Colloid Polym Sci (2004) 282: 946–954
DOI 10.1007/s00396-004-1133-0

ORIGINAL CONTRIBUTION

A. Serghei
L. Hartmann
P. Pouret
L. Léger
F. Kremer

Molecular dynamics in thin (grafted) polymer layers

Received: 10 March 2004
Accepted: 8 April 2004

A. Serghei · L. Hartmann · F. Kremer (✉)
Faculty of Physics, University of Leipzig,
Linnéstr. 5, 04103 Leipzig, Germany
E-mail: kremer@physik.uni-leipzig.de

P. Pouret · L. Léger
Laboratoire de Physique de la Matière
Condensée, Collège de France,
11 Place Marcelin Berthelot,
75231 Paris Cedex 05, France

Abstract Broadband dielectric spectroscopy is employed to study the molecular dynamics in thin polymer layers of (spin-coated) *cis*-1, 4-polyisoprene (PI) and of (grafted and spin-coated) polydimethylsiloxane (PDMS). For the former, besides the segmental and the normal mode relaxation, a confinement-induced mode is observed, which is assigned to fluctuations of terminal subchains. It turns out that the uptake of water has a strong influence on the dynamics of this relaxation, which takes place in the immediate vicinity of the interface. Between grafted and spin-coated PDMS a pronounced difference in the dynamics is observed for layers that are comparable in thickness to the radius of gyration of the confined chain. This is attributed to the different conformation of grafted and spin-coated polymer layers.

Introduction

While the molecular dynamics of low molecular weight glass-forming systems in confining space is well understood, as determined by the counterbalance between surface and confinement effects [1], the situation for polymers is much less clear [2]. For the latter, the conformation of the chain, its interaction with the neighboring surface (grafted or spin coated), and the radius of gyration or the end-to-end distance become important. Chain loops at a free surface of a polymer film may experience an increased mobility. This gives rise—as suggested by de Gennes [3]—to a "sliding mode", which might have an impact on the glass transition temperature of the thin polymer layer. Recently [4, 5] it was shown for the type-A polymer [6] *cis*-1, 4-polyisoprene that "confinement-induced modes" develop if the thickness of the thin layer becomes comparable to the radius of gyration of the polymer chains. Despite this polymer confinement effect the dynamic glass transition corresponding to the segmental relaxation of the chain turned out to be unaffected [4].

Broadband dielectric spectroscopy (BDS) has proven to be an especially suitable tool in studying the dynamics in confinement [1, 7]. Due to the fact that the capacity of a condenser is inversely proportional to the layer thickness, BDS increases in sensitivity with decreasing sample thickness and hence sample amount. With its broad frequency range it enables one to trace the molecular dynamics on length scales spanning the range from a few segments to the end-to-end vector of a chain. In the present article three different topics will be addressed:

1. The confinement-induced mode in thin layers of *cis*-1, 4-polyisoprene
2. The effect of adsorbed water on the dynamics in thin polymer layers as exemplified for *cis*-1, 4-polyisoprene
3. A comparison of the dynamics in thin layers of grafted and spin cast polydimethylsiloxane (PDMS).

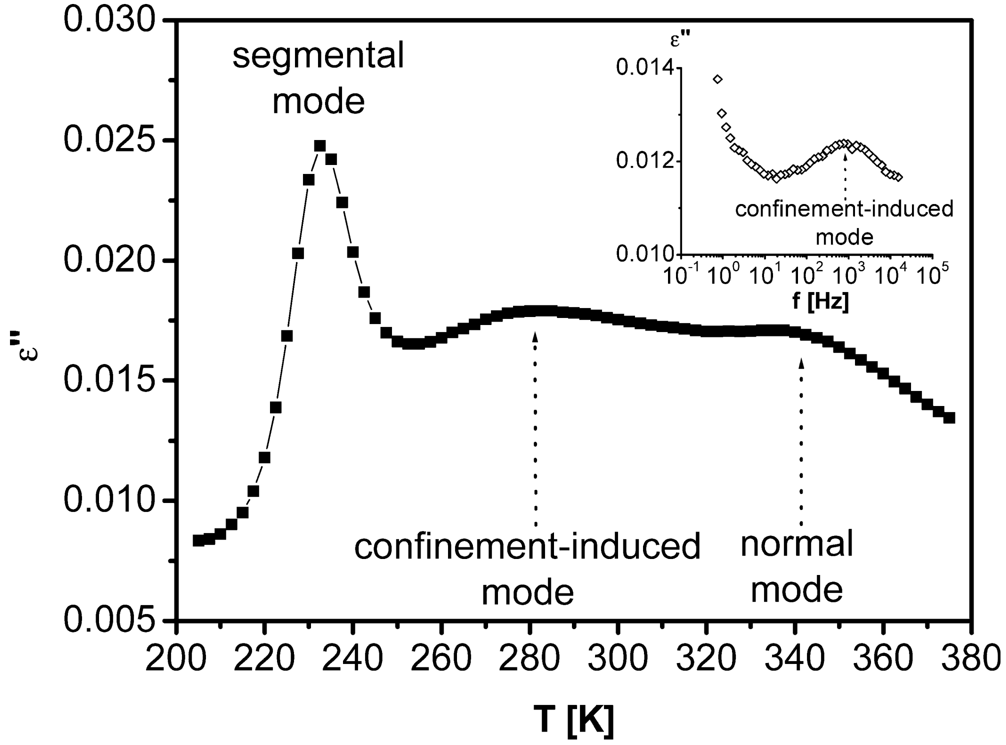


Fig. 1 Confinement-induced mode in the spectra of ϵ'' vs. temperature for PI, 34 kg/mol, 61 nm, measured at 970 Hz. Additionally, the segmental and the normal mode are seen. *Inset*: ϵ'' vs. frequency for PI, 52 kg/mol, 44 nm, measured at 287.5 K. In this and all further figures the experimental accuracy is comparable to the size of symbols if not indicated otherwise by error bars

