Colloid Polym Sci (2004) 282: 882–891
DOI 10.1007/s00396-004-1106-3

ORIGINAL CONTRIBUTION

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Glass transition of polymers confined to nanoporous glasses

Received: 23 February 2004
Accepted: 19 March 2004
Published online: 27 April 2004
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Abstract The glassy dynamics of poly(propylene glycol) (PPG) and poly(methyl phenyl siloxane) (PMPS) confined to nanoporous glasses (pore sizes 2.5–20 nm) investigated by dielectric spectroscopy, temperature modulated DSC and neutron scattering is compared. For both systems the relaxation rates estimated from dielectric spectroscopy and temperature modulated DSC agree quantitatively indicating that both experiments sense the glass transition. For PPG the glassy dynamics in nanopores is determined by a counterbalance of an adsorption and a confinement effect where the temperature dependence of the relaxation times obeys the Vogel/Fulcher/Tammann (VFT-) equation. The former effect results from an interaction of the confined macromolecules with the internal surfaces which in general slows down the molecular dynamics. A confinement effect leads to an acceleration of the segmental dynamics compared to the bulk state and points to an inherent length scale on which the glassy dynamics takes place. The step of the specific heat capacity Δc_p at the glass transition vanishes at a finite length scale of 1.8 nm. This result supports further the conception that a characteristic length scale is relevant for glassy dynamics. For PMPS down to a pore size of 7.5 nm the temperature dependence of the relaxation times follows the VFT-dependence and a confinement effect is observed like for PPG. At a pore size of 5 nm this changes to an Arrhenius-like behavior with a low activation energy. At the same pore size Δc_p vanishes for PMPS. This points to a dramatic change in the character of molecular motions responsible for glassy dynamics and supports further the relevance of a characteristic length scale on which it takes place. Quasielastic neutron scattering experiments on PMPS reveal that the microscopic dynamics characterized by the mean square displacement depends on confinement above the glass transition. The diffusive character of the relevant molecular motions seems to disappear at a length scale of about 1.6 nm.

Keywords Glass transition Polymers · Nanoporous glasses · Glassy dynamics · Poly(propylene glycol) · Poly(methyl phenyl siloxane)

Introduction

If a glass-forming liquid cools down a dramatic increase of the viscosity and the structural (α)-relaxation time τ is observed. Decreasing the temperature by a factor of 2 close to the glass transition temperature T_g at atmospheric pressure leads to an increase of τ by 14 orders of magnitude. This bridges microscopic and macroscopic time scales. The temperature dependence of τ can be approximated by the Vogel/Fulcher/Tammann formula [1, 2, 3] which reads

$$\log \tau = \tau_\infty + \frac{A}{T - T_0}. \tag{1}$$

where τ_∞ and A are constants and T_0 is the so-called Vogel temperature. Besides this strong temperature dependence of the relaxation time a broadening of the relaxation function, a Goldstein/Johari (slow) β-process [4, 5] and an excess contribution to the low energy vibrational density of states (Boson-Peak) [6] are found to be characteristic for glass-forming materials [7]. At a relaxation time which is much lower than that of the α-relaxation an ultra slow relaxation process can be observed [8] which seems to be also related to the glass transition. Thus the dynamic and static features of super-cooled liquids and glasses are distributed over a very wide time and spatial scale and occur in a broad temperature range. Although the phenomena of glass transition is investigated experimentally and theoretically for a long time it is still not completely understood.

The dramatic increase of the relaxation times with decreasing temperature can be most naturally interpreted assuming a cooperative behavior of the relevant molecular motions. The extent of this cooperativity—characterized by a correlation length ξ—is assumed to increase with decreasing temperature [9, 10, 11, 12]. At the glass transition temperature ξ should be in the range of a few nanometers (see for instance [10, 12]). The question is if there is experimental evidence for such a length scale related to those molecular motions which are responsible for the glass transition. Recently some experiments show the existence of dynamical heterogeneities in glass-forming materials, typically found on a length scale of several nanometers [13]. The lifetime of these dynamical heterogeneities is a little bit longer than the relaxation time of the α-process just above T_g. The relevance of a length scale responsible for glassy dynamics can be indirectly proven by investigating the behavior of molecules confined to hosts with confining dimensions on the nanometer scale since ξ cannot exceed the pore size. A limitation of the characteristic length in confinement should lead to an acceleration of the molecular dynamics compared to the bulk (hindered glass transition [10], confinement effect [14]). This is observed for a variety of low molecular weight [14, 15, 16, 17] and polymeric [18, 19, 20] glass-forming systems (see also [14]). Also the transition from a VFT-temperature dependence of the α-relaxation time to an Arrhenius one reported in [16, 20] and the strong decrease of the step in the specific heat Δc_p at T_g with decreasing pore size [18, 20] can be interpreted assuming (the reduction of) a cooperativity length scale. However, it should be noted that purely thermodynamic arguments might be also applied to explain confinement effects [21]. Other considerations are based on the coupling scheme [22].

Apart from the discussed spatial scale arguments the behavior of a confined liquid is more complex. So the molecular dynamics of the confined glass-forming material should also be influenced by surface interactions (adsorption effect), which in general would lead to a slowing down of the relaxation times [14, 17, 18, 23]. Adsorption effects should scale with the surface-to-volume ratio of the confining porous systems. As a consequence the molecular dynamics in confining space is in general determined by a counterbalance between surface and confinement effects.

At the end it should be also stated that the density of a confined glass-forming material can be smaller than that of the corresponding bulk and moreover that the whole thermodynamic state can be different from that of a confined liquid [17]. Experimentally even changes in the fast microscopic dynamics and in the vibrational density of states (Boson Peak) have been observed by neutron scattering [24, 25, 26].

