# Confinement-Induced Relaxation Process in Thin Films of Cis-Polyisoprene

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Broadband dielectric spectroscopy is employed to investigate the molecular dynamics of cis-1,4-polyisoprene (PI) in thin layers down to thicknesses comparable with the chain extension. The segmental and the normal mode dynamics of the PI chains is found not to depend on the layer thickness. Additionally, a novel confinement-induced relaxation process is detected. It is assigned to fluctuations of terminal subchains which are formed due to the immobilization of chain segments at an interface. Most of the experimental findings can be well described by simulations of the chains as ideal random walks.

The (dynamic) glass transition under spatial confinement [1–4] and especially in thin polymer films [5,6] is a topic of current scientific research. Experimental techniques like ellipsometry [7,8], calorimetry [9,10], neutron scattering [11,12], and dielectric spectroscopy [13–15] have been employed. The latter has the advantage that it enables one to study the molecular dynamics of polar molecules in a broad frequency range ($\geq 7$ decades) close to the calorimetric glass transition. It benefits furthermore from the fact that the capacity $C$ is inversely proportional to the sample thickness $d$.

Several approaches were developed to understand the dynamics of molecules under these conditions. Backed by studies on low molecular weight systems [16] it was suggested that the dynamics is the result of a subtle counterbalance between surface and confinement effects. While the former causes a slowing down of the molecular dynamics (and hence an increase in $T_g$) due to attractive interactions with an interface, the latter results in a faster molecular dynamics compared to the bulk (and hence a decrease in $T_g$). Confinement effects come into play if the inherent length on which cooperative rearrangements take place [17] becomes limited by the external confinement.

To explain the glass transition temperature reductions observed for freely standing polystyrene films [8], de Gennes suggested a "sliding model" [18], where for film thicknesses thinner than the coil size motions of chain arcs between the two contacts at a surface become dominant. By that an additional length scale between that of a few chain segments and the end-to-end vector becomes important.

Type *A* polymers [19] (where the dipole moment in chain direction adds up) offer a natural access to study the molecular dynamics at different length scales. The segmental mode which corresponds to the dynamic glass transition represents fluctuations of 2–3 repeat units [20], while the normal mode describing the fluctuation of the end-to-end distance senses the overall chain dynamics. In a study of thin layers of poly(propylene oxide) Kojio *et al.* [21] reported a retardation of the normal mode under confinement while the segmental mode was affected only for a very small thickness (14 nm). A slowed-down normal mode and an accelerated segmental mode were reported in a study of poly(propylene glycol) confined in nanoporous glasses [22]. Petychakis *et al.* reported in [23] a broadening of the normal mode and a faster dynamics in a study of polyisoprene (PI) confined in a nanoporous glass.

In our study four different molecular weights of polyisopropene (34, 52, 60, and 108 kg mol$^{-1}$ having narrow polydispersities ($Mw/Mn = 1.02$–1.04) were investigated. The corresponding radii of gyration are 7, 9, 11, and 13 nm and the end-to-end distances are 18, 22, 24, and 32 nm, respectively. A special arrangement of perpendicularly crossed electrodes obtained by aluminum evaporation in high vacuum was used to contact the samples. The lower electrode, which serves as support for the polymeric film, was deposited by aluminum evaporation on a glass plate while the upper one was evaporated on top of the spin-coated PI layer. There are indications in the literature that such an asymmetric preparation procedure induces also asymmetric interactions at the interfaces [5].

Thin films of polyisoprene were prepared by spin coating from a chloroform solution. The film thickness was adjusted by variation of the solution concentration and of the spinning rate. For thickness determination the capacity of the samples at a frequency of $10^5$ Hz and at 200 K was measured, where the dielectric permittivity is not affected by the dielectric dispersion. The value of $\varepsilon'_\infty$ was assumed to be thickness independent in accord with recent scattering experiments on thin films [24,25]. The films were kept for 5 h in oil-free vacuum at room temperature and subsequently for 10 h at 400 K in a pure nitrogen atmosphere in order to remove solvent and to equilibrate the samples. After this annealing procedure a stability in time and with respect to temperature variation was achieved for all samples.

