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Comparison of mechanical and dielectric relaxation processes in laser-deposited poly(methyl methacrylate) films

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Abstract. Dynamic loss spectra for laser-deposited poly(methyl methacrylate) (PMMA) films are investigated at a frequency of 5.4 kHz with dielectric spectroscopy and mechanical torsional spectroscopy using a double-paddle oscillator as a substrate in a temperature range from room temperature up to 530 K. By comparing both methods, the coupling mechanism of the external force to the molecules and the resulting relaxation processes are discussed. Differences in both loss spectra are ascribed to a different weighting of the contributions of primary and secondary relaxation in the relaxation peak. During annealing above the glass temperature, the local structure of the disordered molecular system is changed. This is accompanied by hardening processes as demonstrated by showing the isothermal development of the mechanical frequency shift and the internal friction of the film. For even higher temperatures, irreversible changes in the polymeric structure occur as observed by infrared spectroscopy and by a weight loss of the film.

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Contents

1. Introduction	2
2. Experimentals and sample preparation	3
3. Results and discussion	4
4. Conclusions	10
Acknowledgments	10
References	10

1. Introduction

Poly(methyl methacrylate) (PMMA) is an important amorphous polymer for industrial and technical applications. Not only window glass, but also advanced materials for holographic data storage or nonlinear optical applications based on PMMA films are discussed [1]. To improve relevant physical properties, and also for fundamental reasons, a better understanding of the glass transition, molecular dynamics and the underlying microscopic relaxation processes in liquid and glassy PMMA films is necessary. Experimental data about the dynamic processes in bulk materials in most cases are gained from dielectric spectroscopy that allows a broad range of frequencies and temperatures [1]–[3]. In addition, there have been various other experimental approaches such as photon correlation spectroscopy [4, 5], multi-dimensional nuclear magnetic resonance [6, 7] and mechanical spectroscopy [8]–[10], which are usually applied at constant temperature below and above the thermodynamic glass transition T_g .

It is well known that, in principle, there are two different relaxation processes in PMMA bulk materials. With decreasing temperature, a rapid increase in viscosity and a slowing down of molecular mobility is observed in the liquid state. At the glass transition temperature T_g , the mobility gets frozen in, i.e. falls out of thermodynamic equilibrium. This main intermolecular internal friction mechanism due to translational movement of molecule chains is correlated to the primary or α -relaxation process. In PMMA, additional intramolecular degrees of freedom are responsible for a faster, so-called secondary or β -relaxation process. The underlying mechanism is usually explained by the hindered rotation of the $-\text{COOCH}_3$ side chain around the C–C single bond that connects this side group to the polymer backbone [2]. The characteristic relaxation time of the β -process shows an Arrhenius-like temperature dependence, whereas the α -process is better described by a Vogel–Fulcher–Tammann law. Both processes are well separated at low frequencies/temperatures. Due to the different temperature dependences of their relaxation times, however, they tend to merge when these timescales attain the same order of magnitude. At high temperatures/frequencies, only one process is observable, known as the α -process (sometimes also α β -process) [11]. Though great efforts have been made to illuminate the molecular mechanisms in the merging region (sometimes also called the splitting region), the details of this phenomenon are far from being understood [1]–[3], [11]–[13].

The aim of this work is to understand the relaxation processes in PMMA films in more detail, using different spectroscopic methods which couple very differently to the molecular system. Firstly, we compare PMMA in bulk form and PMMA prepared as a thin film. Secondly, we try to separate the two contributions of α - and β -processes in PMMA films as far as possible, by comparing dielectric loss data directly with mechanical torsional spectroscopy in

