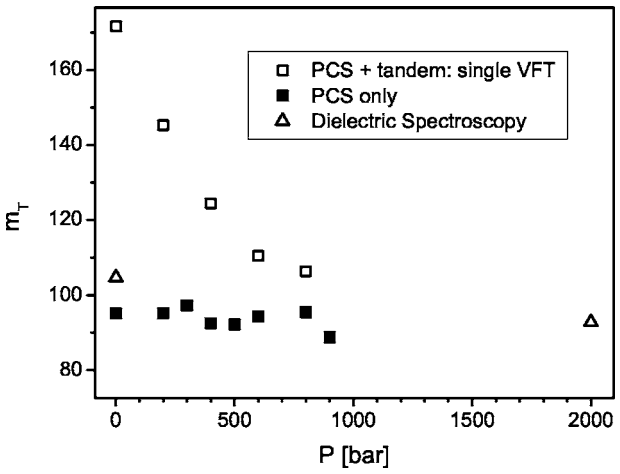

FIG. 9. Fragility m_T of the α process as a function of applied pressure calculated from the fitted VFT parameters (τ_g=100 s) using different ranges of experimental data. Using a single VFT model in the whole temperature range results in unrealistic values of m_T.

show the α traces for the DS results obtained for 1 bar and 2 kbars in a kind of Angell plot. For illustration purposes, in this plot τ_g was assumed to be 1 s in order to bring T_g into the experimentally accessible range and clearly show the difference in the slopes at $T=T_g$ for the two pressures. From this plot the m_T values were calculated and included also in Fig. 9. Clearly, on that basis the finding of the rather weak P dependence of m_T is further supported.

It is interesting to note that the PMPS polymer behaves like a fragile glass-forming liquid and is characterized by high fragility, intermediate nonexponentiality of the correlation function, and a strong dependence of the two characteristic temperatures T_0 and T_g on pressure. It has been shown previously,[22] that the nonexponentiality parameter β_{KWW} and fragility m_T for glass-forming liquids are related by an empirical formula as follows:

$$m_T = (250 \pm 30) - 320\beta_{\mathrm{KWW}}. \tag{8}$$

This dependence is also fulfilled in the case of the PMPS, however, taking the lower bound of the error range, and can

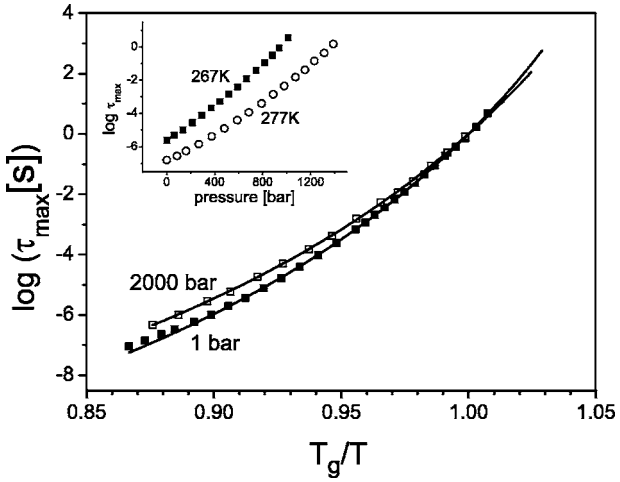

FIG. 10. Graphical illustration of the influence of pressure [P=1 bar (■) and P=2 kbars (□)] on the fragility m_T using the DS results. The inset shows the pressure dependence of α traces at T=267 K and T=277 K using the DS data.

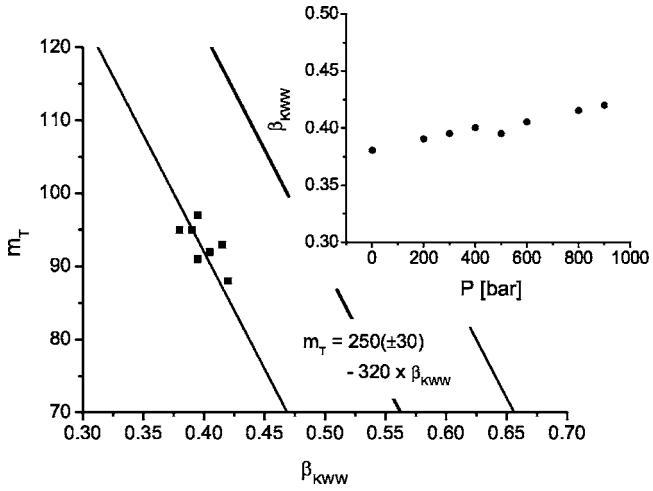

FIG. 11. Plot of the dependence of the fragility m_T on the nonexponentiality parameter $\beta_{\mathrm{KWW}}(P)$ extrapolated to T_g. In the inset the dependence of the extrapolated value of $\beta_{\mathrm{KWW}}(P,T_g)$ on pressure is shown.

