Polymer xxx (2016) 1–14

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Inelastic neutron spectroscopy as a tool to investigate nanoconfined polymer systems

Andreas Schönhals [a], [*], Reiner Zorn [b], Bernhard Frick [c]

[a] Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205, Berlin, Germany
[b] Jülich Centre for Neutron Science, Forschungszentrum Jülich, D-52425, Jülich, Germany
[c] Institut Laue-Langevin, 71, Avenue des Martyrs, Grenoble 38000, France

ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form
26 May 2016
Accepted 1 June 2016
Available online xxx

Keywords:
Confinement
Density of states
Dynamic glass transition

ABSTRACT

The effect of a nanometer scale confinement (pore sizes 7.5 nm down to 2.5 nm) on the vibrational density of states (VDOS) and on the molecular dynamics of Poly(dimethyl siloxane) (PDMS) and Poly(methyl phenyl siloxane) (PMPS) is studied by inelastic neutron scattering. The high penetration depth of neutrons makes neutron scattering a suitable tool for the study of confined systems. Moreover, neutrons are sensitive to light nuclei therefore the confined polymers can be investigated directly, more or less independently of the confining host. Resulting findings are firstly, a reduction of the low frequency contributions to the VDOS below the Boson Peak frequency for both polymers. Including literature data, this reduction can be regarded as a more general feature for glass-forming systems confined by hard walls. Secondly, clear deviations in the temperature dependence of the mean squared displacement of the confined molecules compared to the bulk were found close to the thermal glass transition temperature, whereas localized methyl group rotations were only weakly influenced. Furthermore, the molecular dynamics is accessed. The combination of neutron Time-of-Flight with neutron backscattering, thus covering a broad dynamical range from sub ps to ns, reveal clear influence from confinement on the intermediate incoherent scattering function S(q,t). The latter was obtained by combining the inverse Fourier transform of the individual dynamical structure factors measured by the both methods. The time and q dependence of S(q,t) are discussed in detail for the local methyl group rotations and the segmental dynamics, considering both the interaction of the segments with the pore walls and possible geometrical confinement effects.

1. Introduction

The structure and dynamics of confined soft matter, for example close to surfaces or within porous materials, can deviate strongly from the bulk behavior [1–3]. This is also true for nanoconfined polymers where the chain conformation, the segmental and chain dynamics, and also the flow properties will be influenced by the confinement (see for instance [4–12]). These confinement-induced changes will have a broad variety of implications for practical applications like polymers in ultra-thin films, in microfluidics or in the field of nanotechnology, just to mention a few.

From the theoretical point of view many phenomena in polymers are controlled by length scales. These phenomena concern for instance phase transitions, chain motions and also the segmental dynamics. Nanoconfinement of polymers will be one possibility to study the influence of finite size effects on the structure and dynamics of macromolecules, to identify relevant length scales and to prove theoretical approaches.

This is especially true for the glass transition of polymers, which is related to segmental dynamics. Although the phenomenon of the glass transition is investigated experimentally and theoretically for a long time, it is still not completely understood. Fig. 1 gives an overview of the characteristics effects observed at the glass transition of polymers. One prominent effect concerns the temperature dependence of the viscosity or the relaxation time τ of segmental dynamics (α-relaxation, dynamic glass transition). If a polymer melt is cooled down to the thermal glass transition temperature T_g, the relaxation time changes by 14 orders of magnitude. Close to T_g the temperature dependence of τ might be approximated by the Vogel-Fulcher-Tammann relationship [13–15] given by,

---

[*] Corresponding author.
E-mail address: Andreas.Schoenhals@bam.de (A. Schönhals).

http://dx.doi.org/10.1016/j.polymer.2016.06.006
0032-3861/

Please cite this article in press as: A. Schönhals, et al., Inelastic neutron spectroscopy as a tool to investigate nanoconfined polymer systems, Polymer (2016), http://dx.doi.org/10.1016/j.polymer.2016.06.006