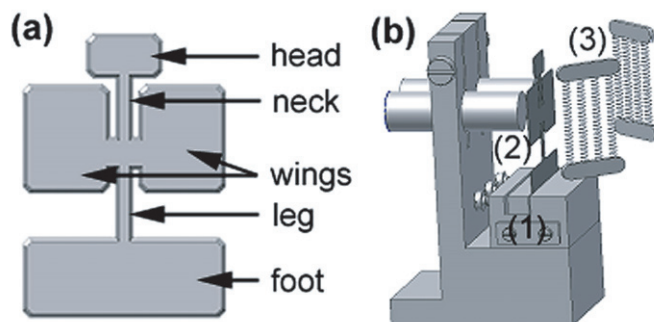


Figure 1. (a) The DPO with its characteristic components. In the AS 2 mode, head and wings are twisting against each other around the neck. (b) The oscillator is mounted in the UHV chamber by dry clamping the foot between two stainless steel jaws (1). Paddle wings and electrodes (2) form capacitors to drive and detect the oscillation. The paddle is heated by radiation from two coils (3).

the temperature range from room temperature up to 530 K. Both experiments are performed at a constant frequency of 5.4 kHz. We investigate films that are produced by pulsed laser deposition (PLD). The films mainly (about 80% of the deposited material) consist of a polymer with reduced molecular mass (corresponding to a number of monomers of about 60) and exhibit an increased mechanical hardness due to a small highly cross-linked fraction [14, 15]. They are in a highly disordered state and contain most likely a large amount of free volume quenched in during the deposition process. Thus, in time- and temperature-dependent annealing experiments in the region of the glass transition, irreversible relaxation processes due to structural rearrangements become visible. In the first part of this paper, we introduce briefly the experimental method of getting the complex shear modulus of thin films by using a double-paddle oscillator (DPO) as a substrate and the dielectric measurement technique. Then we present an overview of the mechanical relaxation spectrum and explain its characteristic features by comparing bulk and thin film PMMA as well as the results from different spectroscopic methods. In the second part of section 3, we discuss the temperature- and time-dependent kinetic processes that lead to significant changes in the relaxation strength of the loss peak. This section is followed by a discussion of the microscopic origin of the observed differences.

2. Experimentals and sample preparation

To perform mechanical spectroscopy in the kHz regime, a DPO, produced from a 300 μm -thick silicon wafer, is used as a substrate (figure 1(a)). It has been shown that the internal friction of the oscillator itself is very low, so that contributions even from thin films to the overall damping can be resolved [16]. A 1.75 μm -thick PMMA film is deposited onto one surface using the PLD method. As determined by x-ray reflectivity measurements, the density of the laser-deposited films is $1.3 \pm 0.1 \text{ g cm}^{-3}$ and therefore comparable with PMMA bulk material (1.2 g cm^{-3}). The deposition is done by focusing a KrF excimer laser beam (wavelength 248 nm, pulse duration 30 ns and laser fluence 1.5 J cm^{-2}) under ultra-high vacuum (UHV) conditions (chamber pressure $<10^{-8}$ mbar) onto a PMMA foil (Goodfellow; $M < 4 \times 10^6 \text{ g mol}^{-1}$) [15, 17]. The DPO is driven in its antisymmetric torsional eigen mode, named AS 2, at a frequency of about 5.4 kHz, where head and neck are twisting against each other [16]. A conventional electrostatic set-up is used

for driving the paddle and detecting the amplitude, as described by Spiel *et al* [18]. During the heating and cooling cycles, the paddle is running in a resonant self-excited loop under UHV conditions. The filtered, phase-shifted and amplified signal is used for driving the paddle and for recording its frequency. All damping data are taken by measuring the decay of free ring-down experiments under stable temperature conditions. The paddle is heated by the radiation of two symmetrically mounted coils taken from commercial projector light bulbs (see figure 1(b)).

By measuring the temperature-dependent damping of the oscillator before and after film deposition and the shift of its eigen frequency, the complex shear modulus $G^*(= G' + iG'')$ of the film can be calculated [16].

