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Influence of Tacticity on the Glass-Transition Dynamics of Poly(methyl methacrylate) (PMMA) under Elevated Pressure and Geometrical Nanoconfinement

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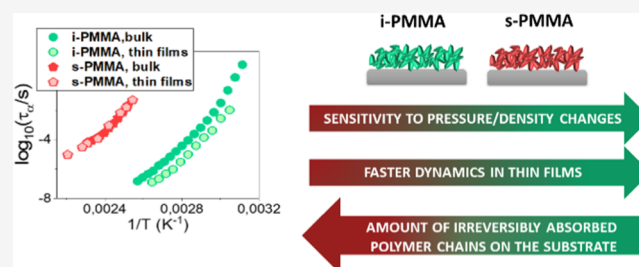
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ABSTRACT: The physicochemical properties of polymers can be modified by spatial configuration. Here, dielectric spectroscopy (DS) was employed to investigate the effect of the tacticity on the glass-transition dynamics of confined polymer films. We have also carried out dielectric relaxation studies at ambient and elevated pressure conditions. High-pressure measurements provide information on the sensitivity of the glass-transition dynamics to density changes, which can be helpful to better understand the confinement effect. For our study, we have chosen a glass-forming polymer, poly(methyl methacrylate) (PMMA), with two different tacticities (isotactic and syndiotactic) and an approximately equal molecular weight. We have shown that the segmental relaxation for the bulk syndiotactic PMMA is observed at a higher temperature range compared to the bulk isotactic PMMA. The experimental data analysis has also revealed that the molecular order influences the behavior of the polymer under increased pressure. The glass-transition dynamics of isotactic PMMA is more sensitive to the pressure/density changes than syndiotactic PMMA. Finally, we have also demonstrated that tacticity has a significant impact on the segmental dynamics of the confined polymer films. Syndiotactic PMMA has a stronger interaction with the substrate than isotactic PMMA, which is indicated by the higher amount of irreversibly adsorbed polymer chains. For this reason, the segmental dynamics of s-PMMA thin films follows the bulk behavior. In contrast, for i-PMMA, the confinement effects are pronounced, and the glass-transition dynamics accelerate with the reduction of the thickness of thin films.



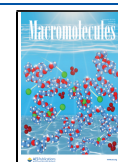
INTRODUCTION

Polymers have been the subject of interest to scientists around the world^{1–14} mainly because of their potential application in medicine, pharmacy, or modern technologies.^{15–25} As known, the polymeric materials' physicochemical properties can modify under the influence of various factors. Literature data show that the chain length (molecular weight) affects the molecular dynamics and the fragility of polymers.^{14,26–28} It has also been observed that molecular weight might affect the crystallization process.^{29–32} The chain length impacts both the crystal morphology and the crystallization rate.^{29,30} The properties of the polymer materials can also be modified by compression. The increased pressure causes changes in the glass-transition dynamics. The percentage of the free volume available for the molecular movements decreases under the influence of the elevated pressure, which induces shifts in the glass-transition temperature.^{33–39} Also, the properties of the polymer glass formers under geometrical nanoconfinement can differ significantly from the bulk behavior.^{9–12,40–46} The most frequently observed effects are the faster dynamics and changes in the glass-transition temperature for both thin films^{42–45} and nanopores-confined systems.^{9–12}

Numerous studies show that tacticity can also dramatically affect the properties of polymers.^{47,48} Tacticity determines how the atoms and the groups of atoms are arranged on the polymer backbone. In the case of isotactic polymers, all of the substituents are on the same side of the polymer chain. The substituents' alternating arrangement characterizes the syndiotactic polymers, while in the atactic polymers, the substituents are randomly distributed along the polymer chain.^{49–53} In addition to that, it has been found that the phase transitions of polymer materials are also influenced by spatial configuration.^{54–56} Experimental evidence reports that tacticity has a significant impact on the glass-transition dynamics.^{52,57–66} For poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylates) (PEMA), it has been observed that different spatial configurations of the polymers are characterized by the various relaxation times and the glass-transition temperatures.^{63,64} As

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shown, isotactic PMMA and PEMA have lower T_g values compared to syndiotactic and atactic stereoisomers.⁶³ Moreover, an increasing amount of the syndiotactic PMMA in the sample causes the vitrification process to occur at higher temperatures.⁶⁷ Based on the calorimetric measurements, it was estimated that for pure isotactic and pure syndiotactic PMMA, T_g is 315 and 397 K, respectively.⁶⁸ The influence of the molecular order on the glass-transition temperature was also observed for polypropylene (PP).⁶⁹ Literature data also show that crystallization kinetics is influenced by the tacticity of the polymers.^{29,70,71} For polypropylene, it has been found that the crystallization rate and melting temperature depend on the spatial configuration.⁷⁰ On the other hand, it has been shown that the degree of isotacticity of PP has a large impact on the nucleation rate, while not as that significant on the crystallization rate and the crystal morphology.²⁹ It should also be mentioned that syndiotactic polystyrene (PS) crystallizes faster than isotactic PS.⁷² Furthermore, isotactic and atactic polypropylenes are characterized by different sensitivities to pressure.⁷³ Tacticity can also affect the thermal stability of a polymer. For example, the thermal stability of atactic and syndiotactic polystyrene (PS) is similar, while isotactic PS degrades at higher temperatures. This fact is related to the greater stability of isotactic PS, which implies restricted molecular mobility.⁷⁴ The behavior of the polymer in confined geometry can also be influenced by the spatial configuration.^{75–81} The literature data show that the segmental dynamics of isotactic PMMA thin films deposited on silicon and aluminum substrates is faster compared to the bulk sample.^{75–78} However, ellipsometric studies suggest that reducing the thickness of the films increases the glass-transition temperature of i-PMMA.⁸⁰ In the case of syndiotactic PMMA, both increase and decrease of the T_g value are possible depending on the degree of syndiotacticity of the sample.⁷⁹ It is worth adding that Grohens et al. have found that the T_g values estimated from ellipsometric and dielectric measurements can differ.⁸⁰ Moreover, for atactic and syndiotactic PMMA thin films, it has been observed that the β -relaxation is sensitive to confinement effects^{78,81} as opposed to an isotactic stereoisomer.^{75,76} From the above considerations, it can be concluded that the polymers' tacticity is an extremely important parameter in the studies of soft matter systems. Understanding the relationship between the spatial configuration and various physicochemical properties is essential to producing polymer materials with desirable behavior and functions.

