The molecular dynamics of polymers in random nanometre confined spaces investigated by relaxational and scattering techniques

A Schönhals[1,3], H Goering[1], K W Brzezinka[1] and Ch Schick[2]

[1] Federal Institute of Materials Research and Testing, Unter den Eichen 87,
D-12205 Berlin, Germany
[2] University Rostock, Department of Physics, Universitätsplatz 3, D-18051 Rostock, Germany

E-mail: andreas.schoenhals@bam.de

Abstract

Dielectric spectroscopy and temperature-modulated differential scanning calorimetry are employed to study the molecular dynamics of oligomeric poly(propylene glycol) (PPG) melts of different molecular weights confined to nanoporous glasses (pore sizes 2.5, 5.0, 7.5 and 20 nm). Moreover, the results obtained for the polymers are compared with those for the corresponding monomer. The experimental results are discussed in the framework of the interplay of confinement and adsorption effects. For large pore sizes (>5 nm) a speeding up of the molecular dynamics is observed (the confinement effect), whereas for small pore sizes (<5 nm) a slowing down of the segmental fluctuations is found (the adsorption effect). In addition, a minimal length scale for the glass transition of 1.6 nm is estimated for PPG confined in nanoporous glasses. This supports the idea that the molecular motions responsible for the glassy dynamics must be describable by a characteristic length scale.

Polarized Raman scattering investigations are carried out to investigate the conformations of the macromolecules inside the pores. These experiments show that the confined polymer chains are locally stretched. This effect increases with decreasing pore size.

1. Introduction

From both the theoretical and the applications points of view, the behaviours of molecules close to interfaces, in thin films and in confining geometries have attracted growing interest in the last decade [1–5]. From the applications point of view, this is due to the necessity of knowing and controlling the properties of molecules on a nanometre scale for applications in

---

[3] Author to whom any correspondence should be addressed.

chemistry, medicine and the field of nanotechnology. From the fundamental point of view, the concern is the investigation of finite-size effects on the properties of matter. The experimental results can be compared with theoretical approaches. An important challenge to the latter is revealing the nature of glassy dynamics, which is an unsolved problem of condensed and soft-matter physics [6–11]. The existence of a length scale which controls the molecular motions responsible for the glass transition can be proven by investigating the behaviour of guest molecules confined to nanoporous host systems. This seems to be a central point in the understanding of the phenomenon of the glass transition [8–10].

A variety of methods have been applied to study the properties of molecules in confined spaces. Some examples are thermal measurements [12–14], optical investigations [15, 16], studies using the surface force apparatus [17–19], NMR studies [20, 21] and Kerr effect measurements [22]. It has been proven by many studies that broadband dielectric spectroscopy (BDS) is very effective in investigating the properties of molecules in the cases of confinement in thin layers [23] and in porous media such as nanoporous glasses and zeolites [5]. This is due to the extraordinarily extended dynamic ranges in frequency and sensitivity which can be covered.

In this paper the influence of nanometre confinement on the molecular dynamics (segmental motions) of polymers studied by BDS and temperature-modulated differential scanning calorimetry (TMDSC) is discussed and compared with results obtained by means of polarized Raman scattering.

2. Experimental details

Poly(propylene glycol) (PPG) specimens of different molecular weights ($M_w \approx 1000, 2000, 3000$ and 5000 g mol^{-1}; $M_w/M_n = 1.03$–1.06) have been selected for the study. The glass transition temperature T_g measured by DSC is 206 K independently of the molecular weight, which can be explained by hydrogen bonding. Dielectric data for the monomer propylene glycol were taken from the literature [24]. For the Raman experiments on the bulk state, a homologous series from propylene glycol up the polymer with $M_w = 5000$ g mol^{-1} was studied.

As host materials, well defined porous glasses with specified pore sizes of 2.5, 5.0, 7.5 and 20 nm and a narrow pore size distribution were used (Geltech Incorporated, USA). Disc-like samples (diameter about 10 mm, thickness 0.3 mm) were prepared for the measurements. All nanoporous hosts were thermally treated at 573 K for 1 h, and evacuated to 10^{-5} mbar for 24 h to remove water and other volatile impurities (such as the solvents needed for the preparation of the disc). Then the discs were slowly cooled down to 373 K under vacuum and the oligomeric melt was injected directly into the vacuum chamber. The pores were filled by capillary wetting at that temperature for 24 h and additionally for 72 h at 348 K under a controlled dry atmosphere. The degree of filling was controlled by weighing.