Dielectric spectroscopy determines the complex dielectric permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, where ε' is the frequency-dependent dielectric constant and ε'' the dielectric loss, proportional to the absorption of energy of the applied electric field in the sample. Dielectric spectroscopy monitors dynamic processes involving reorientations of electrical dipoles or the displacement of charges. In supercooled liquids, it is usually assumed that the dipolar motion is directly coupled to the viscosity for $T > T_g$ and that decoupling processes occur when the system falls out of equilibrium. Combining various techniques, dielectric spectra can be measured in an extremely broad range of frequencies (for details, the reader is referred to [19]). In the present work, we focused on a comparison with mechanical spectroscopy, and for the measurements, a frequency response analyser (Novocontrol α -analyser) covering the mHz–MHz frequency range was used, which determines the sample voltage and the sample current using lock-in techniques. For this purpose, a film deposited on a copper substrate was covered by silver paint, thus representing a parallel-plate capacitor. Cooling and heating of the samples were achieved using a N₂-gas cryostat.

3. Results and discussion

The storage modulus G' gives information about its elastic properties, whereas the loss modulus G'' depends strongly on damping and internal friction due to intra- and intermolecular movements in the polymeric material. In figure 2, as a typical example, the temperature-dependent shear modulus of a 1.75 μm -thick PMMA film is shown during heating. The absolute value of G' (figure 2(a)) is about 11 GPa at room temperature, which is higher than in bulk material, where Muzeau *et al* [10], for example, determined G' to be about 1 GPa. The huge difference can be explained by massive structural changes and partial cross-linking occurring during the deposition process and various foregoing tempering steps that lead to a hardening as will be discussed below. Because of the weakening of the elastic constants due to thermal expansion, etc, G' decreases with increasing temperature. The slight kink at about 375 K marks the glass transition temperature as can also be seen in the G'' curve in figure 2(b). Below this temperature, the sample falls out of thermodynamic equilibrium and the behaviour of $G'(T)$ and $G''(T)$ depends on cooling rate and thermal history. The first maximum in the mechanical loss indicates a maximum of internal friction at around 412 K. As mentioned earlier, two microscopic processes are known in PMMA bulk material, that are responsible for this loss peak, the α -relaxation due to viscous flow and the β -process that is linked to the rotation of side groups. In the kHz frequency range, the relaxation time for both processes is of the same order of magnitude [1, 3]. As a consequence, also in thin films only one rather broad maximum is visible at 5.4 kHz around 415 K.

At even higher temperatures, above about 520 K (see figure 2(b)), the curve strongly decreases due to decomposition and partial evaporation of the polymer film. This was already

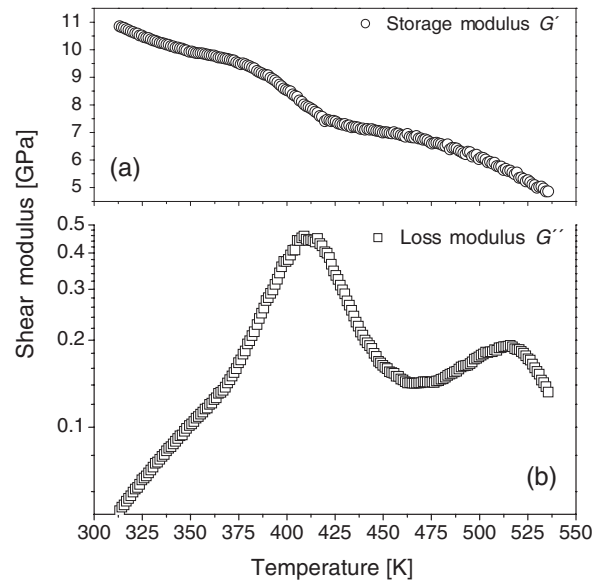


Figure 2. Change of the complex shear modulus of a $1.75\ \mu\text{m}$ -thick PMMA film during heating. (a) Real part G' (storage modulus) and (b) imaginary part G'' (loss modulus). G' decreases with increasing temperature. The first maximum in G'' at about 410 K indicates the merged α - and β -relaxation process due to viscous flow and side group rotations respectively. The second maximum at 515 K is correlated with irreversible changes of the polymeric structure.