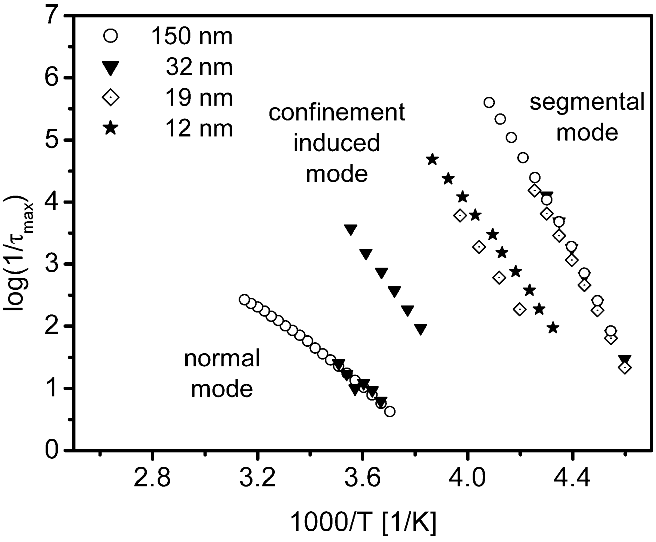


Fig. 2 Activation plot for PI (52 kg/mol) for different film thicknesses, as indicated

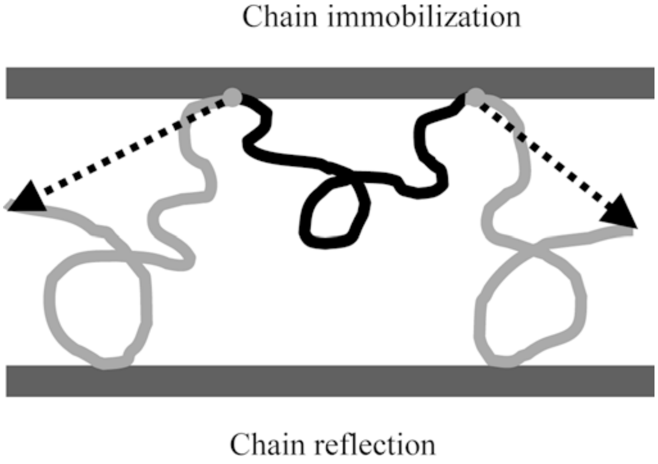


Fig. 3 Sketch illustrating the origin of the confinement-induced mode, which arises from the fluctuations of terminal subchains being immobilized at one interface and reflected at the other one

Dynamics in thin spin-coated films of *cis*-1, 4-polyisoprene

For the type-A polymer [6] *cis*-1, 4-polyisoprene (PI) the dielectrically active molecular dynamics [7, 8] takes place on two different length scales, the segmental mode corresponding to fluctuations of a few polymer segments [9] and the normal mode originating from relaxations of the end-to-end vector of the chain. If the thickness of the polymer layer becomes comparable to the radius of gyration of the chain a confinement-induced mode is detected (Fig. 1) being assigned to fluctuations of terminal subchains, which develop due to the immobilization of polymer segments in interaction with a confining interface. It has the following signature:

a. The confinement-induced mode does not exists for the bulk and shows up only when the film thickness

Fig. 4 Dielectric loss ϵ'' measured at 200 K for PI, 52 kg/mol, 150 nm after different annealing times, as indicated. After 18 h of annealing a decrease by 2–3 decades of ϵ'' is observed