To explore the polymer surface interactions in addition to investigating native porous glasses, the pores were modified by a silanization process before filling. Thereby the surface silanol groups were converted into less hydrophilic trimethylsilyl groups [25].

The equipment used to measure the complex dielectric function $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ (f: frequency; ε': real part; ε'': loss part; $i = \sqrt{-1}$) in the frequency range from 10^{-4} to 10^9 Hz is described elsewhere [26]. Both sides of the glass disc were covered with silver foil of 800 nm thickness to ensure a good electrical contact and a homogeneous measuring field.

The TMDSC measurements were carried out with a Perkin-Elmer Pyris 1 DSC using an empty glass disc with the same pore size as the sample under investigation, as the reference material. The frequency of the measurement was varied from 10^{-3} to 3.4×10^{-2} Hz. All

properties were obtained from heating runs, where the heating rates were chosen between 1 K min^{-1} and 3 K h^{-1} to achieve stationary conditions. For more details, see [25].

The polarized Raman spectra were recorded by a DILOR XY Raman spectrometer in standard backscattering geometry at room temperature. As the excitation source an argon-ion laser with a wavelength of 514 nm was used. The laser power density at the sample surface inside a spot of 70 μm was 0.6 kW cm^{-2}. To exclude the influence of polarization of the spectrometer, a scrambler was applied in the parallel optical path between the collecting lens and the slits optics. The analyser was a polarizing filter foil between the scrambler and the collecting lens. The multi-channel detector was a liquid nitrogen-cooled CCD camera. Further experimental details can be found elsewhere [27].

A treatment of polarized Raman investigations is outlined in [28]. The basic quantity is the depolarization factor ρ defined by

$$\rho = \frac{I_\perp}{I_\parallel} \tag{1}$$

where $I_\perp$ and $I_\parallel$ are the scattered intensities perpendicular and parallel to the polarization of the incident beam. $I_\perp > 0$ and therefore $\rho > 0$ is measured for optical anisotropic molecules where the polarizability has to be described by a tensor. The theoretical consideration [28] gives the following relationships for the depolarization factor:

$\rho = 0$ totally symmetric vibrations of isotropic molecules (totally polarized),

$0 < \rho < 0.75$ totally symmetric vibrations of anisotropic molecules (polarized),   (2)

$\rho = 0.75$ non-totally symmetric vibrations (depolarized).

3. Discussion

Some of the dielectric and thermal data have been published in detail elsewhere [25]. Therefore the most important results will be only briefly summarized. PPG shows a variety of the dielectric active relaxation processes [29]. Most prominent is the α-relaxation (dynamic glass transition) which is related to the thermal glass transition (see the inset in figure 1). Because PPG is a type-A polymer at frequencies below the α-relaxation, a normal-mode process can be observed (see the inset in figure 1), which is related to the global chain dynamics [29].

Figure 1 compares the dielectric loss of PPG in bulk and in native (uncoated) nanoporous sol–gel glasses as regards temperature dependence at a fixed frequency. Again, two relaxation processes can be identified: the α-relaxation at low temperatures and the normal-mode process at higher temperatures. The temperature position of the former is weakly influenced by the confinement, while the latter shifts strongly to higher temperatures with decreasing pore size, connected with a pronounced broadening. The isothermal data are analysed by standard procedures [30] fitting the model function of Havriliak and Negami [31] to the data. By this procedure, the relaxation rate at maximal loss f_p can be extracted. Unfortunately, the two processes strongly overlap in relaxation time distribution. This prevents a reliable estimation and analysis of their dielectric strengths.