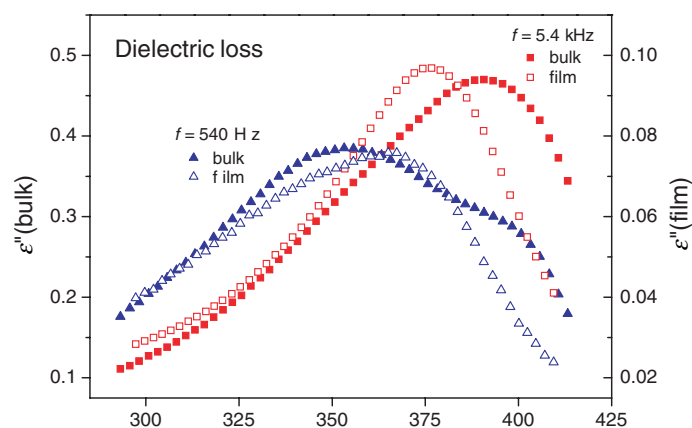


Figure 3. Comparison of the dielectric loss in bulk PMMA and PLD deposited film at 540 Hz and 5.4 kHz.

demonstrated in [15] by infrared spectra of these PMMA films showing large changes in the molecular structure of the material with dramatic rearrangements in the chemical composition of the polymer above 480 K, and also thermogravimetric analysis shows weight losses due to film evaporation at temperatures above 500 K.

Figure 3 shows the measurements of the dielectric loss versus temperature for bulk PMMA and a thin film of PMMA produced by the PLD method for two different frequencies (540 Hz and

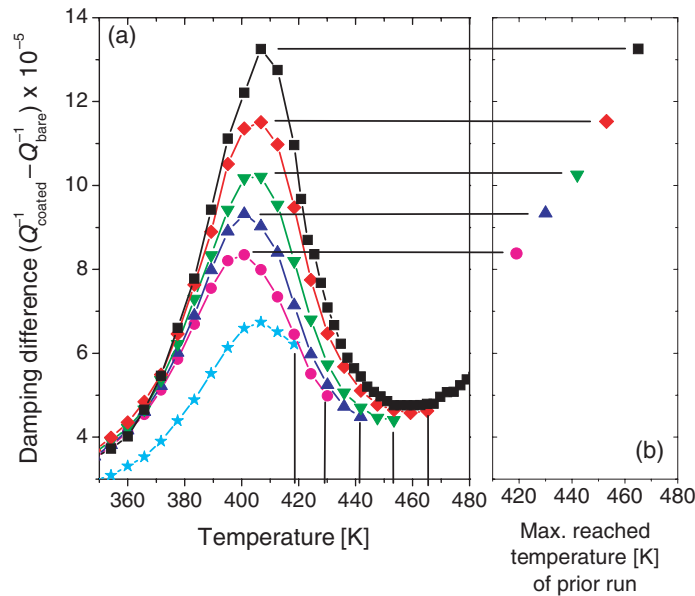


Figure 4. (a) The difference in the damping coefficient between the bare and the coated paddle (with $1.75 \mu\text{m}$ PMMA film) recorded in subsequent heating temperature cycles is shown. With increasing maximum temperature of the prior cycles, the peak maximum increases. This increase in the maximum is summarized in (b).

5.4 kHz) and collected on fresh films. Similar to the mechanical results (cf figure 4), the dielectric loss became reduced on cycling. The data clearly discriminate for the shape, the position and height of the maxima. The different height is partially due to an uncorrected geometry, but probably mainly arises from the different chain lengths and the confined geometry of the film. In the low-frequency measurement, bulk PMMA shows indications for two maxima (α -peak and β -relaxation), whereas the film exhibits one broad maximum at slightly higher temperature. For the high-frequency measurement (5.4 kHz), the maxima for both PMMA materials are shifted to higher temperatures as expected. Again the bulk material exhibits a broader loss peak. In addition, it is remarkable that the peak maximum of the dielectric loss from bulk and film differ by about 15 K. The difference could be originated in the different polymer chain length but also the reduced dimensionality of the film may play an important role [3]. Interestingly, the peak temperature for 5.4 kHz, deduced from the results reported in [3] on spin-coated PMMA films with a thickness of 900 nm, agrees well with the present result. The merging process of the α -peak and the β -relaxation due to the frequency change is more clearly seen for the bulk material. In comparison with earlier measurements of PMMA films at 40 Hz, the merging process is far more developed [20].