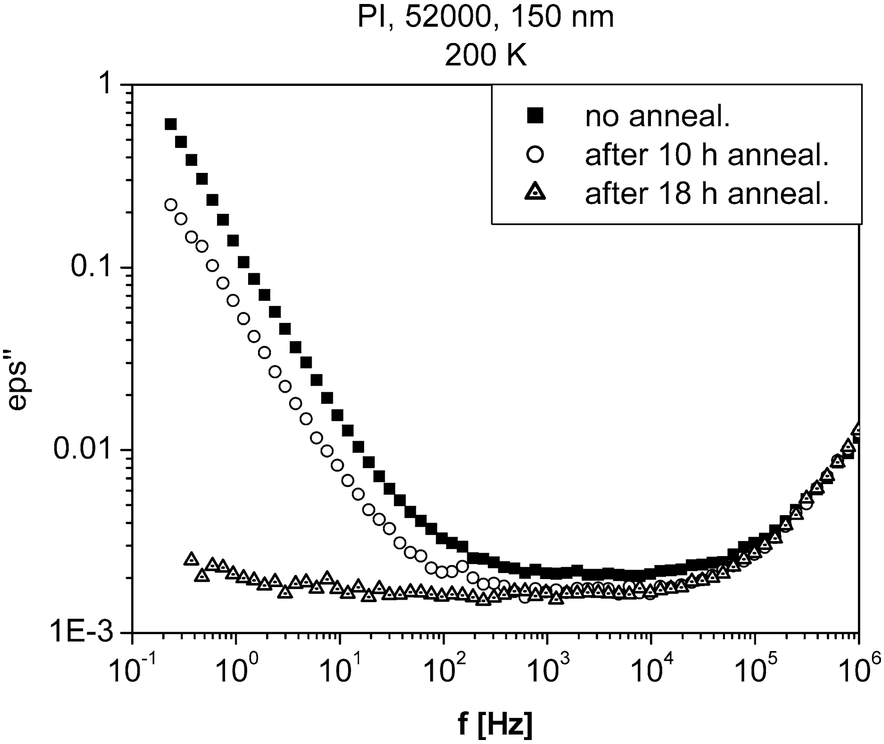
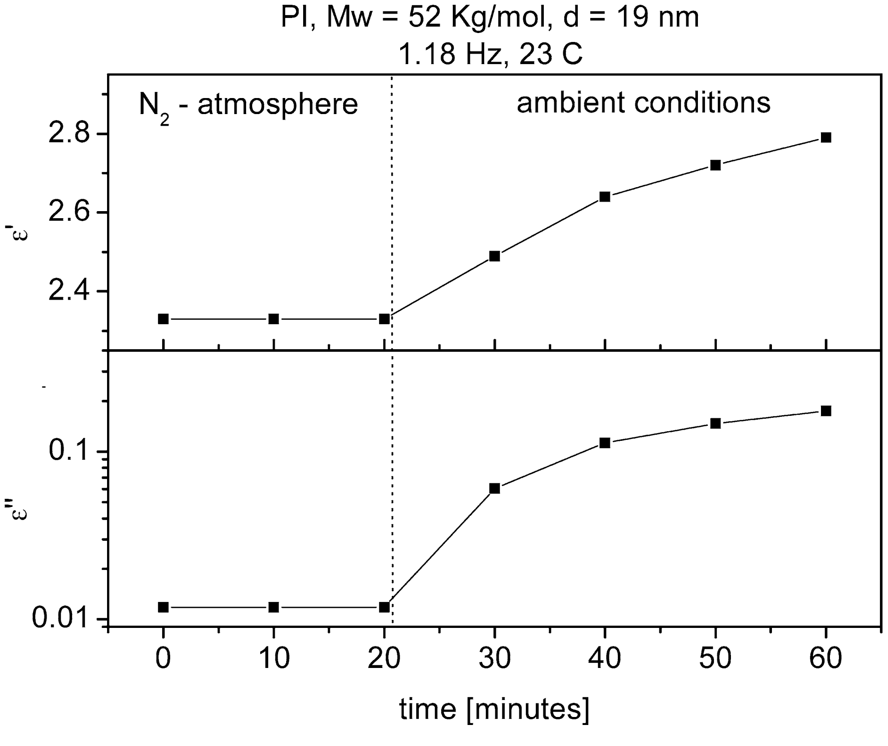


Fig. 5 Time evolution of ϵ' and ϵ'' measured at 1.18 Hz and 23 C for PI, 52 kg/mol, 19 nm. After keeping 20 min in a (water-free) N_2-atmosphere, the sample was measured under ambient conditions



becomes comparable with the size of the PI coil (Fig. 1) because it arises from the chains being in contact with both interfaces

b. The confinement-induced mode becomes faster with decreasing film thickness (Fig. 2) because the distribution of the terminal subchains is shifted to shorter values

c. Its relaxation strength increases at the expense of that of the normal mode because the relative number of immobilized chains increases with decreasing film

Table 1 Parameters for the layers of grafted PDMS

d (nm)	σ	b (nm)
41	0.14	2.6
11	0.038	5.1

d film thickness as determined from capacitance measurements at the lowest temperature, σ grafting density, *b* average distance between grafting sites. The latter two values can be calculated from the film thickness and the molecular weight ($M_w = 170$ kg/mol, $R_g = 21$ nm) according to relations derived in [12]

thickness, while, on contrary, the relative number of free (non-immobilized) chains strongly decreases

d. The relaxation rate of the normal mode is not shifted under confinement because even in thin films there are chains not touching the interfaces and, hence, exhibiting a bulklike-dynamics
e. The confinement-induced mode shows no molecular weight dependence because increasing the chain length also increases the number of contact points of the chain with the immobilizing interface
f. The dynamic glass transition is *not* affected by the confinement because it takes place on a length scale much smaller than the film thickness