be seen in Fig. 11, where the fragility $m_T(P)$ is plotted versus $\beta_{\mathrm{KWW}}(P,T_g)$ extrapolated to T_g. In the inset of the figure the dependence of the extrapolated value of $\beta_{\mathrm{KWW}}(P,T_g)$ on pressure is shown explicitly. As one can see, the change of $\beta_{\mathrm{KWW}}(P,T_g)$ with pressure is small, as was expected from the corresponding change of $m_T(P)$ and Eq. (8). In a previous paper[20] we have shown that within the framework of the VFT model, the Vogel temperature T_0 and the glass transition temperature T_g as well as their pressure dependences are related in the following way:

$$T_0 = CT_g \tag{9}$$

and

$$\frac{dT_0}{dP} = C\frac{dT_g}{dP} + T_g\frac{dC}{dP}, \tag{10}$$

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

Also, in the case of PMPS, this relationship is fulfilled using $dm_T/dP=-0.0035$ kbar^{-1} according to the data shown in Fig. 9. This value is roughly a factor of 2 smaller than the one for a fragile van der Waals liquid (the value for $dC/dP \approx -4.9\times10^{-3}$ kbar^{-1}).

Another useful parameter to characterize the pressure dependence of the structural relaxation time (α process) and compare it to the α' process in PMPS is the activation volume $\Delta V^{\#}$, defined as

$$\Delta V^{\#} = \frac{RT}{2.3}\left(\frac{\partial \log\langle\tau\rangle}{\partial P}\right)_T. \tag{11}$$

It is a measure for the volume requirements which are needed to go from one to another configuration state.[23–26]

Our experimentally obtained mean relaxation times for the α relaxation (cf. Fig. 4) and those for the α' process (cf. Fig. 5) can be presented in the form of isotherms and are shown in Fig. 12 for the α process and in Fig. 13 for the α' process. These relaxation times can be fitted with a pressure analog of the VFT equation as follows:

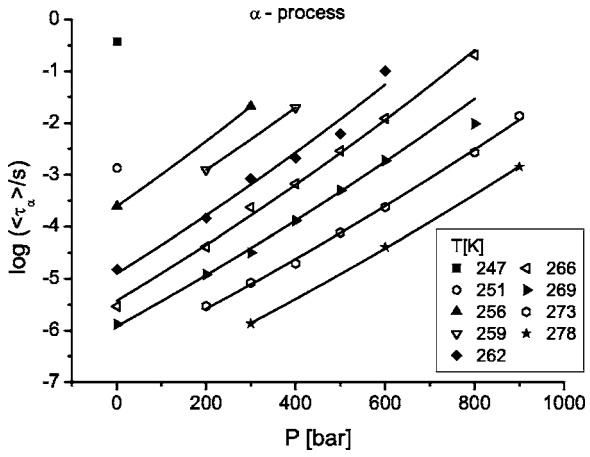

FIG. 12. Pressure dependence of the mean structural relaxation times (α relaxation) for various temperatures. The lines are best fits of Eq. (12) with the common value of $D_p=68\pm30$.

$$\langle\tau\rangle = \tau_a \exp\left(\frac{D_P P}{P_0 - P}\right), \tag{12}$$

where τ_a denotes the corresponding relaxation time measured under atmospheric pressure, P_0 is the pressure of the ideal glass transition at a constant temperature, and D_P is a dimensionless parameter defined analogous to D_T in the temperature dependent VFT equation.