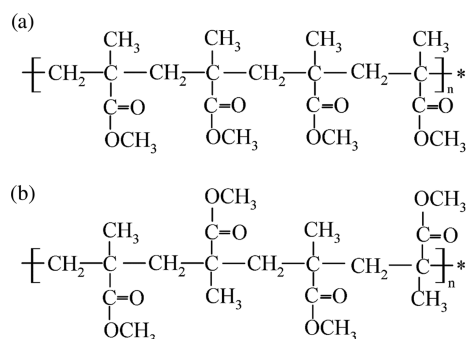
In this paper, we aim to investigate the impact of tacticity on the glass-transition dynamics of confined polymer thin films. For our research, we have chosen a glass-forming polymer, poly(methyl methacrylate) (PMMA), with two different tacticities (isotactic and syndiotactic). At ambient pressure conditions, these two stereoisomers are characterized by various segmental relaxations and glass-transition temperatures.^{63,64,68} Using dielectric spectroscopy (DS), it was observed that the segmental dynamics of PMMA confined thin films was affected by the molecular order. Faster dynamics under geometrical nanoconfinement was observed only for i-PMMA thin film. The average relaxation time for thin films of s-PMMA did not differ from that of the bulk. In contrast to previous studies on the influence of tacticity on the behavior of PMMA, we have combined the results of the dielectric relaxation studies measured under high-pressure conditions for the bulk samples with that for nanometric thin films. This

approach sheds new light on the deviation seen in the confined geometry. To the best of our knowledge, this is the first study that shows that the glass-transition dynamics of s-PMMA is less sensitive to pressure/density changes compared to i-PMMA. The value of the pressure coefficient of the glass-transition temperature, dT_g/dP , is 0.119 and 0.277 K/MPa for the syndiotactic and isotactic samples, respectively. Thus, this could possibly explain also the weaker sensitivity of s-PMMA to the changes in molecular packing induced by geometrical confinement. Moreover, using atomic force microscopy (AFM), we have found that the differences in PMMA thin film behavior can be caused by stronger interactions between the syndiotactic sample and the silicon substrate due to the higher amount of irreversibly adsorbed polymer chains. Our research shows a significant role of tacticity in controlling the glass-transition dynamics under high-pressure conditions and geometrical nanoconfinement. Molecular order influences the sensitivity to density fluctuations and the interaction of the polymer with the substrate, which is extremely essential in the design and application of polymeric materials.

EXPERIMENTAL SECTION

Materials. Two poly(methyl methacrylate) samples of different tacticities and similar molecular weights were tested: isotactic (i% ~ 95%) with $M_w = 11\,700$ g/mol and polydispersity index of 1.17 (labeled as i-PMMA in the text) and syndiotactic (s% > 85%) with $M_w = 10\,200$ g/mol and polydispersity index of 1.13 (labeled as s-PMMA in the text). Samples were purchased from Polymer Source Inc and used as received. The molecular weights, polydispersity indices, and the degrees of tacticity of both stereoisomers were specified by the manufacturer. The chemical structures of the tested polymers can be found in Scheme 1. The values of the glass-transition

Scheme 1. Chemical Structure of (a) Isotactic and (b) Syndiotactic Poly(methyl methacrylate) (PMMA)



temperature, T_g , for i-PMMA and s-PMMA determined from the calorimetric measurements are 320 and 391 K, respectively, which agree well with the literature data.^{62,68}

Film Preparation and Substrate Plasma Treatment. Thin films from i-PMMA and s-PMMA were prepared using spin-coating polymer solution onto a silicon (Si) wafer substrate exposed to air plasma for 20 min. For the substrate, we have used heavily doped 4" diameter silicon wafers of 525 ± 25 μm thickness, with resistivity value in the range 1–3 m Ωcm and orientation of $(100 \pm 0.5^\circ)$. We have used the Henniker Plasma HPT-100 for plasma cleaning of Si substrates. The power was set at 98% with 10 sccm ambient airflow. The polymer solutions with varying mass concentrations (for different thicknesses) were prepared in anhydrous toluene (99.8%) supplied by Sigma-Aldrich and filtered by a 0.2 μm poly(tetrafluoroethylene) (PTFE) syringe filter. We have waited for 24 h before using the solutions to prepare polymer films for better polymer dissolution in the solvent. We have used KLM SCC-200 spin coater for preparing

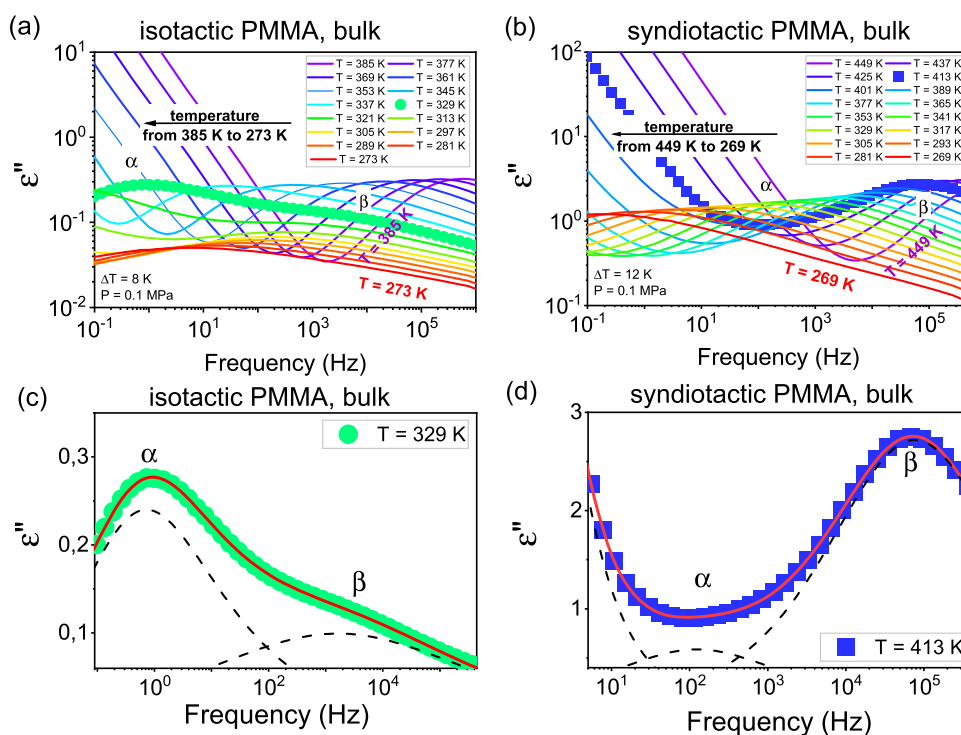


Figure 1. Dielectric loss spectra measured at different temperatures at ambient pressure for (a) isotactic and (b) syndiotactic PMMA. The data were collected on slow cooling (~ 0.3 K/min). Selected dielectric loss spectrum obtained at ambient pressure for (c) isotactic PMMA at the temperature $T = 329$ K and (d) syndiotactic PMMA at the temperature $T = 413$ K. The solid lines are fits of the entire spectrum according to the superposition of the two Havriliak–Negami (HN) functions.

the thin films on the Si substrates. The rotation speed was 2000 rpm, and the spin time was kept at 60 s. We have annealed the prepared films at 340 and 411 K for 24 h under vacuum for i-PMMA and s-PMMA, respectively. The thicknesses of the prepared thin films were verified with spectroscopic ellipsometry.