The activation plot (figure 2) shows that the temperature dependence of the relaxation rate for both processes can be described by the Vogel–Fulcher–Tammann equation [32–34] which reads

$$\log f_p = f_\infty - \frac{A}{T - T_0} \tag{3}$$

where f_∞ and A are constants and T_0 is the so-called Vogel temperature. For high temperatures, the data for bulk and confined PPG coincide, which proves the correctness of the molecular
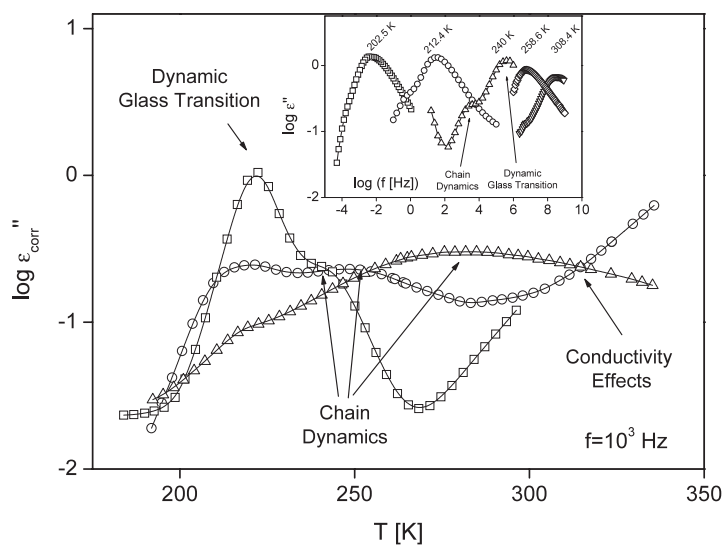
Figure 1. Volume-corrected dielectric loss $\log \varepsilon''_{corr}$ versus temperature at 1000 Hz for bulk PPG ($M_w = 3000$ g mol^{-1}): □: bulk; ○: 7.5 nm pore; ▽: 2.5 nm pore. Curves are guides for the eyes. The inset gives the dielectric loss ε'' versus frequency for bulk PPG ($M_w = 2000$ g mol^{-1}) at the labelled temperatures. Curves are guides for the eyes.
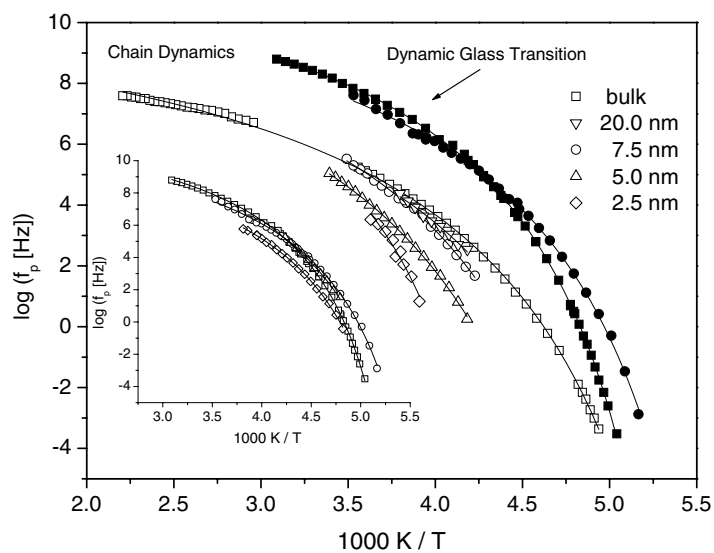
Figure 2. $\log f_p$ versus $1/T$ for the dynamic glass transition (α-relaxation, solid symbols) and for the chain dynamics (normal-mode process, open symbols) at the labelled pore sizes for PPG ($M_w = 3000$ g mol^{-1}). The inset gives $\log f_p$ versus $1/T$ for the dynamic glass transition (α-relaxation) at the labelled pore sizes for PPG ($M_w = 3000$ g mol^{-1}). The curves are fits of the VFT equation to the data.

assignment of the relaxation process in the pores. In the following, only the dynamic glass transition is considered. For a discussion of the normal-mode process, see [25].