For the latter process we were only able to calculate the activation volume via Eq. (11) for four different temperatures due to the reduced number of data points at a given temperature. This result is plotted together with the data of the activation volume for the α process in Fig. 14 as a function of temperature as derived from our light scattering data. From the data shown in the inset of Fig. 10 we were also able to calculate the activation volume from the DS data for two temperatures. These results are also plotted in Fig. 14. The so obtained values of $\Delta V^{\#}$ (calculated in a pressure range up to 800 bars) for the α process are smaller by about 10%, but give a similar temperature trend, as compared to the DLS data: The activation volumes decrease with increasing T, which is usually observed in fragile glass-forming liquids.

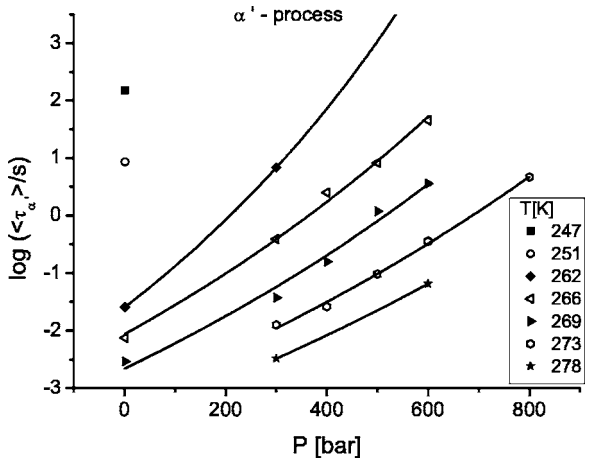

FIG. 13. Pressure dependence of the mean relaxation times of the slow process (α' relaxation) for various temperatures. The lines are best fits of Eq. (12) with the common value of $D_p=30\pm15$.

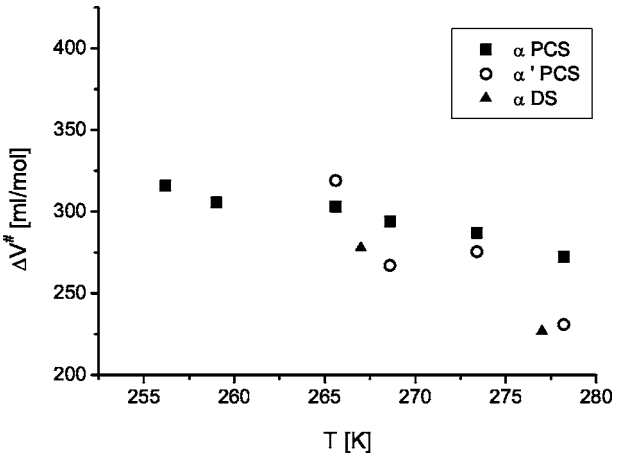

FIG. 14. Activation volumes as a function of temperature for the α and α' processes as obtained from DLS measurements. Data points from DS at $T=267$ and 277 K are also shown.

In addition to that, it seems that the values of $\Delta V^{\#}$ for α and α' are very similar within the experimental uncertainty. This is a surprising finding, since the α' process was thought to be related to a chain motion (end-to-end vector) rather than to a segmental motion alone. However, the activation volume is not directly related to the volume of the entire relaxing molecule, i.e., the value of $\Delta V^{\#}$ for the relaxation of the end-to-end vector is not related to the volume of the entire chain, but rather to the volume of the subunit relaxing in an elementary step. Since the relaxation of the chain can proceed only through rearrangement of monomers, it is not surprising that more cooperative chain modes, involving several polymer segments (monomers), have a similar activation volume to that of local segmental relaxation. Casalini and Roland[27] report in a recent DS study on poly(oxybutylene), a molecule with a dielectrically active normal mode process similar to PPG, that the activation volumes for the α and α' processes are also similar. This is in agreement with our findings for PMPS obtained with light scattering.

In order to compare our results with those obtained by Floudas and Reisinger[28] on *cis*-PI, we have replotted in Fig. 15 some of the data from Figs. 12 and 13 for the α and α' processes at three different temperatures, $T=266$, 269, and 273 K. Floudas and Reisinger have shown that the pressure dependence of the α and α' processes are so different such that the curves cross at high pressures. In our case the pressure dependences are almost identical and therefore, as is evidenced from our Fig. 15, such a crossing is not to be expected.