Methods. Ellipsometry. We have used the spectroscopic ellipsometer Semilab SE-2000 to measure the thickness of the thin films. The measurements were carried out at an incident angle of 70° at ambient conditions. A multilayer model consisting of Si substrate, SiO_x layer, and the PMMA was considered. The SiO_x layer thickness was measured before polymer spin-coating and is fixed while considering the multilayer model. We have obtained the thickness by fitting the ellipsometric angles and the bulk material optical constants.

Dielectric Spectroscopy. Ambient Pressure. Novocontrol Alpha analyzer was used to study the relaxation dynamics of the bulk PMMA samples and confined thin films. For bulk measurements of PMMA, we have used macroscopic amounts of the polymer materials. The samples were placed between two standard plate electrodes with a diameter of 20 mm, separated by a Teflon spacer with ~ 85 μm thickness (see the drawing Figure S1a in the Supporting Information). The highly conductive silicon (Si) substrate on which the polymer film was spin-coated acts as the lower electrode. We have used a 1×1 mm nanostructured die with highly insulating square SiO_2 spacers of 5 μm side length and 60 nm height as the counter electrode. The nanostructured electrodes used in this study were supplied from Novocontrol Technologies GmbH (Germany). They are produced by thermal oxidation and optical lithography on the surface of conductive silicon wafers. The sample capacitor is obtained by covering the Si substrate with the spin-coated polymer film by the upper die equipped with nanostructured insulating spacers. The schematic picture of the dielectric sample array used for thin-film measurements can be found in Figure S1b in the Supporting Information (For more information, also see ref 45). Bulk and thin films were measured as a function of temperature in the frequency range from 10^{-1} to 10^6 Hz. The temperature was controlled with stability better than 0.1 K by Quatro

system. It can be used with all Novocontrol sample cells for dielectric and impedance spectroscopy. This system is a high-quality temperature control system for applications in materials investigations and allows to lower and raise the temperature with high accuracy and repeatability. Dielectric measurements were performed in the temperature range of 273–385 K for i-PMMA and 267–449 K for s-PMMA. We have carried out dielectric measurements for confined samples on both cooling and heating, as it is well established that the segmental dynamics of thin polymer films might reveal non-equilibrium behavior.⁸² In addition to that, it is well known that at high temperatures, there are chances that the polymer films might lose their thermal stability due to dewetting, and the dielectric measurements could potentially be unreproducible. None of such features was observed in the case of the studied PMMA films (see Figure S2 in the Supporting Information).

High Pressure. For dielectric studies carried out at elevated pressure, we have utilized the high-pressure system with MP5 micropump and a control unit (Unipress, Institute of High Pressure Physics, Warsaw, Poland). The pressure was exerted using silicon oil transmitted to the pressure chamber (MV1-30 vessel) by a system of capillary tubes (Nova Swiss). The real and imaginary parts of the complex permittivity were measured within the same frequency range as the ambient pressure data using impedance Alpha-A Analyzer (Novocontrol GmbH, Montabaur, Germany). The temperature was controlled by the highly dynamic temperature control system (Presto W85, Julabo). Dielectric measurements under high-pressure conditions were carried out using a capacitor with the same geometry as that used for ambient pressure measurements (see Figure S1a in the Supporting Information). To separate from the pressure transiting silicone liquid, it was wrapped up with Teflon tape. The schematic picture of the high-pressure capacitor used in this study can be found in the literature (see pg. 75, Figure 4.1b in ref 83).

Differential Scanning Calorimetry (DSC). Calorimetric measurements for bulk samples were carried out using a Mettler Toledo DSC apparatus equipped with a liquid nitrogen cooling device and a ceramic HSS8 sensor. The temperature and enthalpy calibrations were

performed using indium and zinc standards. Bulk polymers were placed in aluminum crucibles and sealed. DSC thermograms were recorded at a rate of 10 K/min in the temperature range from 260 to 480 K and from 328 to 448 K for i-PMMA and s-PMMA, respectively. The glass-transition temperature was determined as the point corresponding to the midpoint inflection of the extrapolated onset and end of the transition curve.

Temperature-Modulated Differential Scanning Calorimetry (TMDSC). For the analysis of the dynamic behavior of the sample in the frequency range from 5 to 30 mHz, we used temperature-modulated differential scanning calorimetry (TMDSC). The measurements were carried out at a heating rate of 2 K/min and temperature amplitude of the pulses of 0.5 K. A multi-frequency temperature-modulated DSC TOPEM allows to get more information about the molecular dynamics as it provides frequency dependence of thermal processes. It overlays a time series of stochastic temperature pulses of different durations with isothermal or ramped temperatures.

Atomic Force Microscopy. For the analysis of residual polymer on the silicon substrate after solvent rinsing, we have used JPK's NanoWizard 3 NanoScience AFM in tapping mode with a silicon cantilever. To obtain good reproducibility and avoid image artifacts, multiple AFM images were taken on different zones of the samples. The surface coverage was estimated using WSxM and ImageJ software. The height image of the surface covered by irreversibly adsorbed polymer chains after solvent rinsing was analyzed.