The data were fitted using the Havriliak-Negami relaxation function [26]. In case of strongly broadened relaxation processes fits of the spectra $\varepsilon''$ vs frequency

did not deliver sufficient accuracy in the determination of the maximum position. Therefore the spectra $\varepsilon''$ vs temperature were fitted using an asymmetric peak fitting function derived from the Havriliak-Negami function (inset, Fig. 1). For samples where the analysis could be carried out in the frequency and temperature representation in parallel it was checked that both procedures are equivalent.

Typical results obtained for a molecular weight of $52 \text{ kg mol}^{-1}$ are shown in Fig. 1 in dependence on the film thickness. Between the segmental and the normal mode a third relaxation process shows up with decreasing thickness. It gains dielectric strength on the expense of that of the normal mode. With decreasing thickness this confinement-induced mode becomes faster (Fig. 2). In contrast the relaxation rate of the segmental and normal mode does not show a thickness dependence. Varying the molecular weight (Fig. 3) shows for the normal mode a shift of the relaxation rate similar to the bulk while the confinement-induced mode and the segmental mode are not affected.

For the assignment of the confinement-induced mode it is assumed that at the contact with one of the two interfaces the chain segments are immobilized. Because of this segmental immobilization, the end-to-end fluctuation of such pinned chains is interrupted and only the relaxation of the terminal subchains is dielectrically active in this case. The confinement-induced mode is assigned to the end-to-end fluctuation of the terminal subchains, which have to be treated as tethered chains with $\tau_{\text{tethered}} = 4\tau_{\text{linear}}$ [27]. This model recovers in a natural way the observed experimental findings: (i) the segmental mode as a local relaxation process is not af-

fected by the confinement; (ii) the confinement-induced mode becomes faster with decreasing film thickness because the terminal subchains become on average shorter; (iii) it shows no molecular weight dependence because with increasing molecular weight $M_w$ the number of contact points $N_C$ of the chain increases correspondingly and by this the length of terminal subchains $M_w^{\text{TSC}} \sim M_w/N_C$ remains on average constant; (iv) the normal mode is not shifted with thickness because even for thin films we still have a certain fraction of free (nonimmobilized) chains which exhibit a bulklike dynamics; (v) it indicates further that its dielectric strength decreases with thickness while the confinement-induced mode gains intensity due to the relative increase of the number of terminal subchains.

For a more quantitative analysis simulations were carried out treating the chain as an ideal random walk in three dimensions taking place between two impenetrable interfaces. The simulations were done off lattice, one step being defined by two independent random angles (the azimuthal and the longitudinal angles from the spherical system of coordinates). Following the idea of the model given above, we assumed that the chain segments coming in contact with an interface are immobilized. The walks penetrating the interface were rejected. We have determined the end-to-end distribution for the free (nonimmobilized) chains as well as for the terminal subchains in dependence on thickness and molecular weight to get information about the normal and the confinement-induced mode and, by this, to test the validity of our molecular model.

The simulations reveal that only in the case when one interface immobilizes chain segments while the other reflects the chains (hard wall behavior) a confinement-induced thickness dependent end-to-end distribution of terminal subchains is found (Fig. 4). It arises from terminal subchains being in contact with both interfaces (inset,
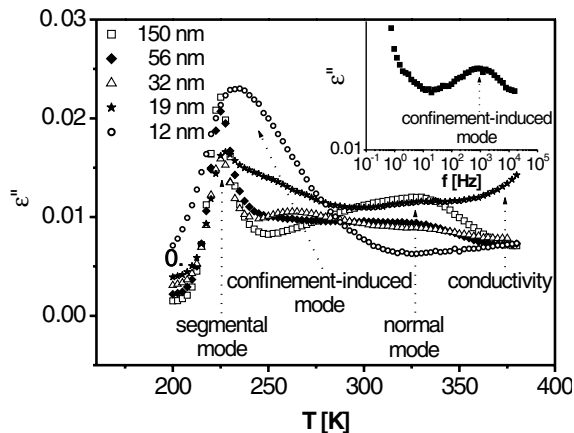