Thus despite the numerous experimental and theoretical results concerning the glassy dynamics of nano-confined supercooled liquids, no general agreement has been achieved yet. Therefore in this contribution the behavior of two polymer model systems confined to nanoporous glasses is investigated by a variety of methods like dielectric spectroscopy, temperature modulated calorimetry, and neutron scattering.

Experimental

Poly(methyl phenyl siloxane) (PMPS) with a molecular weight of 1000 g mol^{-1} is used as one model system. The glass transition temperature T_g is estimated by DSC to 222 K. As a second model system poly(propylene glycol) (PPG) with a molecular weight of $M_W = 3000$ g mol^{-1} is selected. The glass transition temperature was estimated to $T_g = 206$ K and it is known that for PPG T_g is independent of the molecular weight for $M_W \geq 1000$ g mol^{-1}. In contrast to PMPS, PPG is a type-A polymer having a dipole component parallel to the chain backbone. For this class of macromolecules the whole chain dynamics can be observed in addition to segmental fluctuations by dielectric spectroscopy [27].

As host systems silica based nanoporous glasses with mean pore dimensions of 2.5 nm, 5.0 nm, 7.5 nm, and 20 nm are used. According to the supplier, Geltech Inc., USA, the pore size distribution is narrow. Because these glasses are prepared by a sol/gel process they have also a distribution of pore shapes and interconnected cavities [28]. Disk-like samples (thickness = 0.3 mm) with a diameter of 10 mm for the dielectric and neutron scattering experiments were prepared. According to the dimension of a DSC pan the diameter of the samples for the thermal measurements was 6 mm. The procedure to load the confining glasses with the polymeric melt is described in detail elsewhere [18]. To remove water and organic impurities the disk was heated to 573 K for 1 h, evacuated to 10^{-5} mbar, and kept there for 24 h. Then the disk was slowly cooled down to 373 K and the polymeric melt was injected directly into the vacuum chamber. To modify the interaction of the guest molecules with the host a second set of samples was prepared where the surface silanol groups of the native glasses were converted into the less hydrophilic trimethylsilyl groups before filling (coated pores). For details see [18]. After that treatment the pores were filled as described above. The dielectric function $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$ (f—frequency, ϵ'—real part, ϵ''—loss part, $i = \sqrt{-1}$) was measured in the frequency range from 10^{-4} Hz to 10^9 Hz [29]. The outer surfaces of the glass disk were covered by a thin silver foil to ensure a good electrical contact and a homogeneous measuring field. The dielectric data are analyzed by fitting the model function of Havriliak/Negami to the data and the relaxation rate at maximal dielectric loss f_p is estimated. For details see [30].

To study the dynamics related to enthalpy (or entropy) fluctuations temperature modulated differential scanning calorimetry (TMDSC) was employed [31]. These measurements result in a complex heat capacity $c^*(f) = c'(f) - ic''(f)$ (c′—real part, c″—loss part) [32]. Here f is the frequency of the temperature modulation which is varied from 10^{-3} to 3.4×10^{-2} Hz. A Perkin Elmer Pyris 1 DSC was used for the measurements where all discussed data were taken from the heating runs. The heating rates were chosen between 1 K min^{-1} and 3 K h^{-1} to meet stationary conditions. $\tan\delta = c''(f)/c'(f)$ is the part of the phase angle which is due to time dependent processes in the sample but it must be corrected for heat transfer processes [33]. An empty glass disc of the same pore size than the sample under investigation was used in the reference pan.

The neutron scattering experiments have been carried out at the Institute Laue-Langevin, Grenoble using the backscattering spectrometer IN16 with an incident wavelength of 6.271 Å. The energy resolution is $\Delta E = 0.9$ μeV (full width at half maximum) and scattering vector range: $0.2 < Q < 1.93$ Å^{-1}. The scattering contributions from the host, the sample holder and spectrometer background were determined by reference measurements using empty nanoporous glass discs sealed under a He atmosphere. The major part of the scattering results from the protons of the melt and is thus incoherent scattering.

Results

The dielectric response of bulk PMPS is characterized by one relaxation process—the α-relaxation (dynamic glass transition)—related to segmental dynamics [34]. This can be also seen in Fig. 1 where the dielectric loss ϵ'' of PMPS is plotted vs temperature at a fixed frequency. Surprisingly for PMPS confined to nanopores two relaxation processes are observed. The one at lower temperatures corresponds to the α-process of bulk PMPS and is therefore assigned to the dynamic glass transition. The process at higher temperatures shifts with decreasing pore size systematically to higher temperatures. For PMPS in coated pores this process disappears (see inset of Fig. 1) and only a broadened α-relaxation is observed. Therefore the relaxation process at higher temperatures is assigned to polymer segments forming an interfacial layer close to the pore wall with an essential lower molecular mobility than the bulk. These results are quite similar than that found for the glass-forming liquid salol [14, 15].