Recently, it was shown[29–35] that the temperature and pressure dependences of the structural relaxation time in supercooled liquids can be consistently described in terms of a Γ parameter: $\Gamma=\rho^n/T$, where ρ is the density and the exponent n depends on the material. In such a case, plotting τ_α vs Γ results in a master curve for all temperatures and pressures. Roland and Casalini[32] have shown that in the case of poly(propylene glycol) the exponent n is the same for both the segmental (α relaxation) and normal modes (α' relaxation) of the polymer, which means that for both processes the logarithm of the corresponding correlation time is given by the following formula:

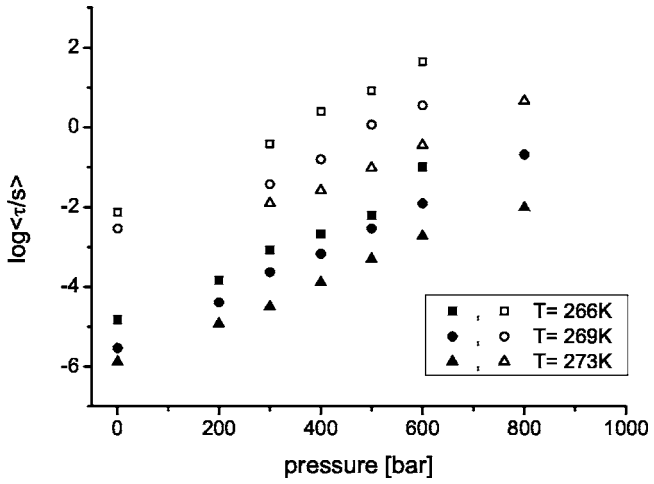

FIG. 15. Pressure dependence of the logarithm of the α relaxation times (solid symbols) and the α' relaxation times (open symbols) for different temperatures as indicated.

$$\log\langle\tau\rangle = \log\,\tau_0 + F(\Gamma), \tag{13}$$

where $F(\Gamma)$ is identical for both processes and the only difference between the α and α' relaxations on the right-hand side of the formula is the corresponding value of $\log\,\tau_0$. Thus, we can write

$$\log\langle\tau^{(\alpha')}\rangle = \log\,\frac{\tau_0^{(\alpha')}}{\tau_0^{(\alpha)}} + \log\langle\tau^{(\alpha)}\rangle, \tag{14}$$

where $\tau^{(\alpha)}$, $\tau_0^{(\alpha)}$, $\tau^{(\alpha')}$, and $\tau_0^{(\alpha')}$ are the relaxation times of the α and α' processes, respectively. From this formula it obviously follows that a plot of $\log\langle\tau^{(\alpha')}\rangle$ vs $\log\langle\tau^{(\alpha)}\rangle$ should be linear with a slope of 1 and an intercept equal to $\log[\tau_0^{(\alpha')}/\tau_0^{(\alpha)}]$. Such a plot for PMPS is shown in Fig. 16.

As one can see, all the experimental temperature and pressure dependent times of the α and α' processes fall on a straight line with a slope of 1. Thus, we can conclude that the scaling of the temperature and pressure dependences of the relaxation times of both the α and α' processes in PMPS can be performed with the same parameter $\Gamma=\rho^n/T$ and the same value of the exponent n.

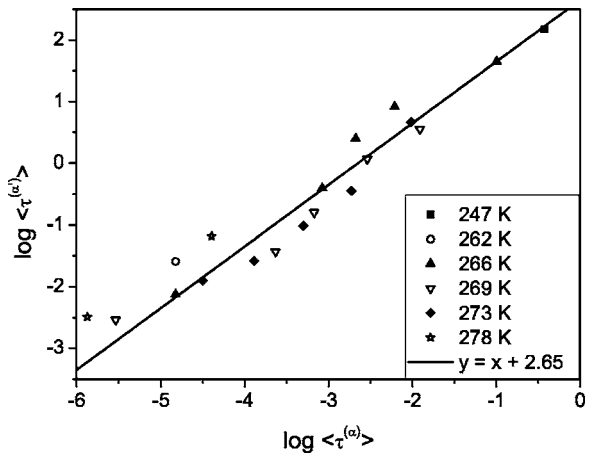

FIG. 16. A plot of $\log\langle\tau^{(\alpha')}\rangle$ vs $\log\langle\tau^{(\alpha)}\rangle$ for all temperatures and pressures measured by DLS.