RESULTS AND DISCUSSION

Ambient and High-Pressure Results. Before investigating the effect of the tacticity on the glass-transition dynamics of the confined thin films, we have characterized the relaxation dynamics of the bulk isotactic and syndiotactic PMMA. For this purpose, we have carried out dielectric measurements at ambient and elevated pressure conditions. We have started our considerations with the analysis of the data collected at atmospheric pressure. Dielectric spectra were recorded on slow cooling (~ 0.3 K/min). The measurements were carried out in the temperature range of 273–385 K and 267–449 K for isotactic and syndiotactic samples, respectively. In Figure 1, we present the representative dielectric loss spectra for i-PMMA (panel a) and s-PMMA (panel b). As shown, two relaxation processes can be observed in the spectra. The first one is the slower process called segmental relaxation (α -relaxation) associated with cooperative segmental mobility and the faster secondary relaxation process. Based on the literature data and our analysis, we believe that this is the so-called Johari–Goldstein β -relaxation (β -JG relaxation), which is the slowest secondary relaxation, considered a precursor of the segmental relaxation (see the Supporting Information for more details).^{64,84–88} At this point, it is worth noting that in the case of s-PMMA, α -relaxation and secondary relaxation are difficult to distinguish, while for i-PMMA, the two processes are more separated from each other. From that, we conclude that the molecular order of the polymer can have an impact on the intensity of the relaxation processes. For syndiotactic PMMA, the secondary relaxation is characterized by a higher intensity than the segmental process. This phenomenon is rarely observed with polymers, but it has been previously seen for atactic and syndiotactic PMMA samples.^{86–88} In the case of i-PMMA, the α -loss peak has a higher intensity than the β -process.

To get more detailed information on the effect of the spatial configuration on the relaxation dynamics of the bulk PMMA, all relaxation processes, segmental and secondary, were fitted using the Havriliak–Negami (HN) function⁸⁹

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{\text{HN}})^{\alpha_{\text{HN}}}]^{\gamma_{\text{HN}}}} \quad (1)$$

where ϵ_{∞} is the high-frequency limit permittivity, $\Delta\epsilon$ is the relaxation strength, τ_{HN} is the relaxation time, α_{HN} and γ_{HN} are the parameters characterizing the shape of the dielectric loss curve, while ω is the angular frequency ($\omega = 2\pi f$). The dielectric loss spectra measured for the isotactic and the syndiotactic samples were fitted as a superposition of the two HN functions. For each set of data, we have made fit twice. First, starting from a higher temperature, and the second time starting from spectra recorded at low temperatures. Importantly, we did not observe any significant differences in the obtained relaxation times. Figure 1 shows representative fits of the HN functions to the raw data for i-PMMA (panel c) and s-PMMA (panel d).

Figure 2 presents the temperature dependence of the segmental and the secondary relaxation times for isotactic

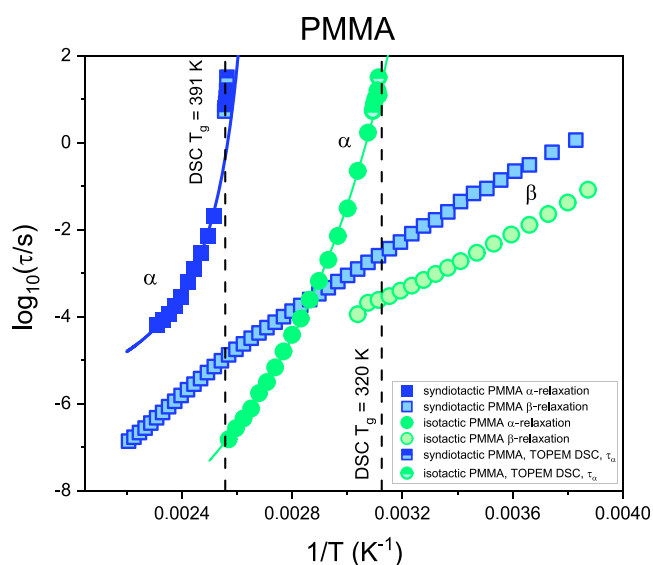


Figure 2. α - and β -relaxation time plotted as a function of the inverse temperature for isotactic and syndiotactic PMMA. The data were collected using DS and DSC (TOPEM - a multi-frequency temperature-modulated DSC technique) techniques. The solid lines are the fitting of the data to the Vogel–Fulcher–Tammann (VFT) equation. The dashed lines indicate the glass-transition temperatures determined from the calorimetric measurements.

and syndiotactic PMMA. As illustrated, the glass-transition dynamics is influenced by the spatial conformation of the tested polymer. For s-PMMA, the α -relaxation process is detected at much higher temperatures than for i-PMMA. For approximately the same relaxation time ($\log_{10}(\tau_{\alpha}/s) \cong -2.1$), the α -loss peak is observed at 336 and 401 K for the isotactic and the syndiotactic samples, respectively. It should be added that due to difficulties in distinguishing between α - and β -relaxation for syndiotactic PMMA, it was impossible to determine the relaxation times from the entire range of the measured frequencies (above 433 K and below 393 K). Moreover, the β -relaxation is faster for the isotactic sample. This fact can be explained based on the coupling model proposed by Kia Ngai.^{84,85,90–94} This model assumes that the coupling between segmental relaxation and JG β -relaxation is correlated with the shape of α -loss peak (see for more details and discussion in Supporting Information). The fact that the

