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Polymer thin film properties as a function of temperature and pressure

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SUMMARY: We report on evanescent wave optical measurements of the glass transition temperature, T_g, of spin-cast PMMA films as a function of film thickness and molecular weight. It was found that for films of high molecular weight PMMA (M_n > 100,000 g mol^{-1}) a strong T_g depression occurs for films that are thinner than 100 nm in case they are deposited on hydrophobic substrates. This strong T_g depression of up to 25°C decreases if similarly thick films of PMMA of low molecular weights are investigated and vanishes completely for PMMA with M_n < 12,000 g mol^{-1}. For films made of these materials T_g is found to be identical to that of the bulk even for films as thin as 5 nm. The results might be interpreted in terms of free volume considerations. To check this assumption we also designed and built a pressure cell that can be used together with the evanscent wave optical techniques for similar measurement, but with the additional option to do the measurements at different pressures up to ca. 100 MPa to further vary the free volume of these polymer films in constrained geometry. Some first results obtained with this setup are also described.

Introduction

During the past years the understanding of the physical properties of polymers in the specific sample format of thin and ultrathin (molecular dimensions) polymer films has become a widely recognized field of research. Generally, it was found that the restricted geometry of

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these films largely alters the thermal properties of the polymers used for film formation. One example is the significant decrease of the degree of crystallization of poly(di-n-hexylsilane) in spin-cast layers that are thinner than 100 nm.[1)] There is also some evidence that the restricted geometry may influence the glass transition temperature T_g of amorphous polymer films and their thermal expansion coefficients.[2-10)] For many systems, a T_g depression can be observed for thicknesses below ca. 100 nm, especially if the films are deposited onto non-attractive surfaces.[3-8)] These findings clearly demonstrate that crucial characteristics of the polymers - such as chain (segment) mobility and free volume are modified for chains that are confined between two interfaces. However, up to now a clear understanding of the various phenomena could not be obtained, and most explanations remain rather qualitative and speculative.

Our studies aim at a comprehensive understanding of the various consequences of confinement on the conformational parameters that describe the structural and dynamic behavior of polymer coils in thin films. Our first approach in this direction is to determine the thickness dependence of the glass transition temperature of polymer films as function of important architectural parameters, such as the influence of end-tethering of the chains,[6)] the polymer / surface interactions[7)] or the molecular weight of the polymers.[8)] Here, we concentrate on the latter parameter and also present first results obtained with a newly designed cell that makes the important thermodynamic parameter pressure available for more systematic studies with thin films.

Results and Discussion

In a first set of experiments we varied the molecular weight of PMMA used for the preparation of such films over a range from 5,000 to 180,000 g mol^{-1}. All layers were deposited by spin-casting onto SiO_x surfaces previously made hydrophobic by gas phase deposition of hexamethyl disilazane. This procedure was employed to minimize the substrate / polymer interactions. The T_g of the samples was determined by using evanescent wave optical techniques, namely optical waveguide and surface plasmon spectroscopies (OWS and SPS) as described in refs. 6-8.