To demonstrate changes in the structure of the PMMA film by performing mechanical spectroscopy, we successively increased the maximum temperature. In figure 4, the resulting temperature-dependent mechanical loss curves are shown. The initial heating was stopped at 419 K just after the loss difference $Q_{\text{coated}}^{-1} - Q_{\text{bare}}^{-1}$ passed through its maximum of 6.8×10^{-5} . During the following cooling cycle, the mechanical loss passes again through its maximum, which is clearly higher than before (8.1×10^{-5}). The data points that belong to the first cooling

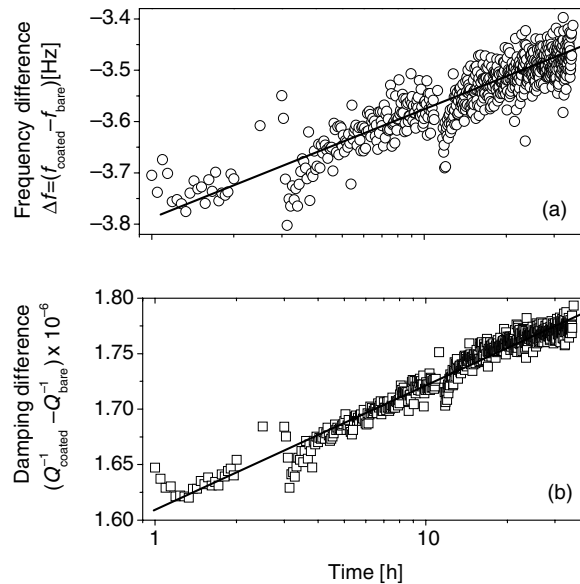


Figure 5. Kinetic processes in PMMA are visualized by the development of the frequency shift (a) and the difference in the damping coefficient (b) between coated and bare paddle (with a $0.9 \mu\text{m}$ PMMA film) on a logarithmic timescale. Three subsequent isothermal measurements at 419 K are shown. After 2 and 12 h, the sample is cooled down to room temperature and then reheated. The straight lines indicate that both quantities follow an exponential law with time.

are reproduced with good accuracy during the second heating up to 430 K. The second cooling and third heating curves are again reversible but the maximum increases in height (9.3×10^{-5}). After heating up to 465 K, the maximum reaches 13.2×10^{-5} , which is more than twice as high as the initial one. The overall observation is that the loss values are reproduced if the maximum temperature is not increased. It should be noted that the cooling (not shown here) and subsequent heating curves lie exactly on top of each other. As soon as a higher temperature has been reached, the maximum loss factor in the PMMA film increases. This tendency is summarized in figure 4(b). Higher values for the mechanical loss factor are directly correlated with higher internal friction in the material. The simple explanation of enhanced molecular mobility due to a higher magnitude of the external stress can be excluded since the amplitude of the macroscopic oscillation has not been changed over the whole measuring process. Below 370 K, the damping difference is reproduced in all temperature cycles (see figure 4). More likely, irreversible changes of the polymeric structure lead to the increase in internal friction. As has been shown in the mathematical analysis of the DPO data [16], the difference between the damping coefficients of the coated and the bare oscillator (that is shown in figure 4) is proportional to the absolute value of the PMMA shear modulus. This leads to the assumption that the observed annealing effect is due to relaxation of the PMMA thin film. The amount of relaxation of the sample depends on the maximum temperature reached and is the reason for the reported structural changes in the arrangement of the molecules. This assumption is confirmed by time-dependent measurements of the frequency shift (figure 5(a)) and the difference in the mechanical loss between coated and bare paddle at a constant temperature of 419 K. For this experiment, a $0.9 \mu\text{m}$ -thick PMMA film was used. The isothermal data were taken in three steps. After two respective 12-hour periods, the sample was

cooled down to room temperature and then reheated to 419 K. After some initial minutes, the values of the foregoing isothermal measurement are reproduced. Over the whole time range of 35 h, both frequency shift and damping difference increase with time and obey an exponential law as indicated by the straight lines in figure 5. The increase in the damping difference has already been attributed to material annealing. It has been shown [16] that an increase in the absolute value of the PMMA shear modulus leads to an increase in the frequency shift as can be seen in figure 5(a). The observed kinetically activated process depends strongly on temperature and can be explained by reorientations of molecule chains and changes in their arrangement.