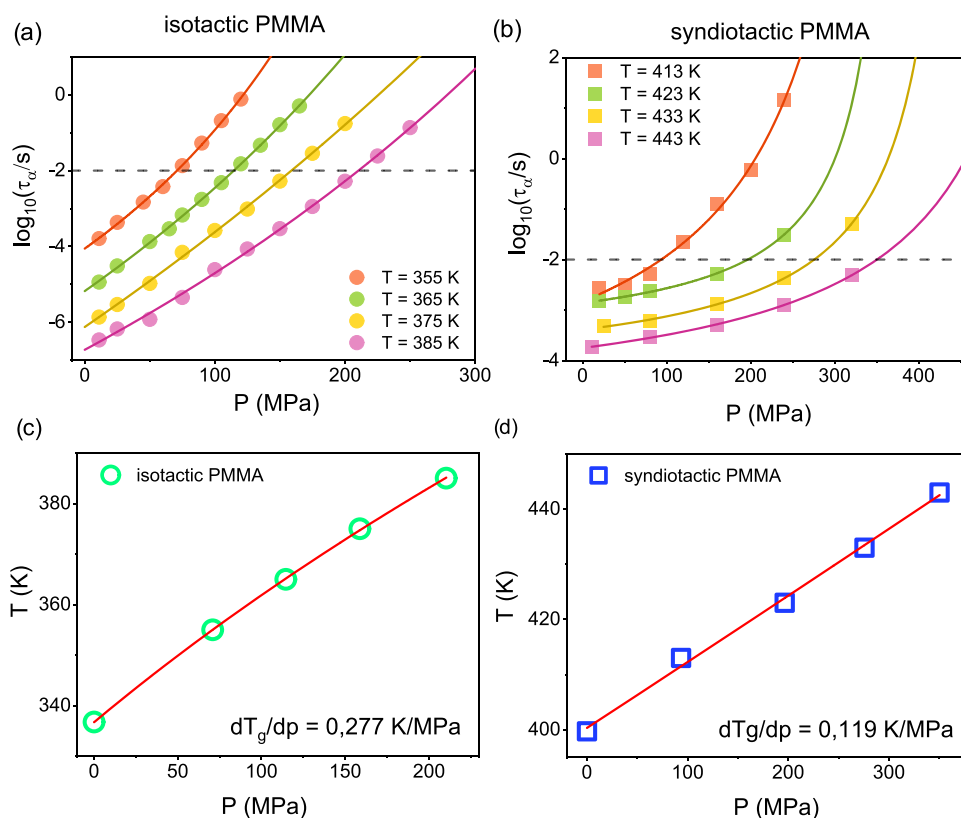


Figure 3. Pressure dependence of the α -relaxation times measured along 4 different isotherms for (a) isotactic and (b) syndiotactic PMMA. The solid lines are fits of the experimental data to the pressure counterpart of the VFT equation. Pressure dependence of the glass-transition temperature for (c) isotactic and (d) syndiotactic PMMA (T_g was redefined as a temperature at which $\log_{10}(\tau_\alpha/s) = -2$). The solid line is the fitting of the experimental data to the Andersson–Andersson equation.

spatial configuration of the polymer influences the glass-transition dynamics has previously been discussed in the literature not only for poly(methyl methacrylate) (PMMA)^{63,64} but also for the numerous glass-forming polymers.^{64,65,73,95}

The temperature evolution of the α -relaxation for both samples was fitted with Vogel-Fulcher-Tammann (VFT) equation.^{96–98}

$$\tau_\alpha = \tau_\infty \exp\left(\frac{D_T T_0}{T - T_D}\right) \quad (2)$$

where τ_∞ is the relaxation time, T_0 is the temperature at which τ_α goes to infinity, and D_T is the fragility parameter. Based on dielectric data, we have defined T_g for both stereoisomers as a T at which $\tau_\alpha = 100$ s. The glass-transition temperature of the tested polymers at ambient pressure conditions is 318 and 387 K for i-PMMA and s-PMMA, respectively. We have also carried out the standard calorimetric measurements (DSC) for the isotactic and the syndiotactic PMMA to confirm our findings. The T_g values estimated from the calorimetric data are 320 K for i-PMMA and 391 K for s-PMMA, respectively. These values agree with the dielectric results and with the literature data.⁶² Furthermore, the effect of the tacticity on the glass-transition temperature was previously discussed for polypropylene (PP). It has been shown that isotactic PP has a higher T_g value compared to an atactic stereoisomer.⁷³ We have also used temperature-modulated differential scanning calorimetry to probe the dynamic glass transition of isotactic and syndiotactic PMMA (TMDSC). In Figure 2, we can see

that for i-PMMA and s-PMMA, the dependencies of the α -relaxation time determined from TMDSC studies coincide with the dielectric data.

It is well known that the glass-transition dynamics is governed not only by the thermal effects but also by the volume effects. The latter ones are particularly important when it comes to polymer materials. Compression is one of the strategies to induce changes in density. In contrast to the temperature, which affects the kinetic energy, increased pressure modifies mostly molecular packing. Therefore, in the next step, we have examined the effect of the high pressure on the segmental relaxation of the isotactic and the syndiotactic PMMA. Dielectric measurements at elevated pressure were carried out along 4 isotherms: 355, 365, 375, and 385 K for i-PMMA, and 413, 423, 433, and 443 K for s-PMMA. In the dielectric loss spectra, we were able to observe the segmental and the secondary relaxation. Both processes shift toward low frequencies with increasing compression. Moreover, similar to the ambient data, the intensity of α - and β -loss peaks is different for isotactic and syndiotactic PMMA. In the case of i-PMMA, the segmental relaxation is characterized by a higher intensity than the secondary process, while for s-PMMA, we have observed the opposite situation. The spectra collected under high-pressure conditions were fitted using the HN function in the same way as the data recorded at ambient pressure. In Figure 3, we present the α -relaxation time as a function of pressure for i-PMMA (panel a) and s-PMMA (panel b). As illustrated, the pressure evolution of the α -relaxation does not follow the Arrhenius behavior. Therefore,