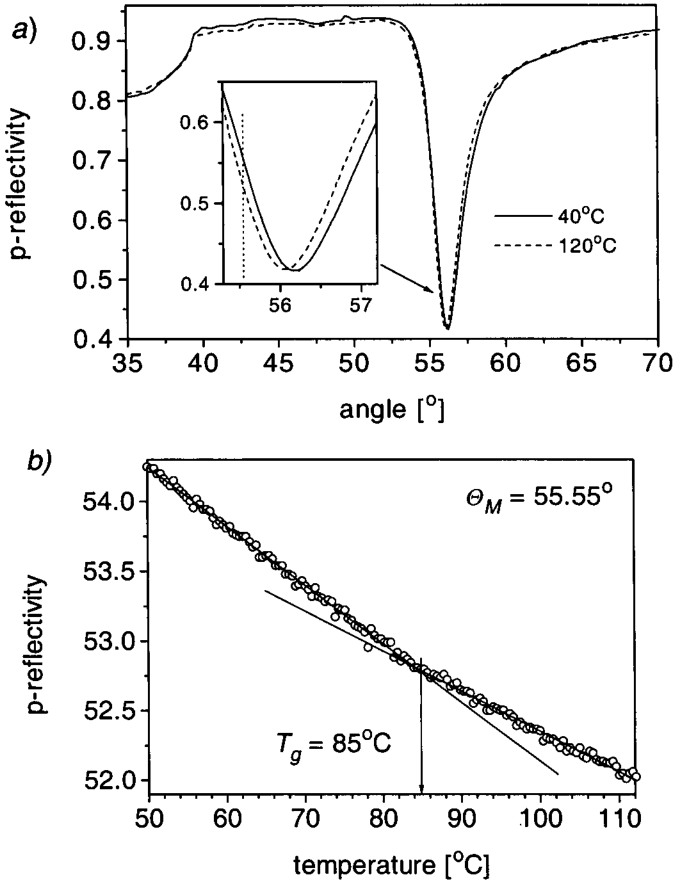

Fig. 1: a) Reflectivity curves (p-light) obtained for a spin-cast film of PMMA (12,300 g mol^{-1}) approximately 380 nm in thickness at two different temperatures (40 °C and 120 °C); b) kinetic scan obtained at Θ_M = 55.55° (see dotted line in insert in Figure 1a) in the low angle slope of the p-mode of this film. The glass transition temperature of this sample was found to be approximately 85 °C as determined by the break between the linear regions in this plot.

Figure 1a shows two typical reflectivity curves obtained from a 380 nm thick PMMA (M_n = 12,300 g mol^{-1}) film at two different temperatures below (40 °C) and above (120 °C) the bulk T_g of this particular polymer. The thickness of the sample was derived from these curves by analyzing them using a Fresnel formalism on the basis of a box model. Details on the exact procedure are published elsewhere.[6-8] Due to different optical thicknesses of the film at these two temperatures a slight shift of the resonance dip to a smaller angle at 120 °C can be seen. This behavior was observed in more detail in a "kinetic scan" during a heating ramp (5 °C min^{-1}) by measuring the reflectivity at an fixed angle of 55.55° slightly below the resonance angle (see dotted line in the inset of Figure 1a). The result of this measurement is shown in Figure 1b. The curve plotted there can be separated into two linear regions and the break between them is taken as the glass transition temperature. The rational for this procedure is the abrupt change of the thermal expansivity and the refractive index increment of the polymer at the glass point. In the case of our optical technique, this behavior manifests itself in a sudden change of the way the resonance shifts with temperature leading to the observed break.[6-8] For the sample shown in Figure 1 we find T_g = 85°C which is in good agreement with the bulk value of PMMA of this specific molecular weight as reported in the literature.[11,12]

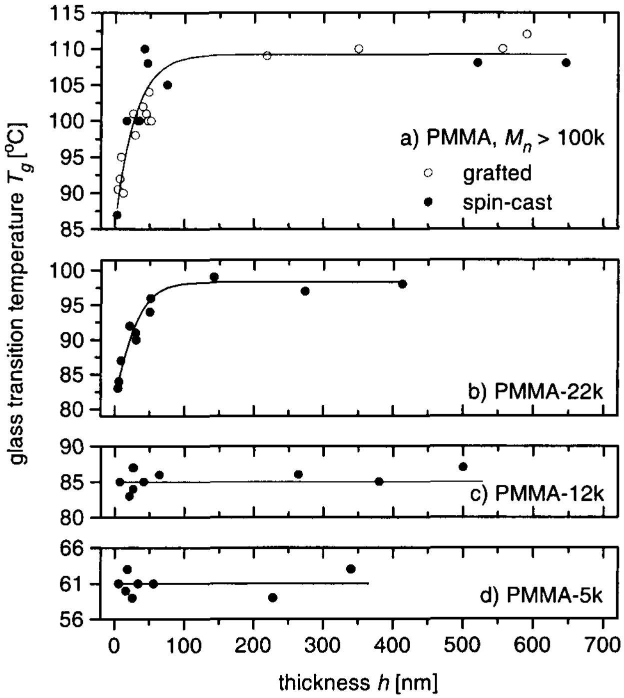

Fig. 2: Glass transition temperatures of PMMA films as a function of thickness for different molecular weights (M_n): a) > 100,000 g mol^{-1}, b) 21,600 g mol^{-1}, c) 12,300 g mol^{-1}, and d) 5,200 g mol^{-1}.