The temperature dependence of the relaxation rate of the α-relaxation shows a non-monotonic dependence on the confinement (see the inset in figure 2). For pore sizes down
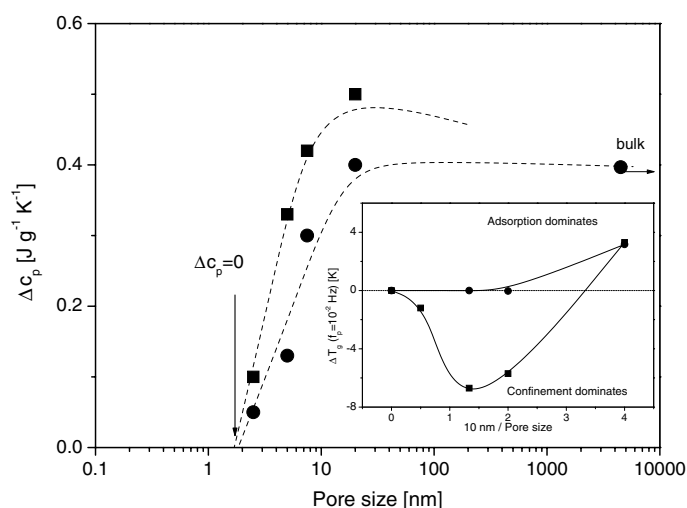
Figure 3. Δc_p versus pore size for PPG ($M_w = 2000$ g mol^{-1}): ●: native pores; ■: silanized pores. The curves are guides for the eyes. The inset shows $\Delta T_g = T_g^{Diel}$(pore) $- T_g^{Diel}$(bulk) versus inverse pore size: ■: PPG ($M_w = 3000$ g mol^{-1}); ●: PG. (The data were taken from [24].) Curves are guides for the eyes.

to 5 nm, the dynamics becomes faster (the confinement effect) but it slows down for smaller pores (the adsorption effect). It has been demonstrated by many examples that the molecular dynamics in a confined space is determined by the counterbalancing of surface and confinement effects [5]. The former result from interactions of guest molecules with the host system at the interface between them; the latter originate from the length scale on which the underlying molecular motions take place. Surface effects cause a decrease, while confinement effects are characterized by an increase of the molecular dynamics with decreasing spatial confinement dimensions. A theoretical approach to understanding the confinement based on the coupling model was published recently [35].

The estimated VFT parameters are used to calculate the dielectrically determined glass transition temperature $T_g^{Diel} = T(f_p = 10^{-2}$ Hz). Its pore size dependence is given in the inset of figure 3. In contrast to the case for monomer PG, where only an adsorption effect is found, in the polymeric pendant PPG the counterbalancing between surface and confinement effects determines the pore size dependence of the dynamic glass transition. This can understood, taking into consideration the different capabilities of the molecules for forming hydrogen bonds with the walls of the pores; the capability is strongly reduced for PPG. Also, the silanization of the internal glass surfaces has only a weak effect on the glassy dynamics of PPG inside the pores, which can be understood on the same basis.