As discussed above in contrast to PMPS poly(propylene glycol) is a typical type-A polymer having a dipole component parallel to the chain backbone [27]. This give rise to a further dielectric active relaxation process—called normal mode process—which can be observed at lower frequencies/higher temperatures than the α-relaxation. The normal mode relaxation is directly related to the self-diffusion of a polymer chain [35]. As for PMPS, PPG confined to uncoated native pores also shows a bimodal relaxation spectra (see Fig. 2). Because PPG is a type-A polymer the process at higher temperatures/lower frequencies was related to the normal mode relaxation in previous publications [14, 18]. However, in the light of the results obtained for PMPS, this interpretation should be carefully checked. It also seems probable that for PPG this relaxation process has to be assigned to an interfacial layer related to adsorption phenomena as for PMPS. If this interpretation is true this relaxation peak overlays the normal mode relaxation which should also take place in uncoated pores. This line of argumentation is supported by Pulsed Field Gradient NMR (PFG NMR) investigations to study the diffusion process of PPG in native uncoated pores directly [36]. The incoherent intermediate dynamic structure factor $S_{inc}(q, t)$ shows a bimodal dependence on q^2t (generalized q-scattering vector, t-diffusion time) which has to be interpreted by a two state model with two different species of polymer segments having two different diffusion coefficients. The lower diffusion coefficient is assigned to polymer segments which are adsorbed at the pore walls. The higher one is due to polymer segments which are located more in the center of the pores. Because diffusion is closely related to the normal mode process it is concluded that it also takes place in uncoated pores.

In coated pores the relaxation process at lower frequencies also disappears for PPG (see inset Fig. 3) and the overlaid normal mode can be observed in dependence of the pore size (see Fig. 3). With decreasing pore size the normal mode relaxation broadens and shift to higher temperatures/lower frequencies. These results are in full agreement with that obtained by PFG NMR [36]. For coated pores the bimodal structure of $S_{inc}(q, t)$ vs q^2t disappears. $S_{inc}(q, t)$ broadens and the estimated diffusion coefficients decreases with decreasing pore size. This can be understood taking tortuosity as well as interaction effects into account.

Results concerning the α-relaxation of PPG confined to nanoporous glasses were discussed recently [18]. Therefore these data will be summarized here only briefly. Figure 4 gives the relaxation map for PPG. The data obtained by dielectric and thermal spectroscopy agree (see inset A, Fig. 4) with each other and their temperature dependence can be described by the VFT-equation. The segmental dynamics of PPG in nanoporous environments is determined by a counterbalance of the confinement and an adsorption effect [14]. For pore sizes down to 5 nm the α-relaxation of the confined PPG is accelerated compared to that of the bulk state (confinement effect, see inset B, Fig. 4) whereas for smaller pore sizes the segmental dynamics slows down (adsorption effect). As discussed in [14] the latter results from interactions of the confined polymer at the interface with the host system, the former originating from a length scale on which the underlying molecular motions takes place. The observation of a confinement effect supports the conception that a length scale is relevant for the glassy dynamics. From the TMDSC measurements the step in the specific heat capacity Δc_p at the glass transition normalized to weight of the polymer melt can be estimated. With decreasing pore size Δc_p drops down dramatically and vanishes at a length scale of about 1.6 to 1.8 nm (see Fig. 5). Below that finite length scale no glass transition can take place for this system. Therefore this value might be considered as a minimal or cut-off length scale for glass transition which would indicate the relevance of an inherent length scale for glass transition. The temperature dependence of the high temperature process of PPG confined to nanoporous glasses seems to be curved in the activation plot (see Fig. 4). However, to get a crude characterization of this

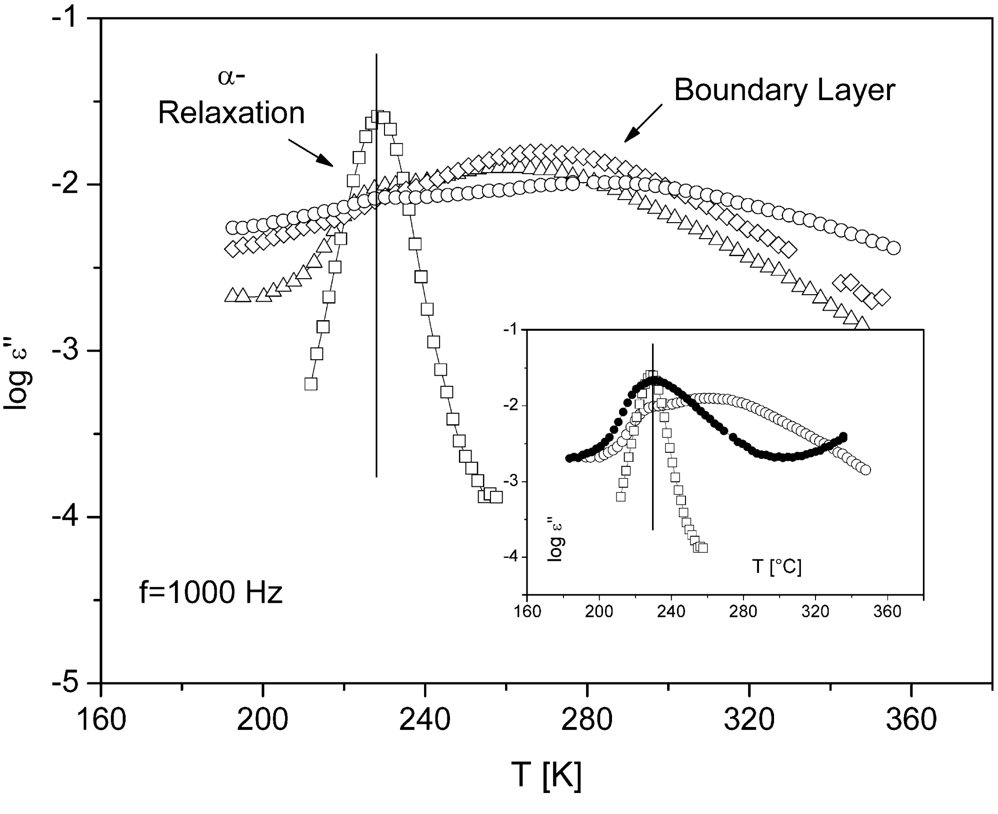


Fig. 1 Dielectric loss ϵ'' of PMPS vs temperature at a frequency of 10^3 Hz for PMPS in the bulk (*open squares*) and in uncoated pores: *open triangles*—7.5 nm, *open diamonds*—5 nm, *open circles*—2.5 nm. The *inset* compares the dielectric spectra of PMPS in the bulk (*open squares*) and for uncoated (*open circles*) and coated pores (*filled circles*) of a size of 7.5 nm

