

H1. NANOMECHANICS AND GLASS TRANSITION OF CONFINED POLYMERS WITHIN SPHERICAL NANOSIZED PARTICLES

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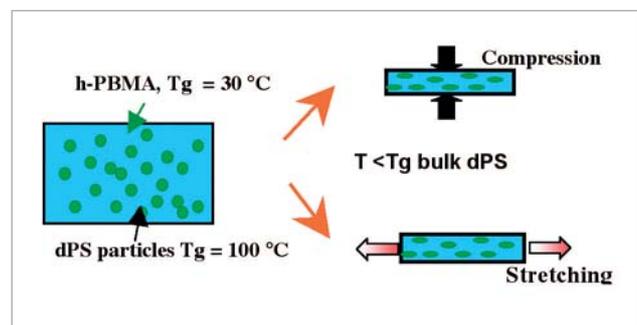
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It is most likely that a polymer's environment affects its dynamics, rheological properties and more particularly its glass transition temperature (T_g). This idea is backed up by "Brillouin Light Scattering", and ellipsometry results from Forrest and al.^{1,3}, and Keddie and al.² on both supported and free standing ultrathin films. They suggest that the T_g of polystyrene is reduced below the bulk values with a decrease in film thickness (h) for $h < 50$ nm. For free standing film, where thickness $h \sim 20$ nm, the T_g is reduced by about 60°C below the bulk value. Other experiments suggest that the T_g of supported polymethyl methacrylate (PMMA) on certain solid surfaces, increases with decreasing film thickness.⁴ However, the situation of a polymer confined within another polymer has not been thoroughly investigated. This situation is particularly crucial for a good number of applications; polymer blends, copolymers, composites... In this work we propose to study the influence of the proximity of two polymers on their glass transition and their dynamics.

We developed a method which combines Nanomechanics with Small Angle Neutron Scattering (SANS) to study the deformation modes of polymers confined within nanosized domains (20 to 200 nm). The work consists of analyzing the deformation modes of deuterated nanosized polymer particles, dispersed individually within matrices of another polymer using SANS (Schema 1). The project involves two major stages: 1) we prepare films containing deuterated polystyrene d-PS nanoparticles, dispersed in a perfectly individual manner within polybutyl methacrylate (PBMA) matrices. 2) Thereafter we apply mechanical stress to the films (compression), and we study the variations of the nanoparticles' form factor. Film preparation was carried out in two steps: 1) Synthesis, via emulsion polymerization, of deuterated d-PS nanoparticles ($T_g^{\text{bulk}} = 100^\circ\text{C}$, diameter ranging from 20 to 200 nm) and hydrogenated h-PBMA particles ($T_g^{\text{bulk}} = 28^\circ\text{C}$, diameter 50 nm). 2) Preparation of films via evaporation of a mixture of h-PBMA and dPS dispersions. PBMA particles were cross-linked during emulsion polymerization with 0, 1, 5 and 10% ethylene glycol dimethacrylate (EGDA). Small angle neutron scattering (SANS) experiments were carried out on the spectrometer PAXY (Saclay).



Schema 1. Experimental procedure

We optimized the experimental conditions for sample preparation in order to achieve perfect dispersion of the dPS particles within h-PBMA matrices. We obtained SANS spectra describing all the characteristics of the form factor of individual particles (Figure 1). The films were compressed at different temperatures in a home-made compression device.

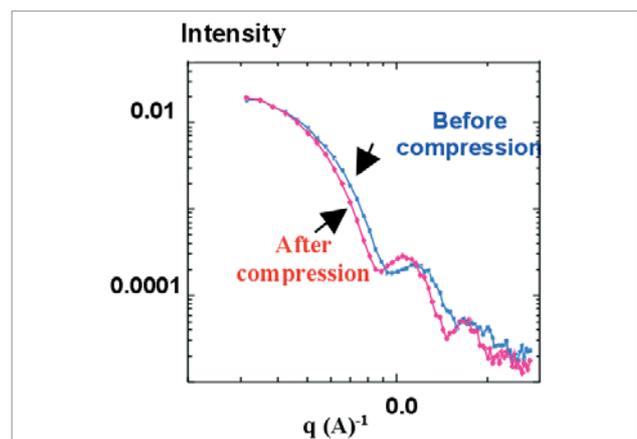


Figure 1. SANS spectra of dPS particles (90 nm, 2%) in crosslinked PBMA matrix (10 % crosslinker), before and after compression at 120°C .