To investigate the thermal relaxation at the dynamic glass transition, TMDSC measurements were carried out. By varying the modulation frequency of the temperature around a linear heating ramp, the temperature dependence of the relaxation rates due to enthalpy (entropy) fluctuations can be measured. The thermal data obtained are in quantitative agreement with the dielectric ones. This indicates that both methods are sensing the glass transition of the polymers inside the pores. The increment of the specific heat capacity Δc_p due to the glass transition decreases strongly with decreasing pore size (see figure 3). This is also in accord with the dielectric results. The extrapolation to $\Delta c_p = 0$ gives lengths of 1.6–1.8 nm. Below that finite length scale, no glass transition can take place for this system. Therefore, this length scale can be considered a minimal length scale for glass transition. This
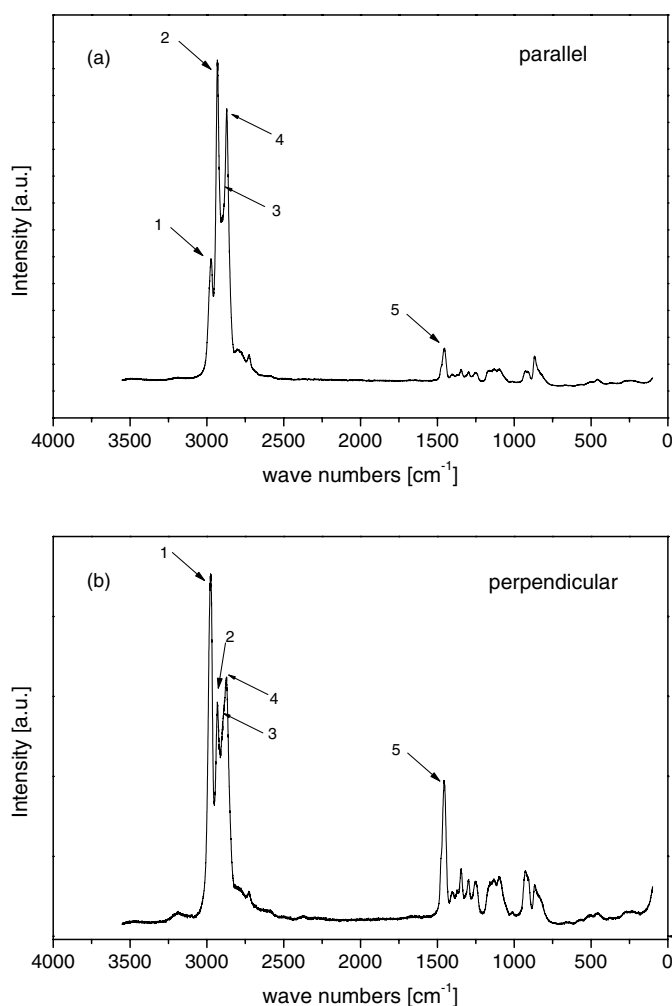
Figure 4. Raman spectra of PPG: 1: 2976 cm^{-1}, CH$_3$ valence vibration, asymmetric; 2: 2933 cm^{-1}, CH$_2$ valence vibration, symmetric; 3: 2906 cm^{-1}, CH$_2$ valence vibration, asymmetric; 4: 2871 cm^{-1}, CH$_3$ valence vibration, symmetric; 5: 1475 cm^{-1}, CH$_2$, CH$_3$ deformation vibrations; (a) scattered intensity parallel to the polarization of the incident beam; (b) scattered intensity perpendicular to the polarization of the incident beam.

supports the notion that the molecular dynamics responsible for the glass transition can be described by a characteristic length. The order of magnitude compares well to that obtained from the fluctuation approach to the glass transition of Donth [10]. Similar results are also obtained for poly(dimethyl siloxane) [36].

The Raman spectra (see figure 4) of PPG show a variety of bands, including ones attributable to the deformation vibrations between 2000 and 1000 cm^{-1} and the valence vibrations between 3100 and 2800 cm^{-1}. The molecular assignments of the vibrations, according to [37], are given in the caption of figure 4. To study the influence of the confinement on the structure of the polymer, the valence vibrations are analysed quantitatively because they are more intense than the deformation vibrations. Moreover, the latter show only a weak dependence on the polarization of the scattered light and for the confined systems the host glasses show substantial background scatter in that wavenumber region.
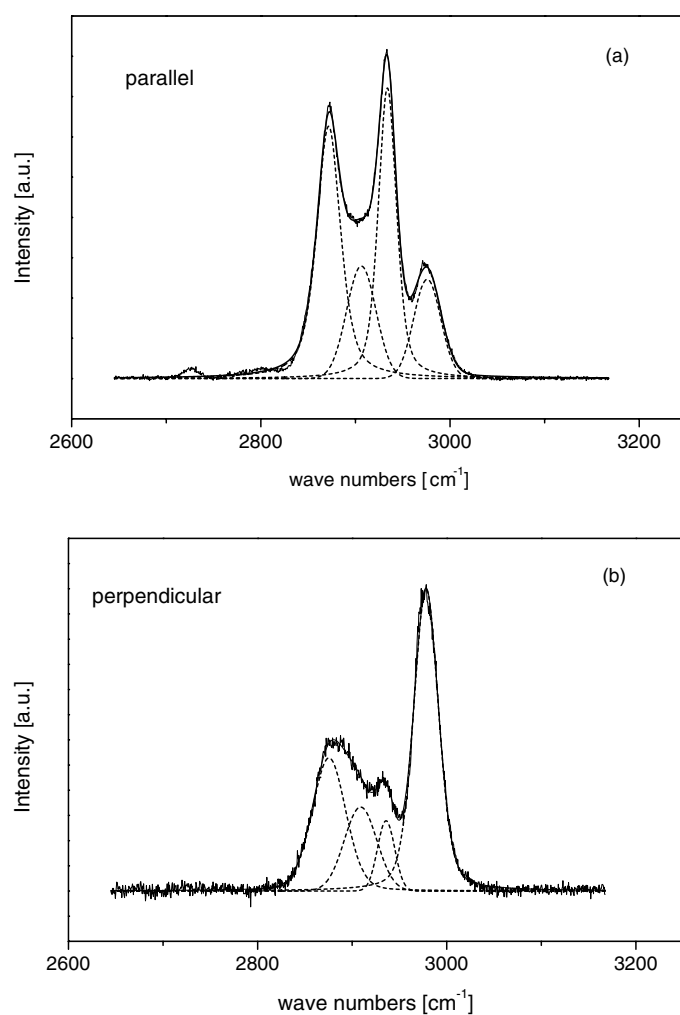
Figure 5. Raman intensities of the valence band vibrations of PPG ($M_w = 2000$ g mol^{-1}). Solid curve: experimental data; dashed curves: fitted functions; (a) scattered intensity parallel to the polarization of the incident beam; (b) scattered intensity perpendicular to the polarization of the incident beam.