The glass transition temperatures of various series of such assemblies are plotted as a function of film thickness in Figure 2. These plots demonstrate clearly that the extent to which the T_g

of a polymer is suppressed, if the material is constrained to an ultrathin film, is not only a function of surface/polymer interactions but also (at least for low molecular weights) depends on the molecular weight of the polymer in question. Films of high molecular weight material (M_n > 100,000 g mol^{-1}) exhibit a pronounced T_g depression of up to 25°C for thicknesses below about 100 nm. Medium molecular weights between 12,000 and around 30,000 g mol^{-1} also exhibit T_g depressions with the extent of this effect diminishing for decreasing molecular weight. Finally, for molecular weights smaller than 12,000 g mol^{-1} no more differences in the T_g of thick and thin films can be observed.

The significant T_g depression that was found for the ultrathin layers of high molecular weight PMMA means that the chains in these films become more and more mobile as the film thickness is decreased. The mobility of polymer chains in the melt can be correlated to the free volume of the polymers. The larger the free volume the higher the chain mobility. This means that the free volume of these PMMA films is largely increased as the material is confined to thinner and thinner films. This argument can be understood because the confinement of the chains certainly reduces the number of conformations that a chain can have. No chain can penetrate the hard wall and it is also impossible that larger segments or loops leave the free surface. These conformational restrictions may lead to situations where larger segments of the chains can no longer arrange themselves in the same dense way as in the bulk. This leads to a higher free volume in these film which then manifests itself in an onset of main chain movement at lower temperatures. For low molecular weights this effect is compensated as the free volume of these polymers is already enhanced due to the higher concentration of end groups.

In order to further explore the effect of confinement on the free volume of polymers it is certainly helpful to use another parameter that influences this physical property, i.e. pressure. The combination of experimental methods for the characterization of thin and ultrathin films such as evanescent wave optical spectroscopies with temperature and pressure control units is a particular challenge. We designed a cell 13) that allows for such measurements and first results obtained from rather thick polymer films show that the instrument can indeed reproduce data that was obtained from bulk measurements. For practical reasons, we used polyethylmethacrylate, PEMA (M_n = 139,000 g mol^{-1}), rather than PMMA in these studies because the T_g of this polymer (ca. 53°C) is somewhat easier to access with our setup. For the same reason we also used a grating rather than a prism for resonant coupling.14) Figure 3 shows two typical reflectivity scans obtained from a rather thick (580 nm), bulk-like PEMA film at 30°C and 100°C and 64 MPa, i.e. above and below the expected glass transition temperature. The two resonance minima, Θ_R, of each curve are again clearly found at different angles for both temperatures indicating differences in the optical thickness of the sample.

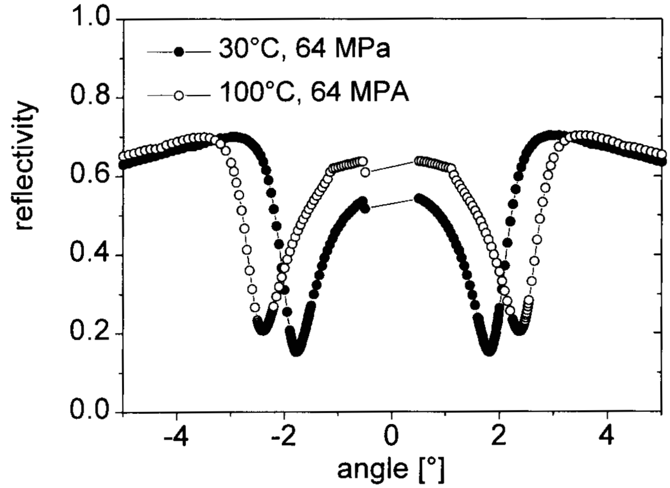

Fig. 3: Reflectivity curves (p-light) obtained for a spin-cast film of PEMA approximately 580 nm in thickness at two different temperatures (30°C and 100°C) and at 64 MPa.