FIG. 1. Dielectric loss $\varepsilon''$ vs temperature $T$ at a frequency of 96 Hz for polyisoprene (molecular weight $M_W = 52 \text{ kg mol}^{-1}$) in thin layers of thicknesses as indicated. Inset: dielectric loss versus frequency for PI ($Mw = 52 \text{ Kg/mol}$) at a temperature of 287.5 K and for a film thickness of 46 nm. (The error bars are comparable with the size of the symbols, if not indicated otherwise.)
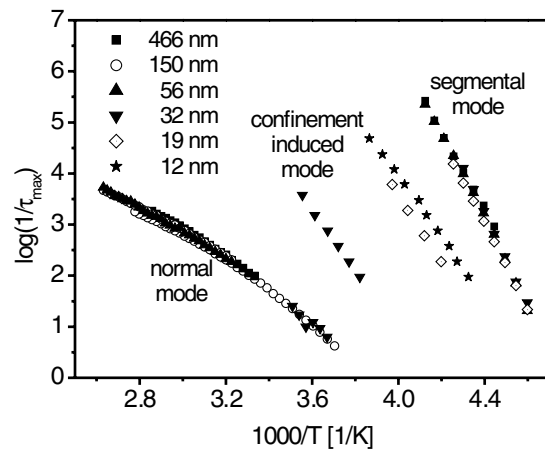


FIG. 2. Relaxation rate $1/\tau_{\max}$ vs inverse temperature for polyisoprene ($M_W = 52 \text{ kg mol}^{-1}$) in thin layers of thicknesses as indicated.
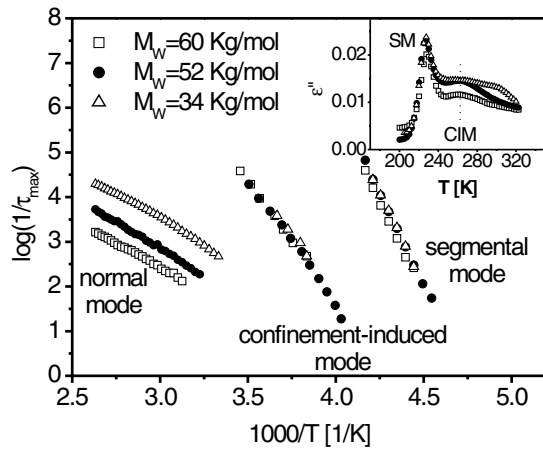
FIG. 3. Relaxation rate $1/\tau_{\max}$ vs inverse temperature for polyisoprene of different molecular weights as indicated. Layer thickness $d = 45 \pm 2$ nm. The inset shows the raw data in the temperature representation.

Fig. 5) and hence exists only when the film thickness becomes comparable with the size of the coil. The asymmetry suggested by our simulations is in accord with a study on thin polystyrene films [5] (where an identical sample preparation procedure was employed as in our experiment) and might be due to the different preparation of the electrodes: on the lower electrode the polymer is deposited by spin coating, while the upper one is evaporated on the top of the polymer layer.

The simulations reproduce qualitatively the experimental findings: (i) the maximum position for the distribution of terminal subchains is shifted to shorter values with decreasing film thickness, i.e., the confinement-

induced mode becomes faster (Fig. 4); (ii) keeping the films thickness constant and varying the length of the chains shows no molecular weight dependence for the distribution of the terminal subchains (inset, Fig. 4); (iii) concerning the normal mode the simulations reveal that its maximum position is not shifted down to $d \sim 2R_{EE}$ while its relaxational strength shows a steep decline with decreasing thickness (data not shown).

For the scaling of the molecular weight of the terminal subchains $M_{\text{TSC}}$ with $d$ the simulations deliver $M_{\text{TSC}} \sim d^{1.7}$. Assuming for the terminal subchains a Rouse-like dynamics (the confinement-induced mode is faster than the normal mode corresponding to the critical molecular weight $M^*$ of PI, with $M^* = 10 \text{ kg mol}^{-1}$) one finds with $\tau_{\text{TSC}} \sim M_{\text{TSC}}^2$, the relation $\tau_{\text{TSC}} \sim d^{3.4}$, in contrast to the experiment, from which $\tau_{\text{TSC}} \sim d^{6.0 \pm 1}$ (Fig. 5). To resolve this discrepancy more refined molecular dynamics simulations are required.