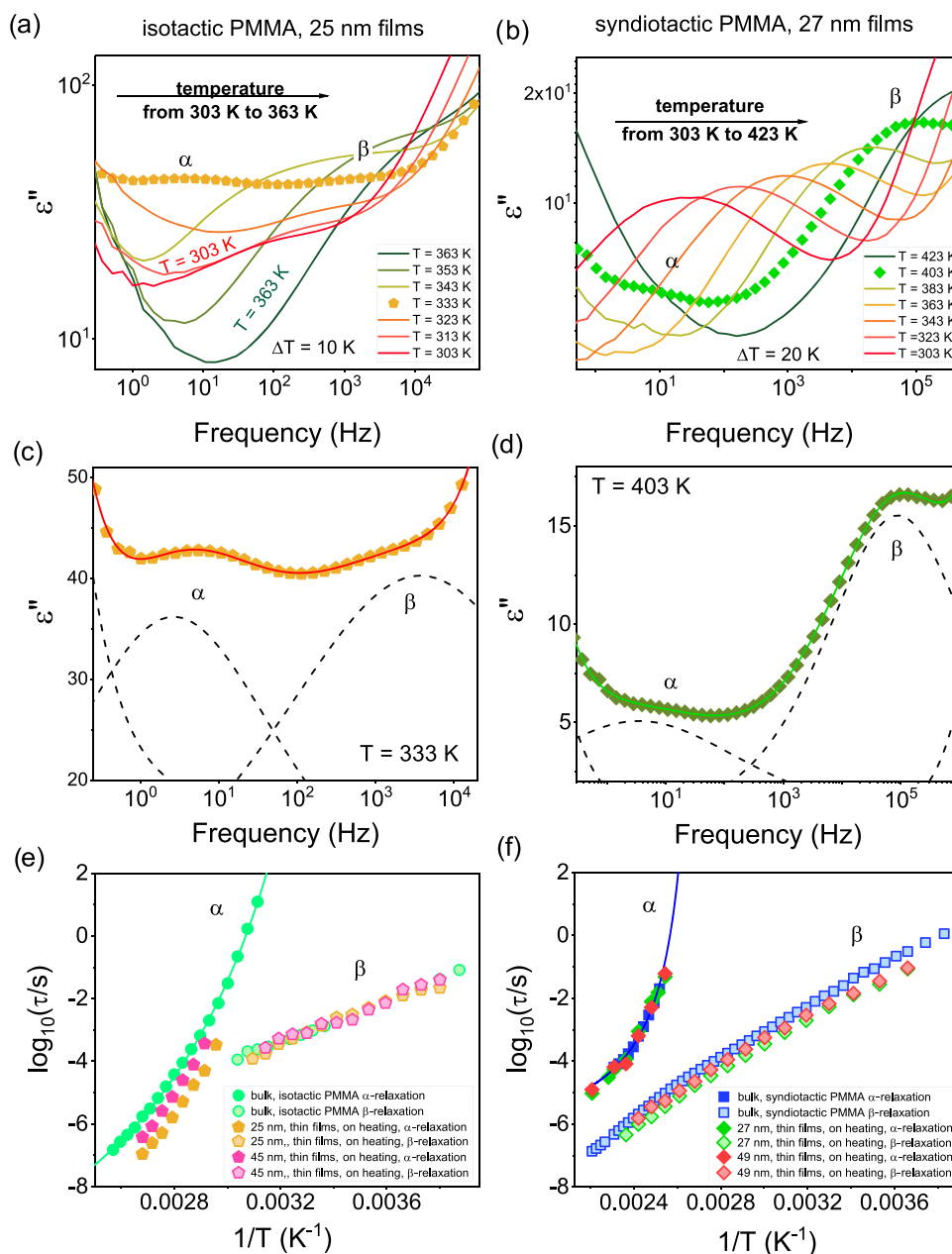


Figure 4. Dielectric loss spectra measured at different temperatures for (a) 25 nm isotactic PMMA thin film and (b) 27 nm syndiotactic PMMA thin film. The sample was prepared on the silicon substrate. Selected dielectric loss spectrum recorded for (c) 25 nm isotactic PMMA thin films at the temperature $T = 333$ K and (d) 27 nm syndiotactic PMMA thin films at the temperature $T = 403$ K. Solid lines are fits of the entire spectrum according to the superposition of the three Havriliak–Negami functions. Temperature dependence of the α - and β -relaxation time for (e) isotactic and (f) syndiotactic PMMA thin films of different thicknesses prepared on the Si substrates. Bulk relaxation times are shown as a reference. The solid line represents the VFT fit to the bulk data.

the obtained isotherms were fitted using the pressure-equivalent of the VFT equation.⁹⁹

$$\log_{10} \tau_{\alpha} = \log_{10} \tau_0 + \frac{D_p P}{P_0 - P} \quad (3)$$

where τ_{ω} , D_p , and P_0 are the fitting parameters. Based on the pressure-equivalent of the VFT equation, the value of the glass-transition pressure, P_g , for each isotherm was calculated. To avoid uncertainty caused by the data extrapolation, we have used $\tau_{\alpha} = 10^{-2}$ s (see in Figure 3a,b, the dashed horizontal lines indicate this value of the segmental relaxation time) to determine the value of the glass-transition pressure from the

dielectric measurements. In this case, we used the same definition to find the T_g at atmospheric pressure. In Figure 3, we have plotted the glass-transition temperature as a function of pressure for i-PMMA (panel c) and s-PMMA (panel d). Based on the $T_g(P)$, we can establish the effect of pressure on the glass-transition temperature of the tested samples. This relation is linear over a narrow pressure range. However, the increase in pressure is accompanied by a nonlinear increase in the glass-transition temperature. For this reason, the pressure dependence of the glass-transition temperature was described using the empirical equation proposed by Andersson and Andersson.¹⁰⁰

$$T_g = k_1 \left(1 + \frac{k_2}{k_3} P \right)^{1/k_2} \quad (4)$$

where k_1 , k_2 , and k_3 are the fitting parameters (collected in Table S1 in the Supporting Information). Also, the ratio k_1/k_3 provides an estimate of the value of the pressure coefficient of the glass-transition temperature (dT_g/dP) at zero pressure limit ($\lim_{P \rightarrow 0}(dT_g/dP)$). The value of $dT_g/dP|_{P=0.1 \text{ MPa}}$ can be determined from the derivative analysis of the Andersson–Andersson equation. This coefficient informs about the pressure sensitivity of the α -relaxation time. Large values of dT_g/dP correspond to the higher sensitivity of the glass-transition dynamics to the pressure/density variation. From the analysis of the experimental data, we have determined the pressure coefficient of the glass-transition temperature for isotactic and syndiotactic PMMA. The value of dT_g/dP is 0.277 and 0.119 K/MPa for i-PMMA and s-PMMA, respectively. Thus, the molecular order has a significant impact on the properties of the studied polymer under high-pressure conditions. The glass-transition dynamics of the isotactic PMMA is more sensitive to pressure/density changes compared to syndiotactic PMMA. It is worth adding that isotactic and atactic polypropylene (PP) are also characterized by different sensitivities to pressure changes. It has been shown that the effects due to compression are more pronounced for the isotactic stereoisomer.⁷⁵

Summarizing this part, we have shown that the polymers' tacticity influences the glass-transition dynamics. In the case of isotactic and syndiotactic PMMA, the relaxation processes are observed in different temperature ranges. For this reason, vitrification of both tested samples takes place at various temperatures, which was confirmed by the calorimetric measurements. The molecular order of the polymers also affects their behavior under increased pressure. The segmental dynamics of isotactic PMMA is more strongly modified by compression compared to syndiotactic PMMA. Recently, it has been demonstrated that the sensitivity of the glass-transition dynamics to the pressure effects can be very useful when it comes to understanding or even predicting deviation from the bulk behavior seen in the confined geometry.^{101–103} Polymer materials confined at the nanoscale level show remarkable changes in the density or molecular packing, which has a significant effect on their glass-transition dynamics.^{104–107} Based on the information that comes from the high-pressure studies, we anticipate s-PMMA might be less sensitive to density fluctuation induced by geometrical nanoconfinement compared to i-PMMA (lower dT_g/dP coefficient).