In addition to these curves, similar scans were taken at other temperatures around T_g and these experiments were then repeated at various pressures between 5 and 76 MPa. The glass transition temperature at a specific pressure was then derived by plotting the resonance angle as a function of the temperature. Two examples of such plots are shown in Figure 4. Θ_R-versus-T curves obtained from the same sample in Figure 3 are shown for pressures of 5 MPa and 76 MPa, respectively. Both curves show the same behavior. With increasing temperature Θ_R shifts linearly to smaller values up to a certain temperature above which again a linear decrease of Θ_R is found but now with a somewhat steeper slope. The break between these two regions again indicates T_g. It can be seen that a smaller value for T_g is found at lower pressures.

In addition to the measurements at 5 MPa and 76 MPa, similar experiments were performed at pressure values between these two limits and the results are shown in Figure 5, where the T_g of this sample is plotted as a function of the externally applied pressure. The observed increase of T_g from 54 to 70°C over this pressure range can be explained by a reduction of the free volume in the polymer and is in good agreement with comparable data from the literature on PMMA.[15,16]

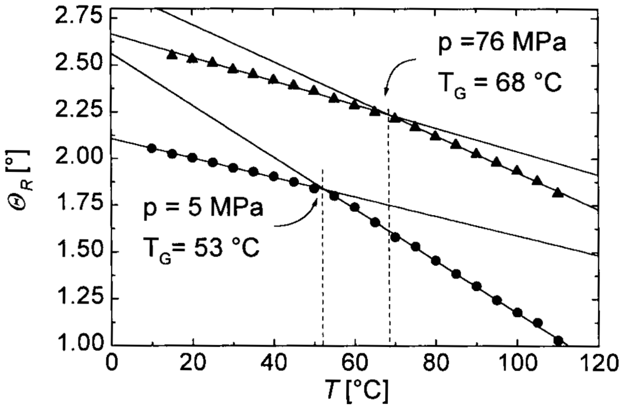

Fig. 4: Resonance angle, Θ_R, as a function of the temperature at 5 and 76 MPa (same sample as in Figure 3). The glass transition temperatures where taken as the break between the linear regions in each curve.

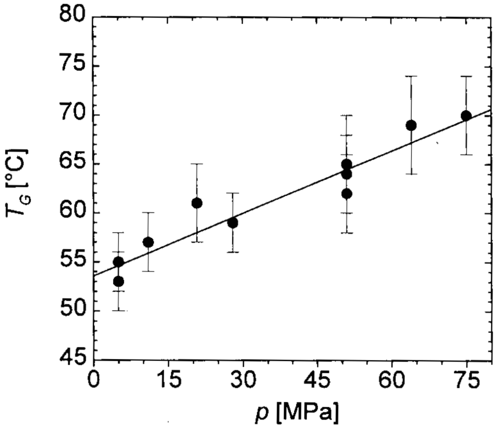

Fig. 5: Glass transition temperature, T_g, of a 580 nm thick spin-cast sample of PEMA (same sample as in Figures 3 and 4) as a function of pressure.

Conclusions

In this study we have shown that the geometrical constraints imposed onto a polymeric material in the sample format of a thin film may largely alter the thermal properties of the polymer. In many cases a drastic T_g depression can be found if the polymer is confined to films with thicknesses that are comparable to the molecular dimensions of the macromolecules. However, it was also shown that the extent of this effect is a function of the molecular weight of the polymers: the strong T_g depressions for films of high molecular weight PMMA cannot be found for similar films composed of low molecular weight analogs. This behavior might be correlated to free volume effects caused by the confinement.

To further explore the operating mechanisms it will be helpful to vary the free volume of these assemblies in a different way, e.g. by applying different external pressures. First experiments with a pressure cell used in combination with our optical techniques show that the well-known bulk behavior of polymethacrylates can be reproduced for thick films (>100 nm). More detailed experiments that aim at the systematic investigation of thin films, where the influence of confinement becomes dominant, are currently performed in our laboratories.

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