In figure 1, we show the spectra of a film containing 90 nm dPS particles within a cross-linked PBMA matrix, before and after deformation. The form factor of the dPS particles changes upon compression which infers that the dPS nanoparticles undergo deformation within the PBMA matrix.

SOFT MATTER

We developed a model for analyzing the SANS spectra of compressed nanoparticles and for calculating the deformation rate λ . In figure 2, we show the nanomechanical spectra, λ vs. temperature for 90 nm and 27.4 nm dPS nanoparticles within cross-linked PBMA matrices (10% crosslink). The 90 nm sized d-PS particles undergo deformation, under compression, for temperatures $T > T_g$ of the bulk polystyrene (100 °C). Whereas the 27 nm sized dPS particles begin to deform at about 20°C below the bulk T_g (Figure 2). These results suggest that the nanomechanical properties and particularly the T_g of 90 nm sized d-PS particles are similar to those of the bulk polystyrene. On the other hand, the nanomechanical properties of 27 nm particles are influenced

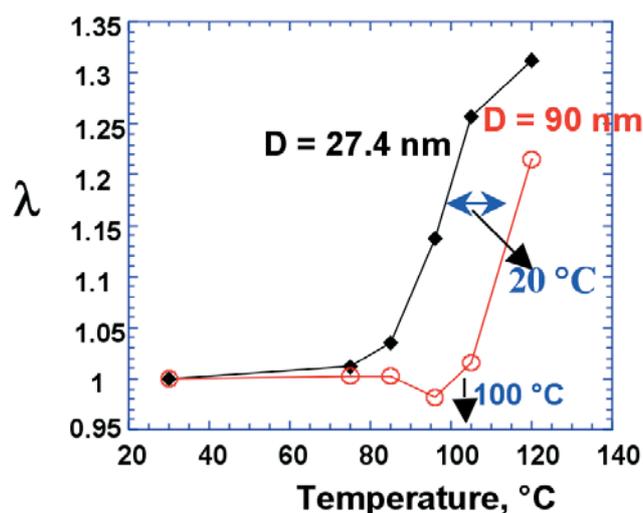


Figure 2. Nanomechanical spectra: deformation rate λ vs. temperature for 90 nm and 27.4 nm dPS nanoparticles in cross-linked PBMA matrices (10% cross-link).

by their environments and their T_g is about 20° C lower than that of bulk polystyrene (Figure 2). The onset temperature for the dPS deformation depends on the T_g of the confined polymer (T_g^{conf}) and is most likely similar to it. In Figure 3, we show the T_g^{conf} values vs. the dPS particle diameter. One can clearly see two behaviors: when the dPS particles are larger than 50 nm, T_g^{conf} is constant and similar to the bulk value. When the dPS particles are smaller than 50 nm, T_g^{conf} decreases continuously as the particle size decreases. This result is similar to that reported on ultra-thin polystyrene films¹⁻³ and is one of the first experiments that clearly show the similarity between confinement in thin polymer film and in blends.

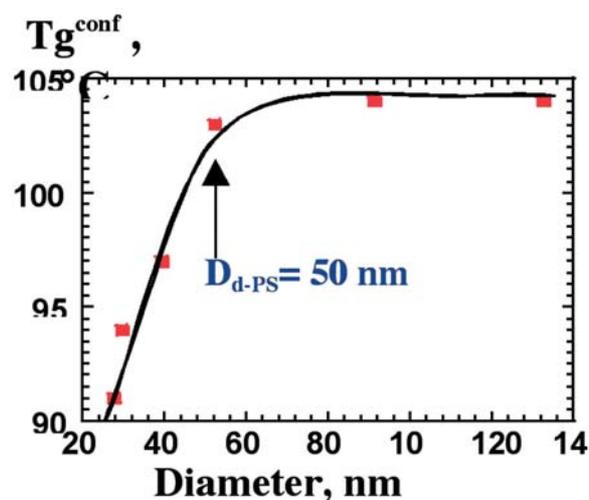


Figure 3. The onset temperature for the dPS nanoparticle deformation, calculated from figure 2, as a function of particle diameter. The PBMA matrices were crosslinked with 10 % cross-linker.

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