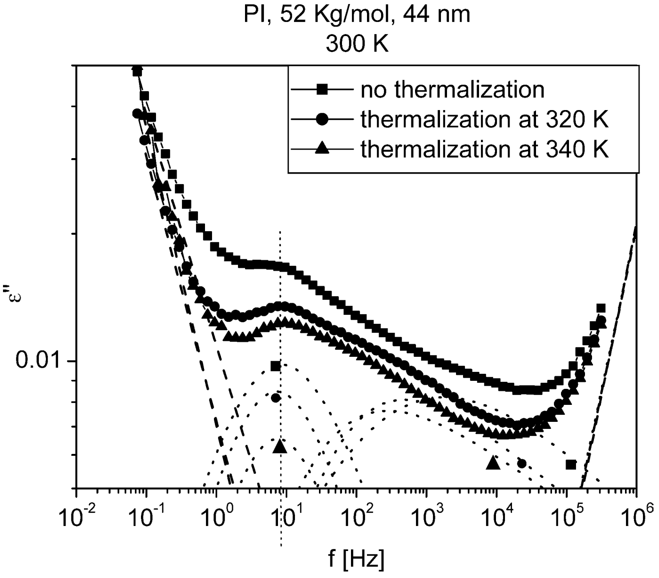


Fig. 6 Dielectric loss ϵ'' versus frequency measured at 300 K for PI, 52 kg/mol, 44 nm after annealing steps at different temperatures, as indicated. The *dotted lines* indicate fits according to the relaxation functions of Havriliak-Negami. The relaxation process at around 10 Hz corresponds to the normal mode while the confinement-induced mode is centered at around 100 Hz–1 kHz. The *dashed lines* of the low frequency side correspond to the conductivity contribution while those appearing at high frequencies are used to fit an artifact

The observed experimental findings can be qualitatively described [5] by simulations in which the confined polymer chains are treated as ideal random walks taking place between two flat walls where one is immobilizing the chain segments in contact while the other is reflecting them (Fig. 3). This asymmetry in the confining surfaces reflects the different type of the lower and upper electrode in the experiment: while the polymers are spin-coated on the former the latter is evaporated on top of the layer. Additional studies to prove this interpretation are in progress.

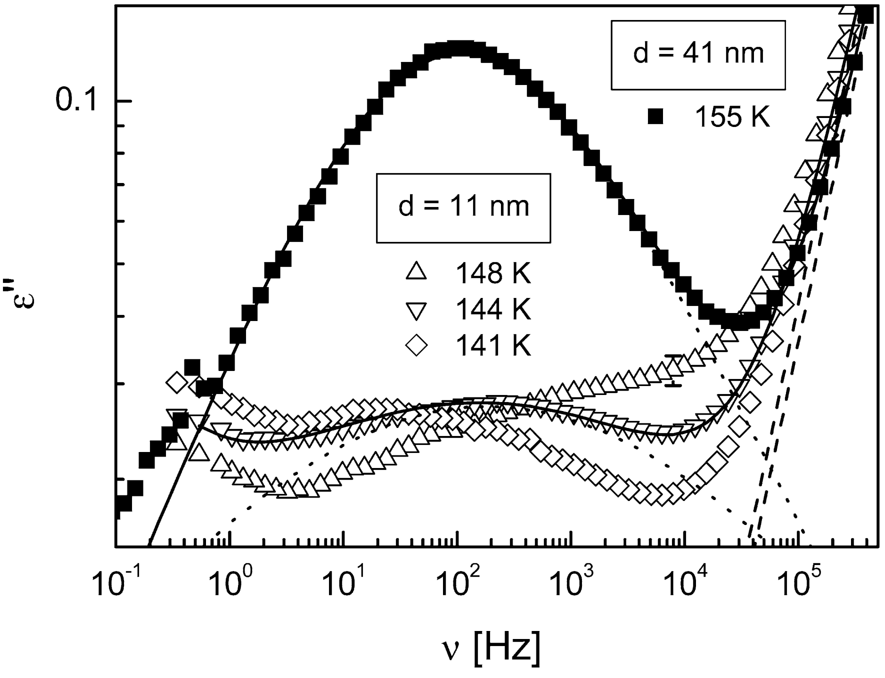
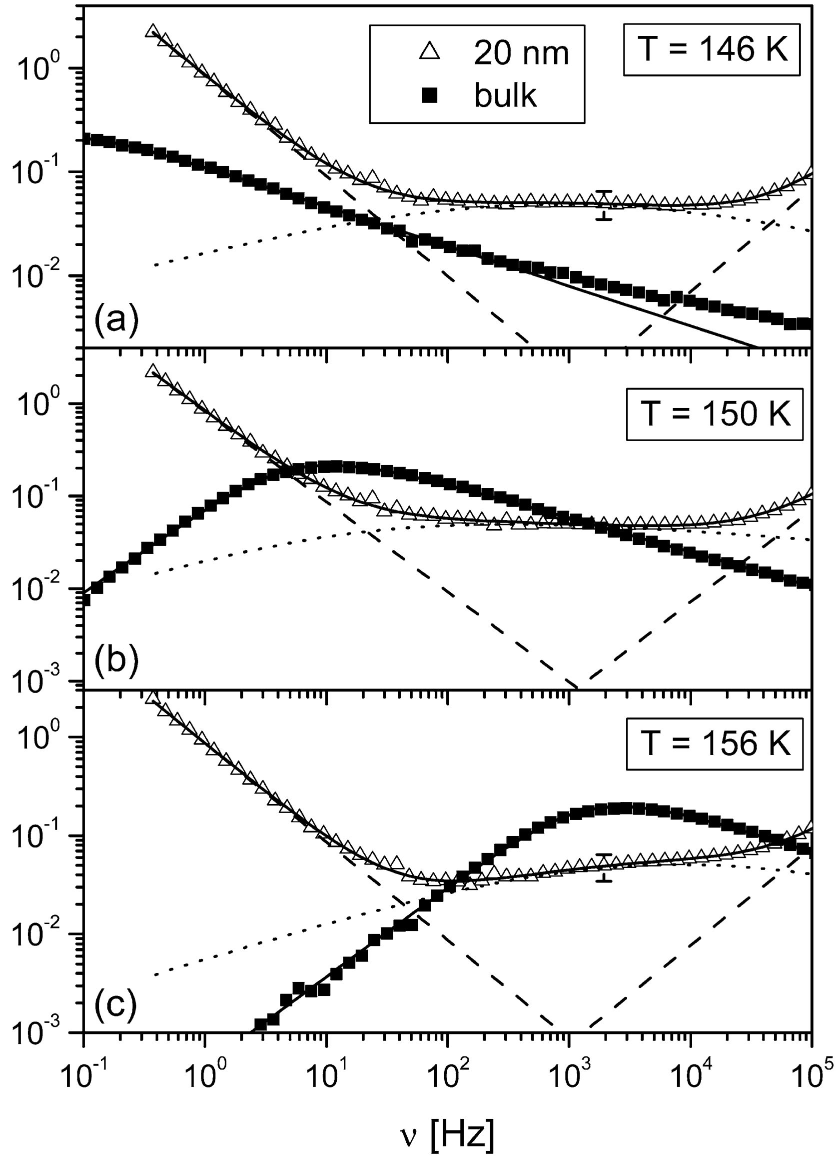


