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Method to probe glass transition temperatures of polymer thin films

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A new methodology was developed to probe glass transition temperatures (T_gs) of polymer thin films supported on gold substrates and confined between two solid (silica and silver) surfaces based on the surface plasmon polariton (SFPP) signals generated by sum frequency generation (SFG) spectroscopy. The detected abrupt change of the temperature-dependent SFPP signal demonstrated the viability of this methodology to determine T_gs of polymer thin films. The measured T_gs for polymer {poly(methyl methacrylate), poly(benzyl methacrylate) and poly(ethyl methacrylate)} thin films supported on gold (Au) substrates showed similar thickness-dependent trend compared to those previously measured using other methods, i.e., the T_g decreased as the thin film thickness decreased due to the free surface effect. However, the measured T_g of the polymer {poly(methyl methacrylate)} thin films confined between two solid (silica and silver) surfaces increased significantly with respect to the bulk value, indicating the strong interfacial effect on the dynamic behaviors of polymer thin films when the free surface was replaced by a buried interface. This new method to measure T_g is general and can be applied to study many different polymer thin films supported on metal surfaces or confined between two solid surfaces with different surface chemistries. More importantly, SFG has the unique selectivity and sensitivity to study surfaces and interfaces, which provides the feasibility to develop SFG into a powerful tool to detect surface, interfacial and bulk T_gs of a polymer thin film simultaneously in the future.

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