Fig. 2 Dielectric loss ϵ'' (corrected for pore volume) vs temperature at a frequency of 10^3 Hz for PPG in the bulk (*open squares*) and in uncoated pores: *open circles*—7.5 nm, *open triangles*—2.5 nm

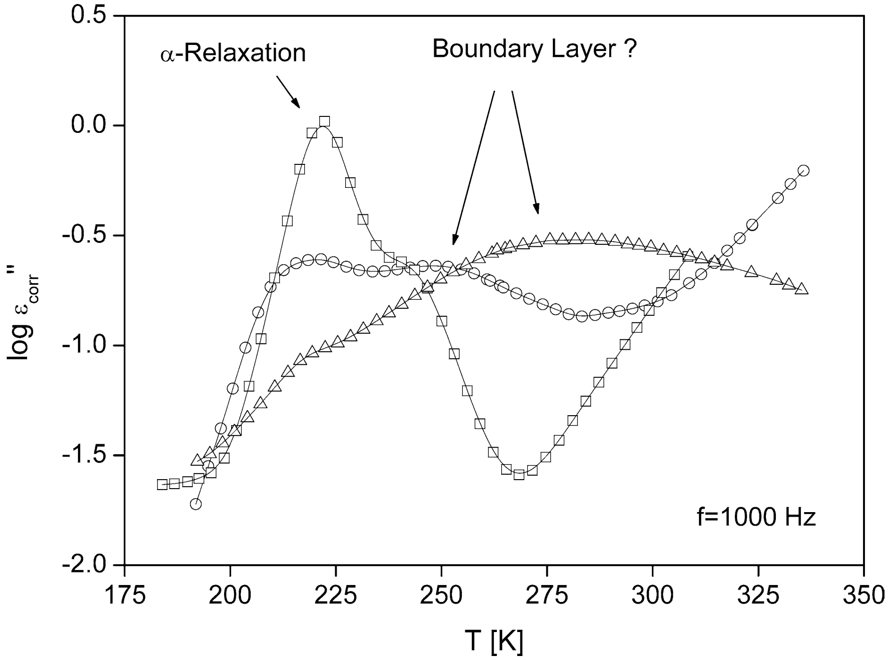
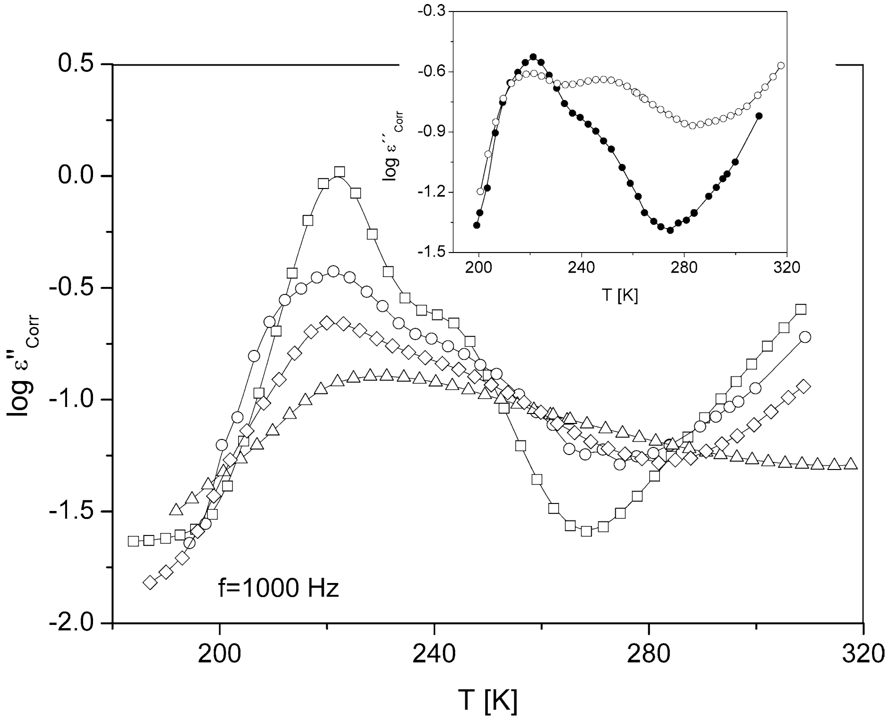


Fig. 3 Dielectric loss ϵ'' (corrected for pore volume) vs temperature at a frequency of 10^3 Hz for PPG in the bulk (*open squares*) and in silanized pores: *open circles*—7.5 nm, *open diamonds*—5 nm, *open triangles*—2.5 nm. The *inset* compares the dielectric spectra of PPG in uncoated (*open circles*) and coated pores (*filled circles*) of a size of 7.5 nm



temperature dependence the Arrhenius equation $f_p = f_\infty exp\left(-\frac{E_A}{k_B T}\right)$ is fitted to the data (E_A—apparent activation energy, f_∞—prefactor, and k_B—Boltzmann constant). This will enable a comparison with the results obtained for PMPS (see below). Both E_A and f_∞ increase with decreasing pore size (see Fig. 6) indicating that the interaction of the polymer segments with the pore wall increases with decreasing pore size.