Thin Films. After analyzing the dielectric data for the bulk isotactic and syndiotactic PMMA at ambient and elevated pressure conditions, we have focused our considerations on thin films of the tested polymers supported on the silicon substrate. We have carried out the dielectric relaxation measurements for 25 and 45 nm i-PMMA films as well as for 27 and 49 nm s-PMMA films. We have used two different thermal protocols to determine the dielectric spectra of the polymer thin films, slow cooling with the rate of ~ 0.3 K/min, and slow heating with ~ 0.3 K/min. The measurements were carried out in the temperature range 303–363 K and 303–423 K for the isotactic and syndiotactic samples, respectively. In Figure 4, we present the representative dielectric loss spectra recorded on heating for 25 nm i-PMMA (panel a) and 27 nm s-PMMA (panel b) films. In the dielectric loss spectra of both

samples, apart from the two relaxation processes (α -relaxation and β -JG relaxation) and the contribution from the DC conductivity, we can also observe an additional signal present in the high-frequency region. The dielectric signal measured using nanostructured electrode arrangement reflects not only the thin films polymer dynamics but also the contribution coming from the non-zero resistivity of the Si electrodes, silicon oxide insulating layer, spacer bars/air gap between the polymer layer, and the upper electrode. To take into account all of the additional contributions present on the spectra of thin films and extract the pure polymer response from dielectric loss, we have used the model presented in a recent paper by Beena Unni et al.⁴⁵

$$\epsilon_{\text{tot}} = \frac{d_{\text{tot}}}{\frac{d_{\text{sam}}}{\epsilon_{\text{sam}}} + \frac{d_{\text{gap}}}{\epsilon_{\text{gap}}} + \frac{d_{\text{oxi}}}{\epsilon_{\text{oxi}}} + \frac{\omega \epsilon_0 A R}{0 - i}} \quad (5)$$

where the gap spacing is $d_{\text{gap}} = 60$ nm (as imposed by the nanostructured upper electrode arrangement), the thickness of the silicon oxide layer is $d_{\text{oxi}} = 7$ nm for 20 min plasma-cleaned surfaces, and the thickness of PMMA films d_{sam} are determined experimentally via ellipsometry. The total thickness of the measured sample is $d_{\text{tot}} = d_{\text{sam}} + d_{\text{gap}} + d_{\text{oxi}}$. Therefore, the collected dielectric loss spectra of the prepared films were fitted using eq 5, assuming that ϵ_{sam} is given by the superposition of the two HN functions and the DC conductivity. In Figure 4, we can see the representative fits of the raw data for 25 nm i-PMMA (panel c) film and 27 nm s-PMMA (panel d) films. In agreement with the results reported by Kremer et al., we have assumed that the specific experimental configuration did not significantly affect the shape and the average relaxation time of the polymer film measured in the geometry of the air gap.¹⁰⁸

In Figure 4, we demonstrate the temperature dependencies of the segmental and the secondary relaxation times for 25 and 45 nm i-PMMA films (panel e) as well as for 27 and 49 nm s-PMMA films (panel f). As illustrated, for the isotactic polymer, the glass-transition dynamics of the confined films are faster compared to the bulk sample. Moreover, our results show that for 25 nm i-PMMA thin films, the deviation from bulk behavior is slightly more pronounced than for the 45 nm polymer layer. This fact indicates that the confinement effects become more visible as the thickness of the film decreases. Our observations are consistent with the previously reported data for isotactic PMMA deposited on silicon^{75,76} and aluminum substrates.^{77,78} It is worth noting that for many other polymers, experiments show that the dynamics accelerate with a reduction of the thickness of thin films.^{45,76,109,110} Furthermore, for i-PMMA, we did not observe that geometrical confinement influenced the β -JG relaxation. It is in accordance with the literature data, which shows the lack of sensitivity of the β -process to confinement effects.^{75,76} In contrast, in the case of s-PMMA thin films, we have observed that the average α -relaxation time does not depend on the film thickness, and its $\tau_\alpha(T)$ dependence follows that of the bulk. Similar observations have also been reported for some other polymers, for example, polystyrene, poly(vinyl acetate), poly(γ -benzyl-L-glutamate), and poly(2-vinyl pyridine).^{111–115} It is also worth mentioning that Geng et al. have shown by the ellipsometric measurements that the molecular weight and tacticity influence the glass-transition temperature of PMMA thin films deposited on a silicon substrate. For high molecular weight ($M_w = 50$ 000 g/mol) of PMMA thin films, it has been shown that an

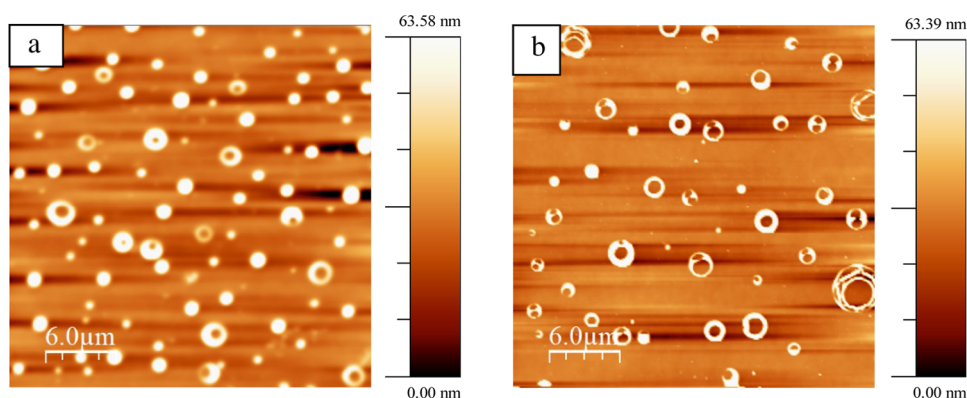


Figure 5. Representative AFM height images showing the residual (a) s-PMMA on Si and (b) i-PMMA on Si after rinsing with the solvent for 60 h.

increase in the percentage of syndiotacticity is accompanied by a decrease in T_g caused by the free surface effects. On the other hand, in the case of low molecular weight ($M_w = 2500$ g/mol), the substrate effects dominate, hence the increase in T_g . Thus, the influence of tacticity on T_g of PMMA thin films is controlled by the interplay between the substrate and surface effects.⁷⁹ Based on that, we can suspect that for our s-PMMA sample with an intermediate molecular weight of 10 200 g/mol, both effects balance each other. Therefore, we did not observe a difference between the glassy dynamics of thin films and bulk. However, it should be recalled that the polymer material used in our research has a higher percentage of syndiotacticity ($s\% > 85$) than the samples discussed in the paper by Geng et al. But meanwhile, Grohens et al. suggested that dielectric and ellipsometric studies may yield different T_g values of i-PMMA and s-PMMA with molecular weights of 35 000 g/mol. Ellipsometric measurements discussed in this paper showed that the glass-transition temperature of isotactic PMMA thin films increased with decreasing film thickness, while the T_g of syndiotactic stereoisomer decreased. On the other hand, the glass-transition temperature of i-PMMA films determined based on dielectric measurements decreases when the layer thickness is reduced, while for s-PMMA films, it is independent of the film thickness for films with less than 20 nm.⁸⁰ The dielectric data presented in the paper is consistent with our observations for isotactic and syndiotactic PMMA films deposited on the Si substrate. Furthermore, we have noticed a very slight acceleration of the secondary relaxation process for s-PMMA films. Faster β -relaxation for polymer thin films has been previously observed for syndiotactic and atactic PMMA deposited on the aluminum substrate.^{78,81} The fact that confinement effects on the α -relaxation are only visible in the case of i-PMMA indicates that the glass-transition dynamics under geometrical confinement is indeed more sensitive to variation in density/molecular packing.