Fig. 7 Dielectric loss ϵ'' of PDMS in grafted films in dependence of the frequency of the electrical field at temperatures as indicated. *Open symbols* denote the loss from a grafted 11 nm thick film, *full symbols* represent a film of 41 nm thickness, which resembles well the dynamics of the bulk. *Solid lines* are the fits of a sum of a conductivity contribution (*dashed lines*) and two Havriliak-Negami functions for the relaxation processes (*dotted lines*) and an artifact at high frequencies (*dashed lines*). Note that the α-relaxation of the 41 nm thick film appears at a temperature being about 11 K higher than for the thinner film. This indicates a much faster dynamics in the film of 11 nm thickness. The relaxation strength for this film is clearly reduced compared to the thick film, the width is increased

Fig. 8a–c Dielectric loss ε'' of PDMS in spin cast films in dependence of the frequency of the electrical field at temperatures of **a** 146 K, **b** 150 K, and **c** 156 K.. *Full squares* denote the loss of the bulk PDMS ($M_w = 139$ kg/mol), *open triangles* that of a 20 nm thick film. *Solid lines* are the fits of a sum of a conductivity contribution (*dashed lines*) and two Havriliak-Negami functions for the relaxation processes (*dotted lines*) and an artifact at high frequencies (*dashed lines*)



The effect of water adsorption on the dynamics of thin *cis*-1, 4-polyisoprene layers

Water is ubiquitous under ambient conditions and it may be adsorbed—more or less (depending on the hydrophilicity)—in thin polymer layers. In view of the fact that many studies on the shift of T_g in thin polymer films were carried out under ambient conditions it is instructive to study this effect systematically. Broadband dielectric spectroscopy is especially suited for that because of the pronounced water absorption and a concomitant conductivity contribution at frequencies smaller than 1 MHz.

Annealing a 150 nm thick PI layer at 120 °C in a water-free atmosphere (under dry nitrogen flow) shows a dramatic effect (Fig. 4). The imaginary part of the dielectric function changes by nearly three decades on the low frequency side after an annealing time of 18 h, as a result of the water desorption. This corresponds to a decrease of the conductivity contribution, which is due to electronic charge carriers. As expected, this effect vanishes at frequencies where molecular relaxations dominate. Alternatively, a significant effect of the water adsorption on the dielectric constant of PI in thin polymer layers (e.g. Fig. 5) is observed by measuring the samples under ambient conditions. Analyzing the influence of adsorbed water on the different modes in PI one finds that the segmental and the normal relaxation do not change in their frequency position (data not shown) while the confinement-induced mode slows down by