The activation diagram for PMPS in uncoated pores is given in Fig. 7. The relaxation rates of the

Fig. 4 Relaxation rate at maximal loss f_p vs 1/T of PPG in uncoated pores: *squares*—bulk, *inverted triangles*—20 nm *circles*—7.5 nm, *diamonds*—5 nm, *triangles*—2.5 nm. *Solid symbols* α-relaxation, *open symbols* low frequency process. The lines are fits of the VFT-equation to the data. The *inset (A)* compares the dielectric data (*open symbols*) with data obtained by TMDSC (*solid symbols*) for uncoated pores. In the *inset (B)* the α-relaxation is enlarged. *stars*—PPG in 7.5 nm coated pores

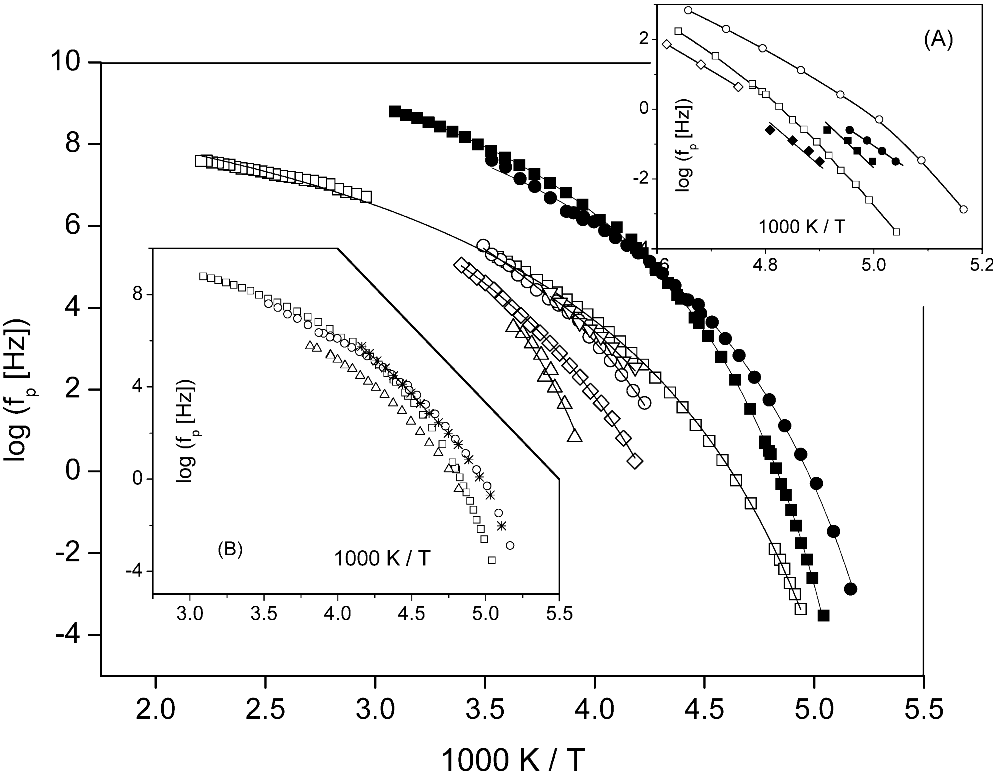
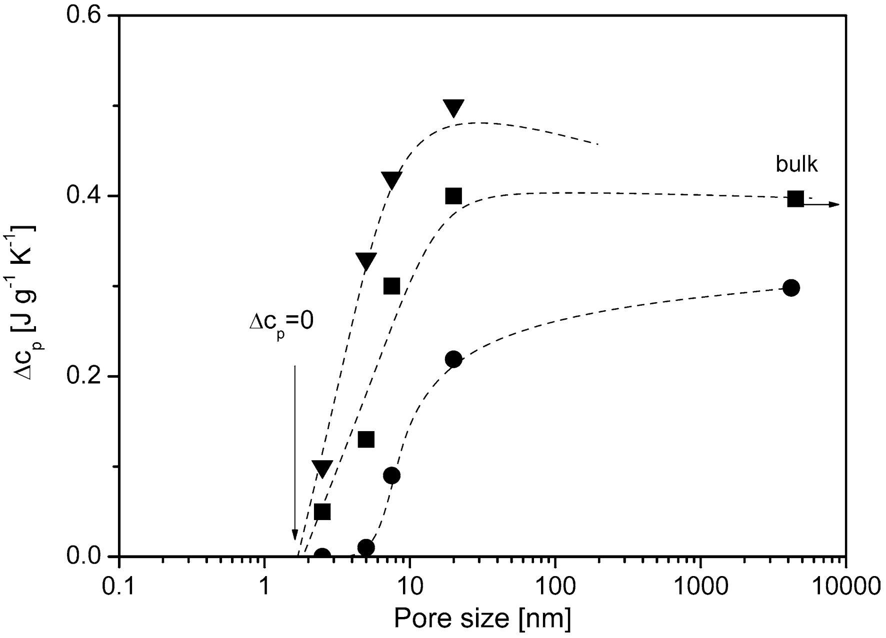