To gain more insight into the segmental mobility of the PMMA confined thin films, we have focused on the polymer chains that are irreversibly adsorbed onto the substrate. We expose the irreversibly adsorbed polymer layer by means of a well-known solvent rinsing approach.^{45,116} For this purpose, we have immersed 25 nm i-PMMA and 27 nm s-PMMA thin films in a good solvent for 60 h. Then, both samples were annealed above their respective T_g values for 12 h in a vacuum. Continuous films were also obtained for both i-PMMA and s-PMMA for a shorter time of rinsing with solvent. However, we intentionally chose ~ 60 h for better removal of the loosely adsorbed chains and hence to reveal the irreversibly adsorbed

layer. It is also worth mentioning that annealing affects solvent rinsing experiments. This can enhance the substrate-polymer interaction.¹¹⁷ In our case, we have annealed both the samples above their respective T_g for the same period of time. The solvent can also influence the solvent rinsing experiments.¹¹⁶ For this reason, we have used chloroform for both samples, which is a good solvent for PMMA considering its Hansen solubility parameters.

The surface coverage of adsorbed polymer observed by AFM is 7.5 ± 0.5 and $13 \pm 1\%$ for i-PMMA and s-PMMA, respectively (the calculation is done after analyzing multiple images at different locations of the samples). The representative AFM height images taken afterward are shown in Figure 5. A higher amount of the remaining polymer chains irreversibly adsorbed to the substrate is observed for syndiotactic films (white regions denote the remaining polymer). Our results suggest that s-PMMA interacts more strongly with the silicon substrate than i-PMMA. Literature data indicate that both the presence of a free surface and interactions with the substrate can significantly affect the dynamics of polymer thin films. Generally, the free surface is responsible for increasing the mobility of the nearby polymer segments. Meanwhile, strong interactions with the substrate slow down the mobility of the polymer chains located in close proximity to the supporting substrate.^{118–120} Based on this, we can suspect that in the case of s-PMMA, the free surface and substrate effects cancel each other out. For this reason, the averaged segmental dynamics of syndiotactic films is similar to the bulk behavior. In contrast, for i-PMMA, the interactions with the substrate are weaker, as evidenced by the lower amount of irreversibly adsorbed polymer chains. Thus, enhanced mobility near the free surface could possibly be the reason that the observed segmental relaxation of i-PMMA thin films is faster compared to the bulk.

Furthermore, molecular dynamics simulations prepared by Soldera et al. show that in the case of i-PMMA, the mobility of the side chains increases the mobility of the backbone and consequently leads to the lower glass-transition temperature.¹²¹ In contrast, Tretinnikov et al. suggest that the limited mobility and higher glass-transition temperature of s-PMMA are associated with the dipole–dipole interactions between the side chains.¹²² Moreover, literature data demonstrate that syndiotactic PMMA has lower intramolecular energies, while isotactic PMMA has lower intermolecular energies, promoting better polymer packing.¹²³ Also, the free volume analysis shows that a better packing of the chain characterizes isotactic PMMA.¹²⁴ Jha et al. proposed that the more favorable arrangement of i-PMMA space groups leads to better packing

and faster dynamics.¹²⁵ Taking on that, we can rationalize our observations, which are the result of the differences in the interaction of the polymer with the substrate and the molecular packing.

CONCLUSIONS

In this work, using dielectric spectroscopy (DS), we have investigated the effect of tacticity of the polymers on the glass-transition dynamics at ambient and elevated pressure conditions. We have also analyzed the influence of spatial configuration on the segmental relaxation of confined thin films. For this purpose, we have used PMMA with two different tacticities (isotactic and syndiotactic) and similar molecular weights. We have shown that for i-PMMA, the α -relaxation process is visible in the lower temperature range than for s-PMMA. This fact is also related to the different glass-transition temperatures of these two studied stereoisomers. Based on dielectric investigations, we have estimated that the glass-transition temperatures are 387 and 320 K for the syndiotactic and the isotactic PMMA, respectively. These values are quite consistent with the values obtained based on our calorimetric measurements and the literature data. We have also found that the spatial configuration has a significant impact on the behavior of the tested polymers under increased pressure. The glass-transition dynamics of isotactic PMMA is more sensitive to pressure changes compared to the syndiotactic PMMA. The pressure coefficient of the glass-transition temperature is 0.277 and 0.119 K/MPa for i-PMMA and s-PMMA, respectively. This could be an indication that the former is more sensitive to density frustration induced by the confined geometry.

We have also demonstrated that the glass-transition dynamics of the isotactic and syndiotactic PMMA thin films are much different in a confined state. In the case of i-PMMA thin films, we have observed faster segmental relaxation compared to the macroscopic sample. Furthermore, the confinement effects become more pronounced with decreasing film thickness. However, for s-PMMA, the temperature dependence of the α -relaxation time resembles the behavior of the bulk sample. We suppose that this is related to the weaker sensitivity to density frustration and stronger interactions of the syndiotactic PMMA with the silicon substrate. In this case, enhanced mobility near the free surface is balanced by strong interactions with the substrate, and averaged segmental relaxation time follows the behavior of the macroscopic/bulk sample.

In conclusion, our research illustrates that the spatial configuration of the polymer affects the glass-transition dynamics under high pressure and geometrical nanoconfinement. Thus, tacticity is an essential aspect in polymer science, as it modifies not only the segmental dynamics but also the sensitivity of a polymer to the changes in molecular packing and the interactions with the substrate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c01341>.

Drawings of the sample geometry used in dielectric measurements of bulk polymers and thin films, list of fitting parameters of the Andersson–Andersson equation for s-PMMA and i-PMMA, discussion on the origin

of the β -relaxation in s-PMMA and i-PMMA, which is based on the high-pressure studies and predictions of the Coupling Model proposed by Kia Ngai (PDF)

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Notes

The authors declare no competing financial interest.

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