In molecular dynamics simulations [28,29] of thin polymer layers confined between smooth and repulsive walls an acceleration of the dynamics was observed. This finding is not in accord with the present study. The reason for the discrepancy might be the influence of the walls [30], which are in our experiment not equivalent (see above) in their interaction with the polymer and certainly not smooth on a molecular scale. Elaborated experiments are required to tackle this problem.

In the present study we have investigated the relaxation dynamics of PI thin films at two strongly different length scales: one defined by 2–3 monomer units and the other by the end-to-end distance of the PI chain. As expected for polyisoprene, two relaxation processes are observed for the bulk: the segmental and the normal mode. When the thickness decreases a novel confinement-induced relaxation process shows up between the normal and the segmental mode. It is assigned to the fluctuation of the terminal subchains formed by the immobilization of the PI segments which are in contact with a
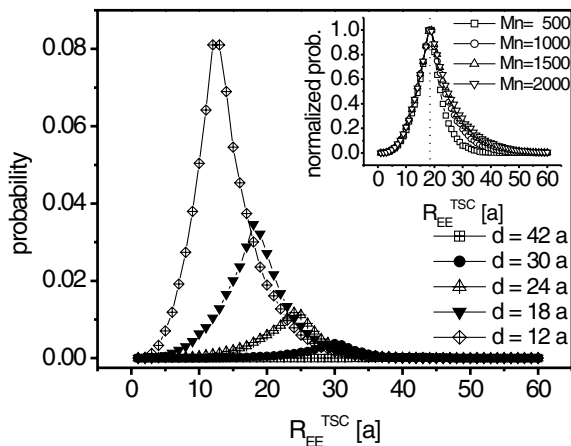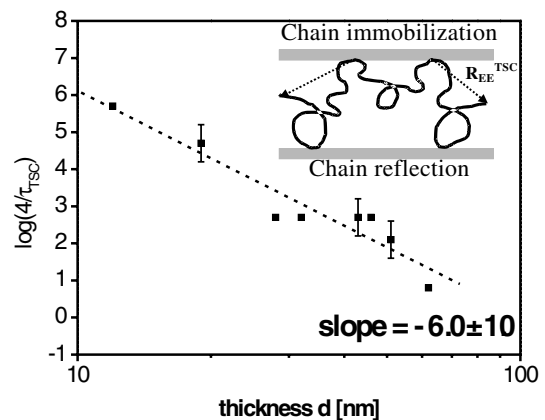


FIG. 4. Simulation of the distribution of the end-to-end vector for terminal subchains in dependence on the separation between an immobilizing and a reflecting interface. The chain is assumed to have as a whole 500 segments. Inset: Distribution of the end-to-end vector for chains of different molecular weights as indicated, for a layer thickness of $18a$, where $a$ is the segment length.



FIG. 5. The relaxation rate of the confinement-induced mode versus film thickness for molecular weights ranging from 34 to 60 kg mol$^{-1}$.

confining aluminum surface. Under increasing confinement this relaxation process becomes faster. No changes in the relaxation rate of the normal mode were found, proving that chains having a bulklike normal mode relaxation dynamics are present in the films, even for thicknesses as small as $d \sim 2R_{EE}$. Its relaxation strength strongly decreases with thickness, as a consequence of the chain interfacial attachment.

The simulations of the chains as ideal random walks reveal the existence of a confinement-induced thickness dependent end-to-end distribution of terminal subchains which originates from chains immobilized at one interface and reflected at the other. Qualitative agreement is found between experiment and simulations. A discrepancy in the thickness dependence of the relaxation rate of the confinement-induced mode still remains. To resolve this, molecular dynamics simulations are required for polymers being confined between an attractive and a repulsive wall.

In contrast to many recent studies we do not observe a shift of the dynamic (and hence the calorimetric) glass transition despite the pronounced chain confinement effect proven by the existence of the confinement-induced mode. This reflects the different length scales at which the dynamics take place, the segmental, the confinement-induced, and the normal mode. These different fluctuations are well decoupled from each other due to the extraordinary flexibility of the polyisoprene chain. This is not the case for polymers having stiffer chains [e.g., PMMA [poly(methyl methacrylate)] in [14,15], PS (polystyrene) in [5]], where confinement effects are well established.

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