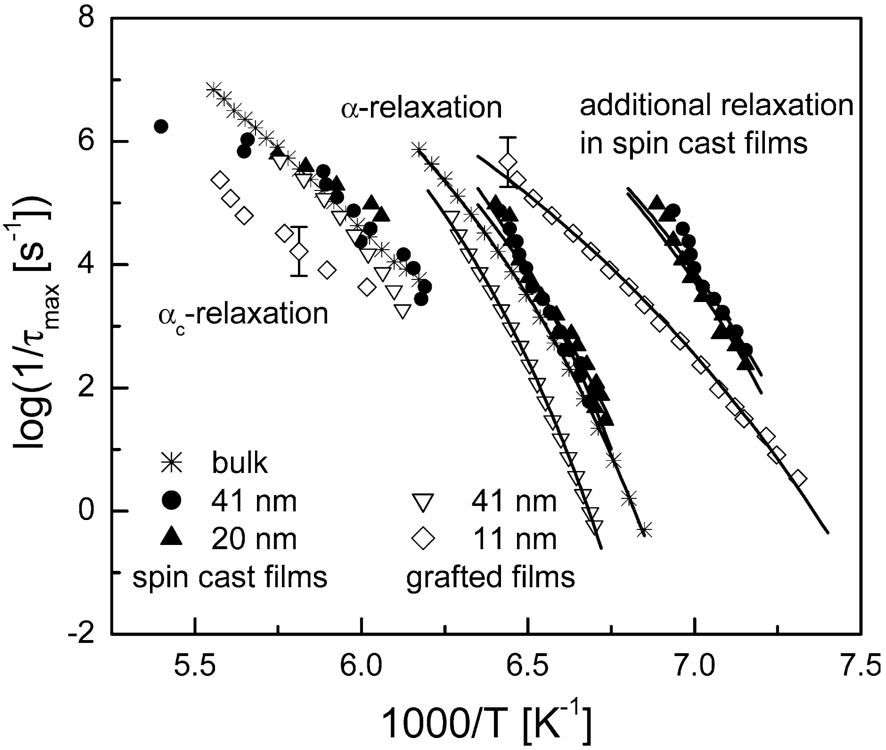


Fig. 9 Activation plot for the molecular dynamics of PDMS in the bulk, as spin cast and as grafted layers as indicated. In all cases the samples were first quenched in liquid nitrogen and then measured during a slow increase of temperature

about a decade after thermalization at 340 K in a water-free atmosphere. This fits well to the nature of this process, which is supposed to take place near an interface.

Molecular dynamics in thin grafted and spin cast layers of poly(dimethyl-siloxane) (PDMS)

For dielectric studies PDMS was grafted on aluminum stripes deposited on a glass substrate. Aluminum evaporated on top of the film after drying the films under vacuum served as upper electrode, as described in more detail in [10, 11]. Parameters for the grafted films and the bulk PDMS are given in Table 1. The preparation of grafted PDMS layers is described elsewhere [12, 13]. Since PDMS has a strong tendency to crystallize, all samples have been quenched ($\Delta T/\Delta t \approx 50$ K/min) in liquid nitrogen after they were capped by a glass container to protect them against ambient humidity. Subsequent heating enables one to measure the α-relaxation in the amorphous polymer below a partial crystallization at around 162 K. A more comprehensive description of the grafting procedure and of dielectric measurements can be found in [14]. Spin cast films were obtained from a solution of the polymer ($M_w = 139$ kg/mol) in toluol and were annealed before evaporation of the upper electrode. Again, PDMS was embedded between aluminum electrodes.

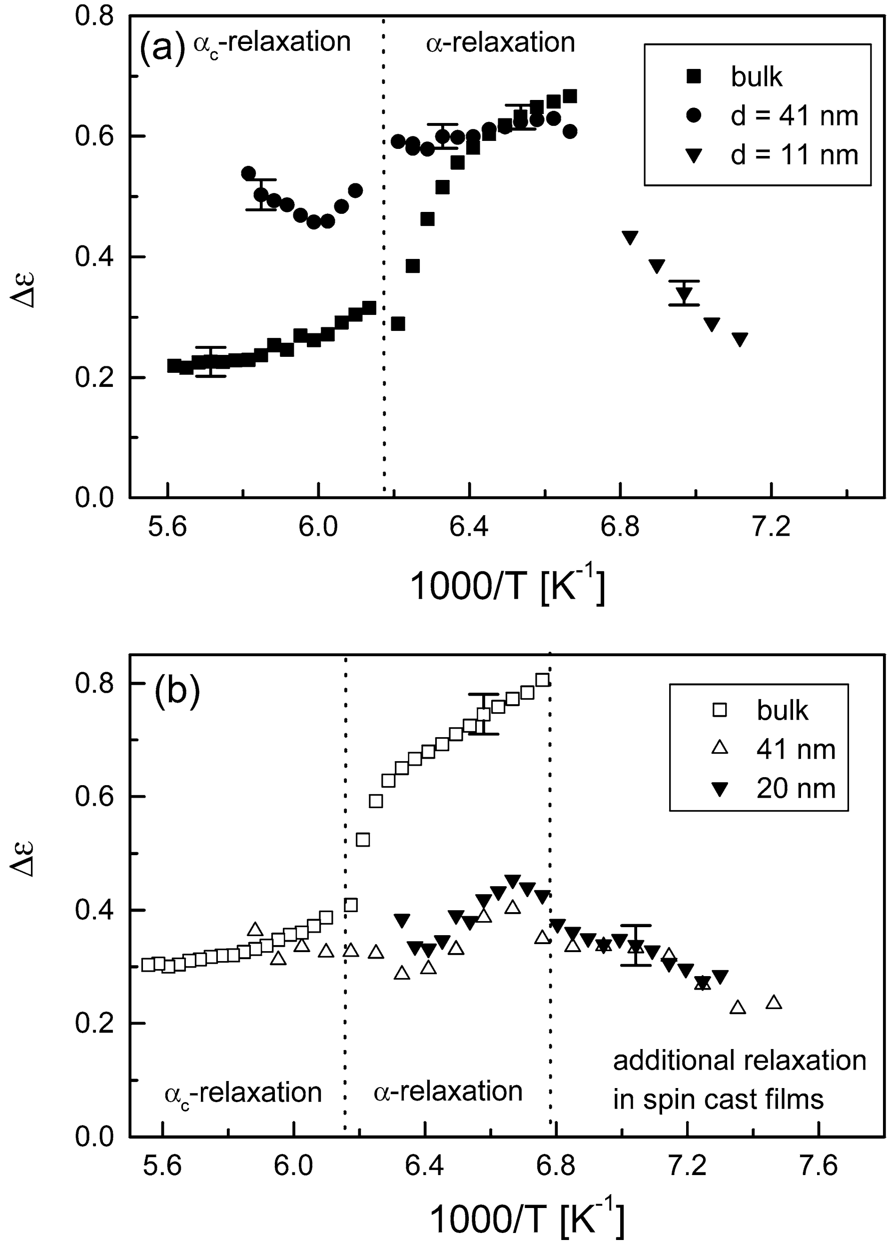
Table 2 Values for parameters of fits of Eq. 1 to the temperature-dependence of the relaxation rate for bulk, grafted and spin cast PDMS, respectively