To extract $I_\perp$ and $I_\parallel$ for the four valence vibrations, a Gauss–Lorentz profile is fitted to each band, where the percentages of Gauss and Lorentz functions are also varied. For comparison, ρ is calculated from the maximum height of the peak as well as from its area. Both quantities are outputs of the fitting procedure. The basis line corrections were carried out by the rubber band method. Figure 5 gives an example of the fitting procedure for PPG with a molecular weight of 2000 g mol^{-1}.

To understand the behaviour of the confined polymers, in a first step a homologous series of PPGs including the monomer and the dimer is studied. Figure 6 shows the molecular weight dependence of the depolarization factor for all valence vibrations. First, we note that the values obtained for the area under the band are similar than those obtained from the maximum height of the peak. For all bands, ρ depends on the molecular weight, but the most prominent change is observed for the peak at 2980 cm^{-1} which is due to the asymmetric CH$_3$ valence vibration.
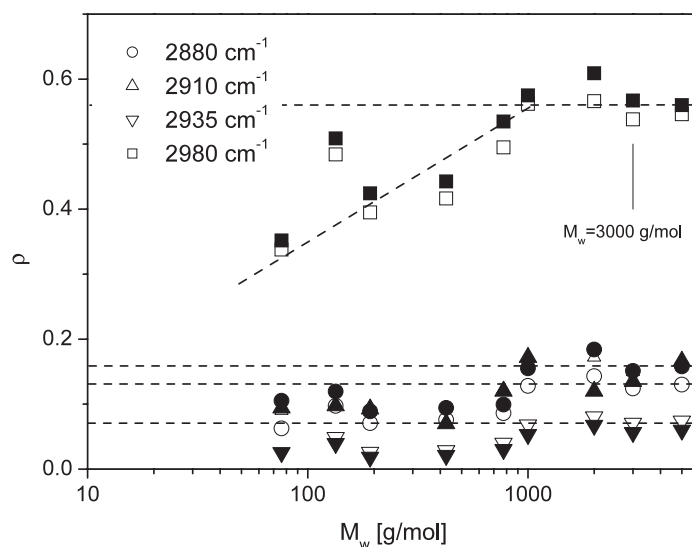
Figure 6. $\rho = I_\perp/I_\parallel$ versus molecular weight for the wavenumbers indicated. Solid symbols: calculated from the area under the band; open symbols: calculated from the maximum height. Lines are guides to the eyes.

For that band, ρ increases systematically from approximately 0.3 to a plateau value of 0.6 which is close to the limit of non-totally symmetric (depolarized) vibrations (see equation (2)). The value for the monomer indicates, according to equation (2), optically anisotropic molecules, but close to the isotropic limit. With increasing molecular weight the valence vibrations become more and more asymmetric, reaching a limiting case (see figure 6). Although the molecular vibrations are localized, they depend on the conformations of the molecule. Therefore the change in ρ with M_w indicates the transition of the average conformation of a small—relatively optically symmetric—molecule to a macromolecule with a random coil conformation. The Gaussian coil limit is characterized by the plateau where the conformations do not change any longer with molecular weight.