CONCLUSIONS

Two relaxation processes, α and α', were measured in PMPS by DLS-PCS. The relaxation time of the α' process is longer by about three orders of magnitude than that of the α relaxation. In the case of DS studies in other materials a similar additional slower process was assigned to the normal modes of the chain. However, it is not clear if this α' process, seen in polysiloxanes and in POB in the DLS experiments, has the same molecular origin and features as that observed in other materials by means of DS. It is also not clear why α' relaxation can be observed in DLS studies only in polysiloxanes and PPG, but not in other polymers. Is it due to the fact that some polymers do not have this process, or is it rather that the process is present in all polymers, but is visible only in some of them because it cannot be resolved from the α relaxation? We should note here that the α' process can be seen in DLS experiment only in those polymers, where the β parameter of the α relaxation is relatively high $(0.6<\beta<0.8)$ and consequently the width of the α process is small.

The pressure dependence of the α' relaxation time was measured for the first time and compared with that of the α process in a broad temperature range. The dynamics of the same polymer was also measured by means of DS in comparable temperature and pressure ranges. Only the α relaxation was seen in the DS spectra.

Isobaric temperature dependence (at all pressures studied) of both α and α' processes can be described by the VFT law. For the α process, where relaxation times could be measured in a broader temperature range, two sets of VFT parameters were obtained for the low $(D_T=12)$ and high $(D_T=2.1)$ temperature ranges, respectively. The D_T parameters are pressure independent and identical for both α and α' processes in the low temperature range. In a plot of $\log\langle\tau\rangle$ vs $(T-T_g)$, taking T_g from the α relaxation, the values of the α and α' relaxation times collapsed on master curves. The crossover from low to high temperature range occurs at $T=280$ K, where both the slope of the Stickel plot and the plot of $\Delta\varepsilon$ vs $\log\langle\tau_\alpha\rangle$ change.

The pressure dependence of the VFT temperature T_0 and the glass transition temperature $T_g(100\text{ s})$ are very similar for both processes, namely, for α relaxation, DLS: $dT_0/dP=19.0$ K/kbar, $dT_g/dP=25.4$ K/kbar; DS: $dT_g/dP=24.3$ K/kbar; and for the α' process $dT_0/dP=23.4$ K/kbar and $dT_g/dP=24.7$ K/kbar. The values of T_0, T_g, and fragility m_T and their pressure dependences are related in the usual way.[20]

The value of the nonexponentiality parameter β_{KWW} of the α process is increasing with increasing temperature in the isobaric experiments. The change of β_{KWW} at T_g with pressure fulfills the usual correlation between β_{KWW} and fragility, observed in other glass-forming liquids.

The activation volumes of the α and α' processes in PMPS are very similar and decrease slightly with increasing temperature. A similar pattern of behavior was also observed recently by means of dielectric spectroscopy in polypropylene glycol (PPG).[36,37]

Temperature and pressure dependences of the relaxation

times of both α and α' processes in PMPS can be expressed in terms of the parameter $\Gamma=\rho^n/T$, with the same value of the exponent n for both processes. It is worthy to note that the α' process observed in dielectric spectra of PPG has been attributed to the motion of the whole polymer chain (normal mode). Since the α' relaxation measured in PCS experiments in PMPS has very similar features to the α' process in DS spectra (in PPG), we can conclude that the α' process in PMPS (measured by PCS) has the same molecular origin as the α' process in PPG.

An additional support for the assignment of the α' process in PMPS to the more cooperative relaxation modes of the polymer chain is presented in our next paper, where the structural relaxation of three poly(methyl-*para*-tolylsiloxane) samples of different molecular weights (from 4500 to 42 000) was studied by means of PCS.[38] For one of the samples the PCS results were compared with the data obtained from mechanical relaxation, dielectric spectroscopy, and computer simulations. We found that the relaxation time of the α' process is proportional to the molecular weight of the polymer, justifying the assignment of this process to the normal modes of the chain. Simulated correlation functions of the bond orientation, phenyl ring orientation, dipole moment orientation, and density fluctuations also exhibit a bimodal decay without taking explicitly into account the end-to-end vector of the chain. Thus, the α' relaxation can be assigned to the more cooperative chain modes, and depending on the probe and method used, it can or cannot be seen in the spectra or correlation functions measured.