Fig. 5 Δc_p vs pore size for PPG (2000 g mol^{-1}) and PMPS: *filled inverted triangles*—PPG in uncoated pores; *filled squares*—PPG in coated pores, *filled circles*—PMPS in uncoated pores. *Lines* are guides for the eyes



high temperature/low frequency relaxation process which is assigned to the dynamics of segments forming a surface layer have approximately an Arrhenius-like temperature dependence. The estimated activation energies and the prefactors are quite high. Therefore this Arrhenius-like dependence is probably an apparent one. If a broader temperature range could be covered it is expected that f_p is curved vs 1/T as for PPG. Both E_A and f_∞ increase with decreasing pore size like for PPG (see Fig. 6). The values are even

Fig. 6 Activation energy of the relaxation process assigned to the interfacial layer vs pore size: *filled inverted triangles*—PPG, *filled circles*—PMPS. *Lines* are guides for the eyes. The *inset* shows the correlation of log f_∞ and E_A in the compensation plot

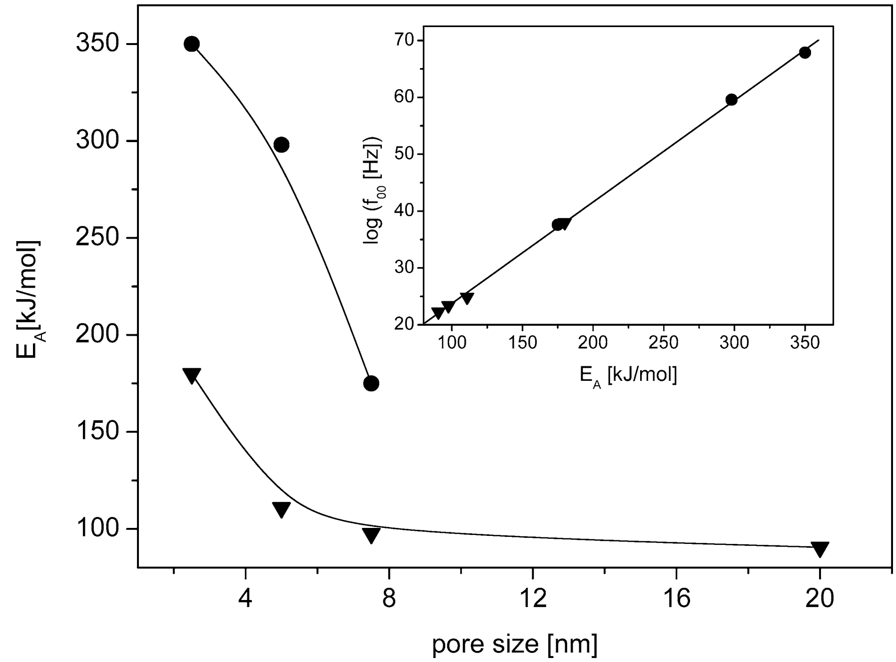
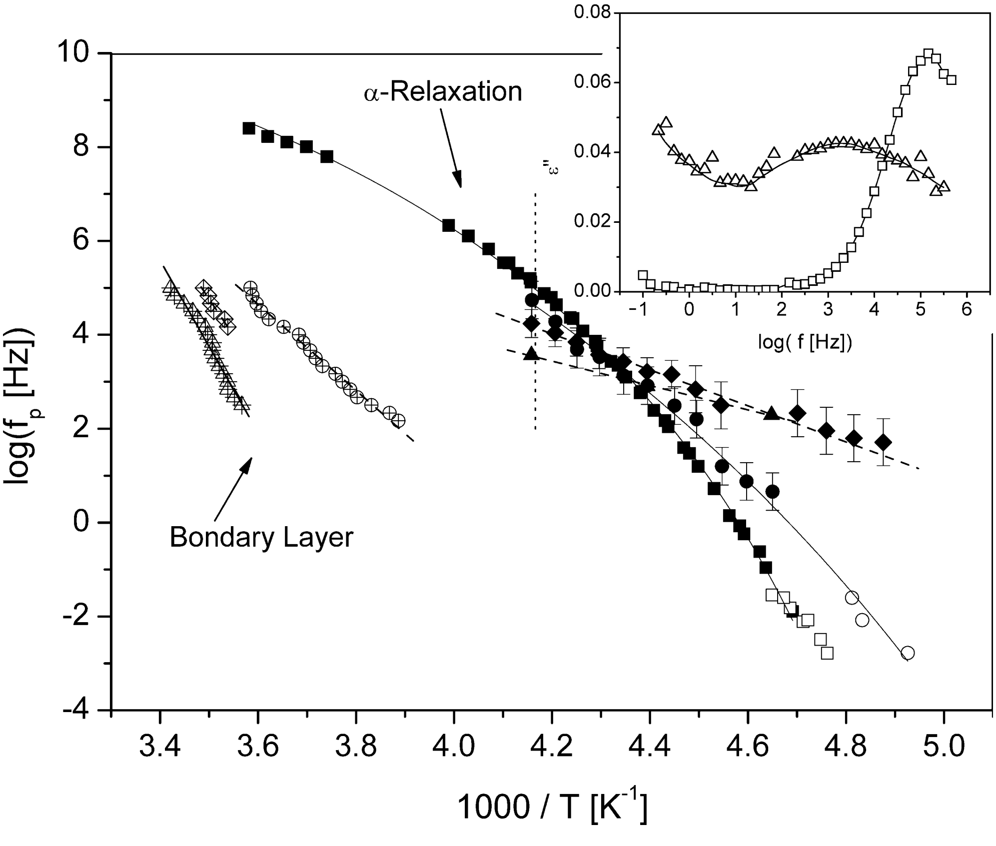