The value obtained for the dimer seems not to fit into that dependence. This derivation can be understood, taking it into consideration that it is well known that dipropylene glycol can form ring-like structures. Clearly these rings can have different conformations to linear molecules. For further discussion, see [27].

To study the influence of the confinement on the conformation of the polymer chain, a PPG with a molecular weight inside the plateau region ($M_w = 3000$ g mol^{-1}) was selected for the further studies (see figure 6). As a first result, we state that confining the polymers into the nanoporous glasses does not result in a band shift compared to the bulk state situation, within the experimental error. Therefore the same analysis as was applied for the bulk state can also be applied for the confined systems. Figure 7 gives the dependence of the depolarization factor versus inverse pore size. With decreasing pore size, ρ decreases systematically. Following the lines of the argumentation given above, this means that by confining the macromolecular chains into the nanoporous glasses, the average conformation changes from a Gaussian coil to a structure which is, on a localized level, more stretched. The values for the depolarization measured for the silanized pores are systematical larger than those for the native system. So it can be concluded that polymer surface interactions increase the chain stretching.
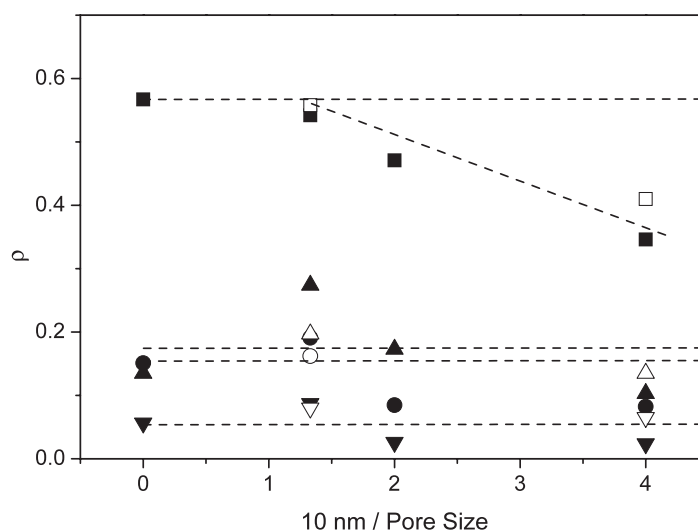
Figure 7. $\rho = I_\perp / I_\parallel$ versus inverse pore size. The symbols indicating the different wavenumbers have the same meanings as in figure 4. Open symbols: silanized pores; solid symbols: native pores.

4. Conclusions

The segmental dynamics for various oligomeric PPG melts ($M_w \approx 1000, 2000, 3000$ and $5000 \, \text{g mol}^{-1}$) confined in nanoporous glasses (mean pore dimensions 2.5, 5.0, 7.5 and 20 nm) is studied by dielectric spectroscopy and temperature-modulated DSC. For the dynamics glass transition (α-relaxation), a non-monotonic variation of the glass transition temperature with decreasing pore size is found by both dielectric spectroscopy and temperature-modulated DSC. For larger pore sizes (>3 nm), the glass transition temperature decreases, while for small confining dimensions (<3 nm), T_g increases with decreasing pore size. This behaviour is completely different from that obtained for the monomer, where an increase of T_g with decreasing pore size is always found. This is discussed in the framework where the molecular dynamics in a confined space is determined by the counterbalancing between surface and confinement effects [5]. The increment of the specific heat capacity Δc_p decreases strongly with pore size and can be extrapolated to zero at a finite length scale. It is concluded that this length scale can be regarded as a minimal length scale of cooperativity for the glass transition. Polarized Raman scattering investigations of a homologous series of PPGs in the bulk state show a transition between the molecular conformations of a low-molecular-weight molecule and a macromolecule with a random Gaussian coil conformation. For the confined systems, the local chain conformations of a polymer chain are stretched compared to those in the bulk state, which increase with decreasing confining dimensions.