Sample	$-\log(\tau_\infty)$	B (K)	T_0(K)
Bulk ($M_w = 139$ kg/mol)	14.5	763	124
Grafted films ($M_w = 170$ kg/mol)			
d = 11 nm	14.5 (fix)	1093	103
d = 41 nm	14.5 (fix)	696	129
Spin cast films, α-relaxation			
d = 20 nm	14.5 (fix)	759	123
d = 41 nm	14.5 (fix)	635	128
Spin cast films, fast process (T ≤ 150 K)			
d = 20 nm	14.5 (fix)	686	115
d = 41 nm	14.5 (fix)	707	114

In the fits the high temperature limit of the relaxation rate for the spin cast and the grafted sample is kept fixed at the value found for the bulk liquid

Representative isothermal representations of the dielectric loss ϵ'' of PDMS in the bulk and as thin spin cast and grafted films are shown in Figs. 6, 7 and 8, respectively. In the bulk and in the thick grafted film PDMS shows an α-relaxation, i.e., the dynamic glass transition of the amorphous PDMS after the samples have been quenched. At 162 K PDMS undergoes a partial crystallization. Thus, at higher temperatures the dynamics in the remaining amorphous regions is slowed down due to interactions with the crystalline regions; the corresponding relaxation process is the α_c-relaxation [14, 15].

Fig. 10a, b Relaxation strength $\Delta\epsilon$ vs. inverse temperature for PDMS in grafted films (**a**) and in spin cast films (**b**). In both cases the values of the bulk are given for comparison. Note that $\Delta\epsilon$ is obtained from fits of the Havriliak-Negami function to the dielectric loss whereas the activation plot stems from evaluation of the loss in its isochronal representation [14]. Thus, for the thin grafted layer only a few values can be obtained due to its high width, the conductivity contribution and the artifact at high frequencies, which restrict the accessible frequency range



The grafted layer of 11 nm thickness (Fig. 7) reveals a broadened α-relaxation, which is shifted in its maximum to lower temperatures corresponding to a shift to higher relaxation rates with respect to the bulk. The broadening of the α-relaxation in the thin film is due to the polymer–substrate interaction leading to a more heterogeneous environment for the fluctuating dipoles than in the bulk. The grafted layer of 41 nm thickness shows the same behavior as bulk PDMS except that the maximum temperature of the α-relaxation is slightly shifted to higher temperatures, corresponding to a slowing-down with respect to the bulk. Since the thickness of grafted layers is determined by the grafting density (Table 1) and thus by the chain conformation, the latter turns out to be the determining parameter for the rate of the α-relaxation as it can be seen in the activation plot (Fig. 9). Also for the grafted film of 11 nm, an α_c-relaxation appears as a high-temperature shoulder of the α-relaxation [14], indicating that even in the thinnest films a partial crystallization takes place. Activation plot for the molecular dynamics of PDMS in the bulk, as spin cast and as grafted layers as indicated. In all cases the samples were first quenched in liquid nitrogen and then measured during a slow increase of temperature.