Since mechanical torsional strain and electric field couple to the molecules in a different way, a comparison between mechanical and dielectric losses is illuminating and helpful in gaining a deeper understanding of the nature of the different relaxation modes and their merging process. The main dipolar moment of PMMA is located in the carboxyl group in the side chain of the molecules. An alternating electric field would therefore reorient those side groups whose dipolar vector does not coincide with the axis responsible for the rotational movement. Because of the amorphous structure in PMMA and the randomly arranged molecular coils, there are at any time enough side groups that fulfil this condition and hence the strength of the β -relaxation in the dielectric loss exceeds that of the α -relaxation by far [2, 3]. Especially at low temperatures, where the viscosity is high and translational diffusion is constricted, the β -peak dominates the dielectric loss spectrum [13]. With increasing temperature around the thermodynamic glass transition, viscous flow sets in. The translational motion of polymer chains, representing the α -relaxation, is only weakly dielectrically active by itself, but is coupled to the side chain rotations.

In case of a macroscopic mechanical shear stress, the situation is vice versa. The corresponding strain of the PMMA film has to be relaxed by a translational motion of molecule chains against each other. For polymers, flow is connected to motion of the whole chain and this corresponds to length scales larger than the length scales responsible for the α -relaxation. For entangled polymers, the flow transition is well separated from the glass transition and even shows a different temperature dependence. After PLD treatment, the polymer may have a low molecular weight (this means it is not entangled) but, additionally, the polymer is partially cross-linked. This influences the flow transition in different ways, unknown in the present case. There is no direct way to yield the shear stress by only side group rotations and it is difficult for the macroscopic mechanical force to couple directly to the localized side groups. On the other hand, it is conceivable that the rotational mode is activated by an oscillating translation of molecular chains especially if the frequency corresponds to the β -relaxation time in the merging region. In this case, changes in the coil structure lead to locally unfavourable sites and hence to a rotation of side groups. That is why the reported relaxation strength of the α -peak in mechanical loss experiments in the time domain, as well as in the frequency domain, exceeds that of the β -peak [9, 10].

In figure 6, typical loss spectra for both methods are shown for 1.75 μm -thick PMMA films directly after growth by the PLD process. The frequency is held constant at 5.4 kHz and the temperature programme has been chosen to be the very same. Every data point has been measured under equilibrium temperature conditions. Obviously, both experimental methods result in only one dominant relaxation maximum. But the positions of the maxima and the shapes of the curves are significantly different.

First we consider the peak position at 380 K for the dielectric loss and at 410 K for the mechanical loss. This difference is too large to be explained by experimental artefacts. The length scale of a rotating side group is significantly smaller than that of a completely moving

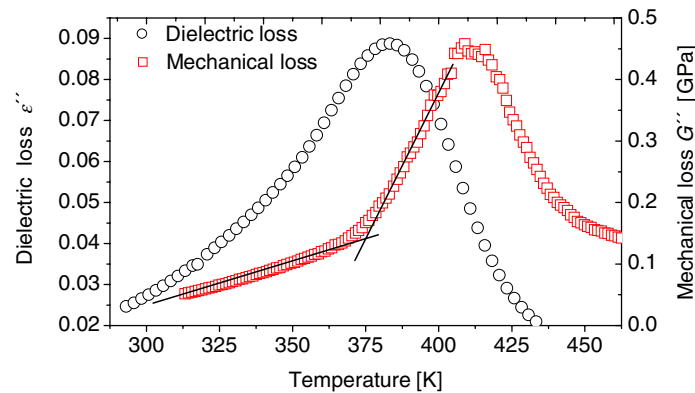


Figure 6. Comparison of the temperature-dependent mechanical (squares) and dielectric loss (circles) in a PMMA film measured at 5.4 kHz. Both curves show a clear maximum that is at about 410 K and at 380 K for the mechanical and dielectric cases, respectively. The low-temperature tail of the mechanical loss shows a kink (indicated with two straight lines), at 375 K, in the regime of the glass transition. There is no such kink observable for the dielectric measurement.