References

[1] Drake J M, Klafter J and Kopelman R (ed) 1990 *Dynamics in Small Confining Systems* (Pittsburgh, PA: Materials Research Society)

[2] Drake J M, Klafter J, Kopelman R and Troian S M (ed) 1995 *Dynamics in Small Confining Systems II (Mater. Res. Soc. Symp. Proc. vol 366)* (Pittsburgh, PA: Materials Research Society)

[3] Drake J M, Grest G S, Klafter J and Kopelman R (ed) 1998 *Dynamics in Small Confining Systems IV (Mater. Res. Soc. Symp. Proc. vol 543)* (Pittsburgh, PA: Materials Research Society)

[4] Frick B, Zorn R and Büttner H 2000 *Proc. Int. Workshop on Dynamics in Confinement; J. Physique* IV **10**

[5] Kremer F, Huwe A, Schönhals A and Różański A S 2002 *Molecular Dynamics in Confining Space in Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) p 171

[6] Anderson P W 1995 *Science* **267** 1615

[7] Angell C A 1995 *Science* **267** 1924

[8] Sillescu H 1999 *J. Non-Cryst. Solids* **243** 81

[9] Ediger M 2000 *Annu. Rev. Phys. Chem.* **51** 99

[10] Donth E 2001 *The Glass Transition* (Heidelberg: Springer)

[11] Debenedetti P G and Stillinger F H 2000 *Nature* **410** 259

[12] Jackson C L and McKenna G B 1996 *Chem. Mater.* **8** 2128

[13] Jackson C L and McKenna G B 1991 *J. Non-Cryst. Solids* **131** 221

[14] Simon S L, Park J-Y and McKenna G B 2002 *Eur. Phys. J.* E **8** 209

[15] Keddie J L, Jones R A and Cory R A 1994 *Europhys. Lett.* **27** 59

[16] Forrest J A, Dalnoki-Veress K, Stevens J R and Dutscher J R 1996 *Phys. Rev. Lett.* **77** 2002

[17] Granick S 1991 *Science* **253** 1374

[18] Klein J and Kumacheva E 1995 *Science* **269** 816

[19] Cho Y-K, Watanabe H and Granick S 1999 *J. Chem. Phys.* **110** 9688

[20] Stapf S, Kimmich R and Seitter R-O 1995 *Phys. Rev. Lett.* **75** 2855

[21] Rittig F, Huwe A, Fleischer G, Kärger J and Kremer F 1999 *Phys. Chem. Chem. Phys.* **1** 519

[22] Schwalb G and Deeg F W 1995 *Phys. Rev. Lett.* **74** 1383

[23] Hartmann L, Fukao K and Kremer F 2002 *Molecular Dynamics in Thin Polymer Films in Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) p 433

[24] Gorbatschow W, Arndt M, Stannarius R and Kremer F 1996 *Europhys. Lett.* **35** 719

[25] Schönhals A, Goering H and Schick Ch 2002 *J. Non-Cryst. Solids* **305** 140

[26] Schönhals A, Kremer F and Schlosser E 1991 *Phys. Rev. Lett.* **67** 999
        Kremer F and Schönhals A 2002 *Broadband Dielectric Measurement Techniques in Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) p 35

[27] Goering H, Brzezinka K W and Schönhals A 2003 in preparation

[28] Weidlein J, Müller U and Dehnicke K 1982 *Schwingungsspektroskopie* (Stuttgart: Thieme) p 14

[29] Schönhals A 2002 *Molecular Dynamics in Polymer Model Systems in Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) p 225

[30] Schönhals A and Kremer F 2002 *Analysis of Dielectric Spectra in Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) p 59

[31] Havriliak S and Negami S 1966 *J. Polym. Sci.* C **14** 99

[32] Vogel H 1921 *Phys. Z.* **22** 645

[33] Fulcher G S 1925 *J. Am. Ceram. Soc.* **8** 339

[34] Tammann G and Hesse G 1926 *Z. Anorg. Allg. Chem.* **156** 245

[35] Ngai K 1999 *J. Phys.: Condens. Matter* **11** 119

[36] Schönhals A, Goering H and Schick Ch 2003 in preparation

[37] Sverdlov L M, Kovner M A and Krajnov E P 1970 *Vibrational Spectra of Multi-Atomic Molecules* (Moscow: Nauka) p 185