Fig. 7 Relaxation rate at maximal loss f_p vs 1/T of PMPS: *squares*—bulk, *circles*—7.5 nm, *diamonds*—5 nm, *triangles*—2.5 nm; *solid symbols* dielectric α-relaxation, *open symbols* TMDSC data; *crossed symbols* low frequency process. The *lines* are fits of the VFT equation to the dielectric data. The *dashed lines* are fits of the Arrhenius equation to the corresponding data. The *inset* compares the dielectric loss of PMPS in the bulk (*open squares*) and confined to 2.5 nm (*open triangles*) at 240 K (see *dotted line* in the main figure)



higher than those found for PPG indicating that the boundary layer for confined PMPS has a lower molecular mobility than that formed for confined PPG. This can have several reasons. Firstly, the chain structure of PPG is more flexible than that of PMPS, leading to higher molecular mobility expressed by a lower glass transition temperature. Therefore the adsorbed segments of the surface layer can also have a higher molecular mobility. Secondly, the bulky phenyl rings may in addition lead to a restricted mobility close to surfaces. In the inset of Fig. 6 it is shown that log f_∞ increases with the activation energy E_A where both sets of data collapse into one line. This is an expression of the well-known compensation law indicating the cooperative nature of the underlying motional processes [37, 38].

The dielectric α-relaxation is analyzed with regard to the relaxation rate of maximal loss f_p (relaxation time $\tau = 1/(2\pi f_p)$). For bulk PMPS the temperature dependence of f_p obeys the VFT-equation where like for PPG the relaxation rates estimated by dielectric and thermal spectroscopy agree quantitatively. For PMPS confined to 7.5-nm pores at high temperatures the relaxation rates seems to be close to that of the bulk. However, close to the glass transition temperature the molecular dynamics of PMPS embedded in pores shows a strong confinement effect where again the dielectric and the thermal data agree with each other. This confinement effect provides evidence that a length scale is also relevant for glassy dynamics in PMPS. At the pore size of 5 nm the temperature dependence of f_p changes from a VFT-like behavior to an Arrhenius one. This is further supported by the inset of Fig. 7 which compares the dielectric loss of PMPS in the bulk and confined to pores of 2.5 nm directly at the same (high) temperature. The loss peak for the confined PMPS is shifted by two decades to lower frequencies compared to the bulk. The change in the temperature dependence of the relaxation rates indicates a dramatic change in the molecular dynamics. For PMPS in 5.0-nm nanopores an activation energy E_A of 73 kJ mol^{-1} is estimated which is decreased to 50 kJ mol^{-1} for PMPS confined to 2.5-nm pores. The change of the heat capacity Δc_p at T_g normalized to the mass of confined polymer is plotted vs pore size in Fig. 5. As for PPG, Δc_p decreases strongly with decreasing pore size also for PMPS, and vanishes at a pore size of 5 nm. This is exactly the same confining length scale at which the temperature dependence of f_p changes from the VFT- to an Arrhenius behavior. These data provide strong evidence that a minimal length scale of about 5 nm is relevant for glassy dynamics in PMPS.

Neutron scattering experiments have been carried out only for PMPS. The full set of data obtained for native (uncoated) pores will be published in detail elsewhere [39]. Here only data measured by elastic scans on the backscattering spectrometer IN16 are reported. Such measurements provide an overview about the temperature dependence of the microscopic dynamics. Assuming a Gaussian form for the elastically scattered intensities the effective mean square displacement $<r^2>_{\mathrm{eff}}$ is extracted by

$$I_{el}/I_0 = exp\left[-\frac{Q^2\langle r^2\rangle_{eff}}{3}\right]. \tag{2}$$

In Eq. (2) I_{el} and I_0 are the elastically and totally scattered intensities, respectively, where I_0 was measured below 2 K. Q is the scattering vector. From the resolution of IN16 ($\Delta E \sim 1$ μeV) the time scale on which the scattering particles (mostly hydrogen) attain this effective mean square displacement can be estimated to $t = h/\Delta E \sim 4$ ns. Figure 8 compares the temperature dependence of $<r^2>_{\mathrm{eff}}$ for PMPS for different pore sizes. In the temperature range around 100 K the methyl group rotation shows up as a sharp step in $<r^2>_{\mathrm{eff}}$. This is a localized process and therefore it is only weakly influenced by the confinement (although in the quantum regime some influence is detected for methyl groups of toluene in confinement [40]). Around 225 K changes appear in $<r^2>_{\mathrm{eff}}$ which are related to the glass transition. For unconfined glass-forming liquids an increase of $<r^2>_{\mathrm{eff}}$ is found to be characteristic, indicating the diffusive character of the underlying motional process [41]. This is also found for the confined polymeric melt. However, both the absolute value of $<r^2>_{\mathrm{eff}}$ and its temperature dependence characterized by the derivative $\frac{d\langle r^2\rangle_{eff}}{dT}$ for $T > T_{g,\ \mathrm{Bulk}}$ (see inset of Fig. 8) decrease greatly with decreasing pore size. This behavior is qualitatively similar to what was found for thin supported polymer films with decreasing film thickness [42]. One simple way of extrapolating $\frac{d\langle r^2\rangle_{eff}}{dT}$ to zero would be to extend the slope between the last two points linearly which, following the above interpretation, could means that the diffusive character of the local dynamics disappears. From this we may then estimate a length scale of about 1.6 nm (see Fig. 8) which can be regarded as a minimal length scale for microscopic segmented dynamics. With increasing confinement and increasing surface/volume ratio the mean squared displacement approaches the extrapolation of the low temperature behavior. Again this could mean that essentially only local motions remain for the adsorbed PMPS layer.