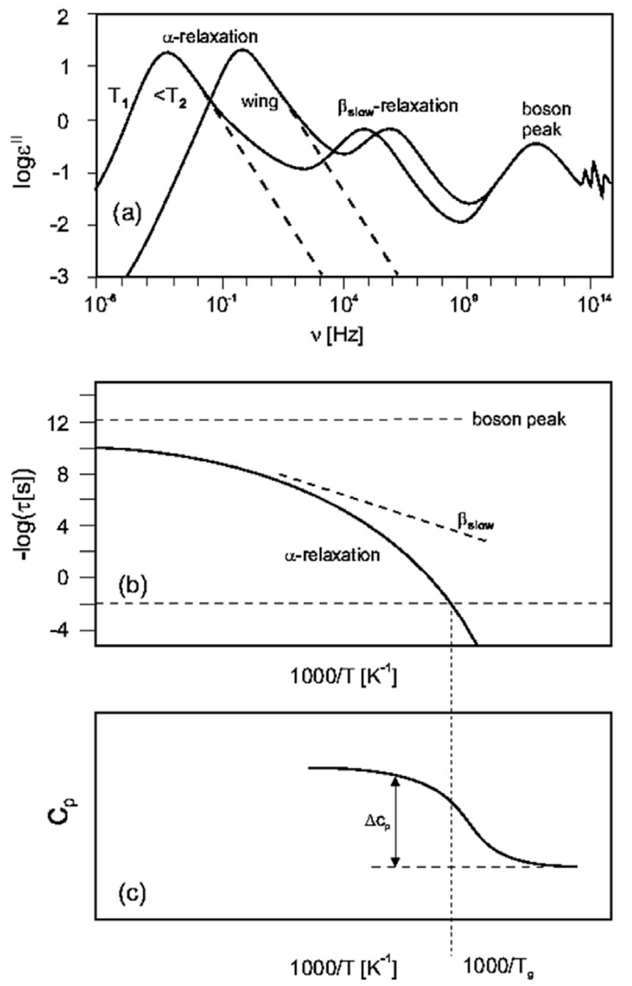

Fig. 1. Scheme of the dynamic features taking place at the glass transition for amorphous polymers: (a) imaginary part ε'' of the complex dielectric function versus frequency for two temperatures T_1 and T_2. The different processes are indicated. (b) Relaxation map (relaxation rate versus inverse temperature) for the different processes. (c) Thermal glass transition, where the specific heat capacity is plotted versus inverse temperature. The figure was reproduced from Ref. [49] with permission.

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

where A and τ_∞ are constants. T_0 is the so-called Vogel or ideal glass transition temperature found 50 … 70 K below T_g. The question is whether this strong temperature dependence is due to an underlying length scale, which controls segmental dynamics as assumed in some theoretical approaches (see for instance [16–19]). Nanoconfinement has been suggested as a method to test this more intuitive idea. If the growing of the length scale of cooperative motions is restricted within a spatially confined geometry, modes with larger length scales are cut out, which should result in characteristic changes in the temperature dependence of the corresponding relaxation time $\tau(T)$. Thus, if the strong temperature dependence of the relaxation time of the dynamic glass transition is caused by a length scales which grow with decreasing temperature, one should expect that the temperature dependence of τ becomes weaker in a spatially limited environment. This means that the molecular motions become accelerated compared to the unconfined state. For a strongly confined state it might also appear that the glass transition is completely suppressed [20].

Besides the α-relaxation a so-called Johari-Goldstein (slow) β-process has been discussed to be characteristic for the glass transition [21,22] (see Fig. 1). It is a localized relaxation process and often it has been considered as a precursor of the dynamic glass transition (for a discussion see Ref. [23]). The β-relaxation separates from the α-process in the frequency range from 10^7 Hz to 10^8 Hz ($T \cong 1.2\ T_g$). In addition to the Johari-Goldstein (slow) β-process, further localized processes can be observed for polymers, which can be assigned directly to certain chemical groups. One example is the rotation of the methyl group [24–26].

One further feature of polymer glasses or glasses in general are characteristic excess contributions to the vibrational density of states $g(\omega)$ (VDOS) compared to the Debye vibrational density of state due to the propagation of sound waves ($g(\omega) \sim \omega^2$) in the frequency range $\omega \approx 1 \ldots 5$ THz (Boson Peak, BP) [27]. There are several indications that the Boson Peak might be related to the glass transition. In the framework of the fragility concept to the glass transition [28,29] it has been found that the Boson Peak is pronounced for "strong glasses" while it is by trend weak for fragile glass formers [30] and that the frequency of the BP position might be lower for fragile compared to strong glasses [28]. Till now the molecular origin of the BP is not completely understood and two main theoretical approaches are discussed. In the first approach, the modes of the BP are different from sound waves and originate from (quasi) localized modes, which are due to peculiarities of the interatomic forces in the material (e. g. groups of atoms subject to a soft potential) [31–33]. In the second class of theoretical models, the BP of the amorphous system is considered as a frequency broadened Van Hove singularity of crystalline systems [34]. This means that the VDOS of an amorphous material is just a modification of the vibrational density of states of the corresponding crystalline system due to random fluctuations of force constants [35]. The investigation of the Boson Peak of confined polymers can shine some light on its molecular origin.

Although the idea to confine polymers to nanoporous materials to substantiate relevant length scales experimentally seems to be rather simple, one has to keep in mind that ideal nanoconfined systems do not exist. In real systems the polymers will interact with the confining walls, which can lead to adsorption, distortions, or changes in the density compared to the bulk value [36,37].

Inelastic neutron scattering is a valuable technique to investigate soft matter systems [38,39] even in the nanoconfined state [40,41]. This is directly due to high penetration depth of neutrons. Moreover, by a suitable choice of isotopes the confined polymer can be selectively studied. The aim of the presented work is threefold. In a first step, the influence of a nanoscale confinement on the vibrational density of states in the frequency range of the excess contribution to the vibrational density of states is investigated. Secondly, the question how the localized dynamics of the methyl group rotations is changed by the confinement is addressed. Last but not least, the alteration of the segmental dynamics (dynamic glass transition, α-relaxation) is discussed in detail. Some of the results have been published elsewhere [40–48].

2. Inelastic neutron scattering

Inelastic Neutron Scattering is related to the dynamics of nuclei on nanoscopic length and time scales where dynamics refer to both vibrations and molecular fluctuations [50]. In an inelastic neutron scattering experiment both the transfer of momentum,

$$\hbar\vec{q} = \hbar\left(\vec{k}_f - \vec{k}_i\right) \tag{2}$$

and the transfer of energy