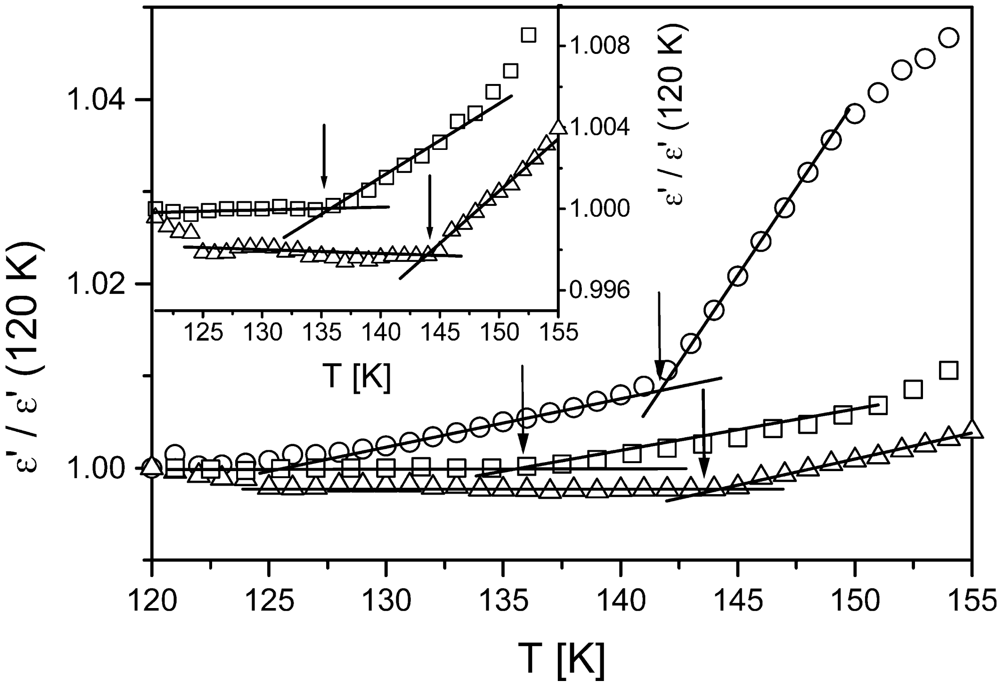


Fig. 11 Determination of the glass transition temperature T_g by capacitive scanning dilatometry as explained in the text for PDMS in grafted and in spin cast layers. *Triangles* denote the normalized values of ϵ' of the 41 nm thick grafted film ($T_g = 144 \pm 2$ K), *squares* represent an 11 nm thick grafted film ($T_g = 136 \pm 2$ K) and *circles* denote a spin cast film of 20 nm thickness ($T_g = 142 \pm 2$ K). In all cases data were taken at a frequency of 5×10^5 Hz. The *inset* magnifies the data of the two grafted films. In this case, T_g is clearly lowered in the thin film, while for the spin cast films a value almost equal to that of the bulk is obtained

The α-relaxation in thin spin cast films in Fig. 8 shows up at the position of the corresponding process in the bulk (Figs. 8b and c). Additionally, a weaker process appears at lower temperatures for both the film of 20 nm thickness and that of 41 nm (Fig. 8a). At the present state an assignment of this process remains speculative. Assuming that it is caused by fluctuations of dipoles, which are situated in the polymer-substrate interface, it could be assigned to the α-relaxation in a layer that has a higher molecular mobility than in the bulk due to an altered chain conformation in this region. This is similar to the "liquid-like layer" close to the upper surface of polymer films, as proposed by Fukao [16]. While in grafted films the altered chain conformation extends over the whole film thickness, only a part of the film is affected in spin cast films. This assumption unambiguously explains the difference in the dynamics of grafted and spin cast films. Also for the latter α_c-relaxation appears as high-temperature shoulder.

Figure 9 summarizes the above findings in an activation plot. The temperature-dependence of the relaxation rate can be described in all cases by the Vogel-Fulcher-Tammann (VFT)-equation:

$$1/\tau = 1/\tau_\infty \exp\left[\frac{-B}{T - T_0}\right] \qquad (1)$$

where $1/\tau_\infty$ is the relaxation rate in the high temperature limit, B denotes a constant and T_0 is the Vogel temperature. Results for the fit parameters are given in Table 2. In grafted films the α-relaxation becomes faster with decreasing grafting density. Hence, the reason is an alteration of the chain conformation. In contrast, the spin cast films reveal a bulk-like α-relaxation independent of the film thickness, and additionally a faster process that is assigned to segmental fluctuations in a layer of increased mobility. This finding requires further experimental investigation. Even the thinnest films undergo a cold crystallization independent of the inner film architecture, as is well known for bulk PDMS [15].

Figure 10 displays the relaxation strength for both, grafted and spin cast films as a function of inverse temperature. While for grafted films the relaxation strength of the 41 nm thick film and of the bulk coincide, $\Delta\epsilon$ in the spin cast films and in the thin grafted film is reduced by a factor of 2–3 with respect to the bulk. This reduction can either be attributed to an partial immobilization of dipoles in the polymer-substrate-interfaces or to a restriction of cooperative fluctuations in these regions as discussed by Fukao et al. [17].

The measured temperature-dependence of the capacitance, and hence the real part ϵ' of the dielectric function, can be used for the determination of the glass transition temperature T_g as shown in Fig. 11. This procedure is similar to the technique of capacitive scanning calorimetry, which has already been applied for thin films [16]. Thus, T_g can be identified as "kink temperature" since the coefficient of thermal expansion, and hence the capacitance, are altered at this temperature. While for the 11 nm thick grafted PDMS film T_g is reduced by about 8 K; there is only a negligible change between the bulk and the thick grafted film and the thin spin cast films. These findings are confirmed by values for T_g that are obtained from VFT fits to the relaxation rates in Fig. 9 as the temperature where the relaxation time is equal to 100 s.

Conclusions

For the type-A polymer *cis*-1, 4-polyisoprene it is shown that, despite a pronounced chain confinement effect (as proven by the development of novel modes), the dynamic glass transition is *not* influenced. The results can be qualitatively comprehended by simulating the chain as ideal random walk between an immobilizing and reflecting interface. The uptake of water in PI has a pronounced effect on the dynamics of the terminal subchains, which are always located in the vicinity of a boundary layer; obviously the water acts there as a plasticizer making the dynamics faster. For polydimethylsiloxane one finds a clear difference in the dynamics of grafted and spin-coated layers under the condition that the layer thickness becomes comparable to the radius of gyration of the polymer chains. This effect is attributed to the different conformations of the polymer in grafted and spin cast films.

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