polymer chain. At a given temperature, the characteristic relaxation time for the β -process has to be smaller because of that simple geometric argument. If the frequency f of the external force is constant, the temperature at which the relaxation rate of the side group rotation equals this frequency must be reached at lower temperatures compared with the slower moving molecule chains. From an Arrhenius diagram given by Garwe *et al* [1], the peak maximum temperature for bulk PMMA at 5.4 kHz is at 416 K for the α -process and at 377 K for the β -process. In a similar diagram of Fukao *et al* [3], these peak positions in the temperature range can be extrapolated from low frequencies (where α - and β -processes resemble clearly separated peaks) to be at 407 K for the α -relaxation and 387 K for the β -process. In all these experiments, a separation of 20–40 K in the relaxation rate plot does not imply well-separated peaks in the loss function, especially as both peaks are broad and the amplitude of the α -relaxation is small. But this separation compares well with older literature data of the dielectric and the mechanical β -peak positions for bulk PMMA, which has been given in the book of McCrum *et al* [9]. At a given constant frequency, the loss maximum obtained from dielectric experiments is at a significantly smaller temperature than the maximum gained from mechanical measurements. All this agrees well with the results in figure 6 and hence the observed difference in the peak position can be explained.

Secondly, we analyse the shape of the peak. In the mechanical case, a kink in the low-temperature tail of the peak is observed (figure 6) at about 375 K. Such a kink is known to be a characteristic behaviour for the glass transition in polymers and is also found in other materials [21]. The glass transition temperature of bulk PMMA is given as 390 K by the manufacturer. Since the number of monomer units is larger than 4000 in the bulk material and about 60 in the film as has been observed using size exclusion chromatography [17], the glass transition is shifted to lower temperatures in the film. With an empirical model [22], the expected shift due to the chain length dependence can be calculated to be about 20 K. This is precisely what is observed here. The crucial point, however, is that the kink is visible in the mechanical loss but not in the dielectric measurement. This strongly supports the assumption that the peak in the mechanical loss is mainly due to the α -relaxation process.

To summarize this analysis, the merged peak in the dielectric loss of PMMA films is mainly caused by the β -relaxation mechanism, whereas the α -process provides only a minor contribution. In the mechanical loss spectrum, the observed merged peak is explained the other way round. Now basically the α -mechanism causes the relaxation maximum and the side group rotation plays an inferior role. One has to point out in this context that there is no significant change in the figures if, instead of the shear modulus, the shear compliance is calculated. The curve shape for both is very similar and it is therefore accepted (see for instance [10]) to compare the dielectric loss that indeed represents a compliance directly with the imaginary part of the shear modulus.

4. Conclusions

We showed temperature-dependent mechanical loss spectra at 5.4 kHz of PMMA films produced by PLD. High-temperature effects can be explained by an irreversible destruction of the polymer itself. Dielectric measurements compare bulk PMMA and PLD thin films at different external frequencies. The molecular rearrangement and loss of free volume result in an enhanced aging of the material that can be seen in an increase of the internal friction and the relaxation strength in the mechanical loss. As well as in the dielectric loss spectra, the mechanical loss measurements exhibit one merged peak at high frequencies. The weighting of the two contributions of α - and β -relaxation is vice versa. Indeed, we were able to demonstrate that the significant differences in both spectra occur because of different coupling processes of the external forces to the film. In the mechanical experiment, the merged maximum is dominated by viscous flow and the α -relaxation, whereas the dielectric loss peak is strongly dominated by hindered side group rotations and the β -process.

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