Conclusion

Broadband dielectric spectroscopy on poly(propylene glycol) and poly(methyl phenyl siloxane) confined to nanoporous glasses shows that for both systems an interfacial layer is formed close to the pore wall for native unsilanized internal surfaces. This adsorbed surface layer has an essential lower molecular mobility than the molecular mobility in the bulk. For silanized pores the relaxation processes assigned to this surface layer disappears. This supports the conclusion that adsorption phenomena play an essential role for the dynamics of molecular systems confined to nanoporous host systems.

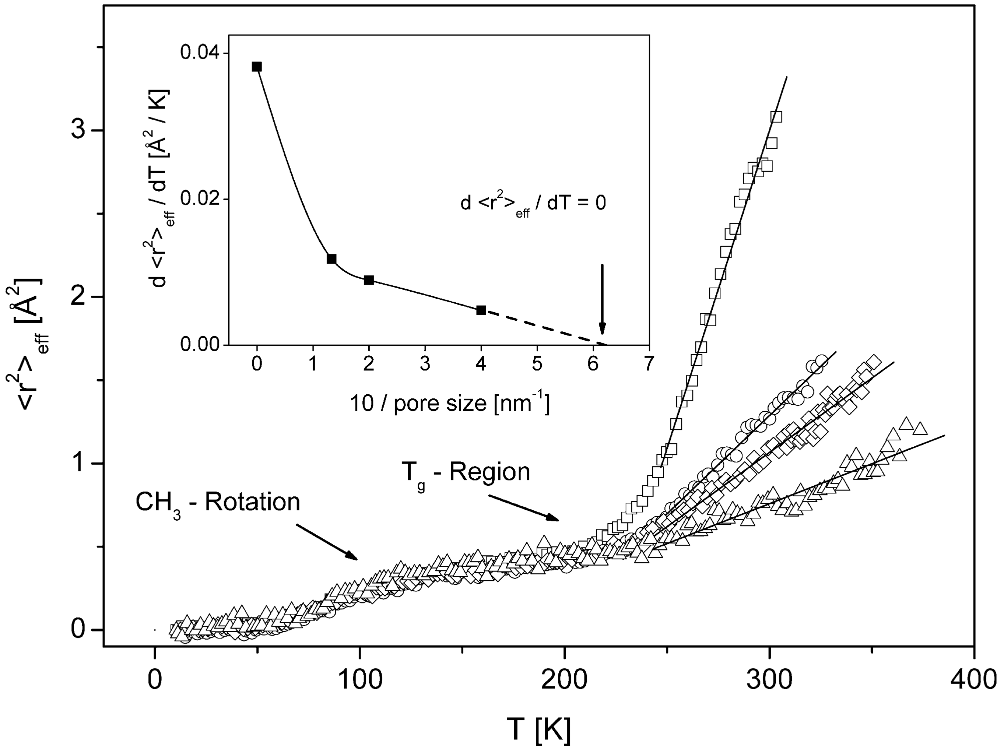


Fig. 8 Temperature dependence of $<r^2>_{\mathrm{eff}}$ of PMPS for the different pore sizes: *open squares*—bulk, *open circles*—7.5 nm, *open diamonds*—5 nm, *open triangles*—2.5 nm. The *inset* gives the slope $\frac{d\langle r^2\rangle_{eff}}{dT}$ for $T > T_{g,\ \mathrm{Bulk}}$ vs inverse pore size

The α-relaxation results obtained by broadband dielectric and thermal spectroscopy give indications that an inherent length scale is relevant for glassy dynamics. Firstly, an acceleration of the molecular dynamics compared to the bulk state (confinement effect) is observed for both systems. A confinement effect is expected if a length scale is involved in the molecular dynamics with corresponds to the confining dimensions of the host material. Secondly, the step in the specific heat capacity Δc_p at the glass transition normalized to the weight of the confined polymer vanishes at a finite length scale also for both systems. Within the current interpretation of glass transition this means that below this finite value no glass transition can take place. Therefore it can be regarded as a minimal or cut-off length scale for glass transition. For PGG a value of 1.8 nm is estimated. Furthermore the relaxational experiments carried out on PPG show that the molecular dynamics in confining space is determined by an interplay of confinement and adsorption effects in general. The latter results from interactions of the confined polymer molecules with the host system at the interface between both.

For PMPS Δc_p goes to zero at 5 nm. At the same confining length scale the temperature dependence of the relaxation rates changes form a VFT- to Arrhenius-like behavior with a low activation energy which depends on pore size. This points to a dramatic change in the character of the underlying motional processes which seems to change for a cooperative to a localized one. These results are in full agreement with quasi-elastic neutron scattering experiments. These experiments show that the microscopic dynamics characterized by the temperature dependence of the mean square displacement $<r^2>_{\mathrm{eff}}$ is also strongly influenced by the confinement. Above $T_{g,\ \mathrm{Bulk}}$ for the confined PMPS the temperature dependence of $<r^2>_{\mathrm{eff}}$ characterized by the derivative $\frac{d\langle r^2\rangle_{eff}}{dT}$ is much weaker than for the bulk and $\frac{d\langle r^2\rangle_{eff}}{dT}$ decreases with decreasing pore size. The diffusive character of the microscopic dynamics seems to disappear at a length scale of about 1.6 nm.

Acknowledgements The financial support by the "Deutsche Forschungsgemeinschaft" (Projects Scho 470/6, Sp 152/44–2) and of the "Fonds der Chemischen Industrie" is gratefully acknowledged. We also thank the Institute Laue-Langevin for enabling the neutron scattering experiments.

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