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[1] T. Kanaya, A. Patkowski, E. W. Fischer, J. Seils, H. Gläser, and K. Kaji, Acta Polym. **45**, 137 (1994).
[2] D. Boese, B. Momper, G. Meier, F. Kremer, J.-U. Hagenah, and E. W. Fischer, Macromolecules **22**, 4416 (1989).
[3] S. W. Smith, B. D. Freeman, and C. K. Hall, Macromolecules **30**, 2052 (1997).
[4] M. E. Baur and W. H. Stockmayer, J. Chem. Phys. **43**, 4319 (1965).
[5] S. Yano, R. R. Rahalkar, S. P. Hunter, C. H. Wang, and R. H. Boyd, J. Polym. Sci., Polym. Phys. Ed. **14**, 1877 (1976).
[6] G. P. Johari, Polymer **27**, 866 (1986).
[7] K. Adachi and T. Kotaka, Macromolecules **17**, 120 (1984).
[8] K. Adachi and T. Kotaka, Macromolecules **18**, 466 (1985).
[9] T. Kanaya, A. Patkowski, E. W. Fischer, J. Seils, H. Gläser, and K. Kaji, Macromolecules **28**, 7831 (1995).
[10] C. M. Roland, M. Paluch, and R. Casalini, J. Polym. Sci., Part B: Polym. Phys. **42**, 4313 (2004).
[11] B. Momper, Th. Wagner, U. Maschke, M. Ballauff, and E. W. Fischer, Polym. Commun. **31**, 186 (1990).
[12] G. Fytas, G. Meier, and Th. Dorfmüller, Macromolecules **18**, 993 (1985).
[13] M. Paluch, J. Chem. Phys. **115**, 10029 (2001).
[14] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
[15] S. Havriliak and S. Negami, Polymer **8**, 161 (1967).
[16] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **102**, 6251 (1995); **104**, 2043 (1996).
[17] H. Kriegs *et al.* (unpublished).
[18] A. Schönhals, Europhys. Lett. **56**, 815 (2001).
[19] M. Paluch, J. Gapinski, A. Patkowski, and E. W. Fischer, J. Chem. Phys. **114**, 8048 (2001).
[20] A. Patkowski, M. Paluch, and J. Gapinski, J. Non-Cryst. Solids **330**, 259 (2003).
[21] R. Böhmer and C. A. Angell, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer Verlag, Berlin, 1994).
[22] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[23] A. Zussman and E. Rapoport, J. Chem. Phys. **61**, 5098 (1974).
[24] G. Fytas, A. Patkowski, G. Meier, and Th. Dorfmüller, J. Chem. Phys. **80**, 2214 (1984).
[25] H. Leyser, A. Schulte, W. Doster, and W. Petry, Phys. Rev. E **51**, 5899 (1995).
[26] M. Paluch, S. Pawlus, and C. M. Roland, Macromolecules **35**, 7338 (2002).
[27] R. Casalini and C. M. Roland, Macromolecules **38**, 1779 (2005).
[28] G. Floudas and T. Reisinger, J. Chem. Phys. **111**, 5201 (1999).
[29] C. Dreyfus, A. Le Grand, J. Gapinski, W. Steffen, and A. Patkowski, Eur. Phys. J. B **42**, 309 (2004).
[30] C. Dreyfus, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski, and R. M. Pick, Phys. Rev. E **68**, 011204 (2003).
[31] C. Alba-Simionesco, A. Cailliaux, A. Alegria, and G. Tarjus, Europhys. Lett. **68**, 58 (2004).
[32] C. M. Roland and R. Casalini, J. Chem. Phys. **120**, 10640 (2004).
[33] R. Casalini and C. M. Roland, Phys. Rev. E **69**, 062501 (2004).
[34] C. Alba-Simionesco, D. Kivelson, and G. Tarjus, J. Chem. Phys. **116**, 5033 (2002).
[35] G. Tarjus, D. Kivelson, S. Mossa, and C. Alba-Simionesco, J. Chem. Phys. **120**, 6135 (2004).
[36] S. P. Andersson and O. Andersson, Macromolecules **31**, 2999 (1998).
[37] C. M. Roland, T. Psurek, S. Pawlus, and M. Paluch, J. Polym. Sci., Part B: Polym. Phys. **41**, 3047 (2003).
[38] A. Patkowski, J. Gapinski, T. Pakula, and G. Meier Polymer (submitted).