Direct Observation of the Length of Molecular Cooperativity in Melts of Ultrathin Glass Formers

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ABSTRACT

Many modern and future technological applications involve ultrathin polymer films with a thickness below the 100-nanometer scale, where statistical bulk averaging is jeopardized and interfacial constraints dictate transport properties. In such confined polymeric systems, transport properties strongly depend on molecular relaxation and structural phases that deviate from the bulk. In this paper, we investigate the length scale of molecular cooperativity in a glass forming amorphous polymer, compare it to the critical film thickness below which the glass transition deviates from bulk values, and illustrate its impact on a nano-electromechanical system (NEMS) application. Thereby, an elaborate scanning force microscopy (SFM) friction-velocity temperature analysis is introduced as a material characterization tool. It provides fundamental insight into the glass forming process, and consequently, the glass transition value in ultrathin spin coated polymer films.

Keywords: Thin films, NEMS, glass transition, polymers, shear modulation SFM

1 INTRODUCTION

Our fundamental understanding of nanoscale material properties is still in its infancy in thin film technologies, such as NEMS/MEMS, and optoelectronic and photonic systems, involving polymeric materials. A particular challenge is the determination of kinetic properties such as the molecular mobility in constrained ultrathin film systems. Kinetic properties are paramount for material engineering and processing, as they dictate the material's relaxation behavior. In polymeric materials, the relaxation properties are intimately related to the glass forming process. Since Adam and Gibbs [1], structural relaxation near the glass transition is visualized in terms of a correlated motion of polymer segments or domains, giving rise to dynamic heterogeneities [2-7]. While the time scale of dynamic heterogeneities can be directly inferred from scattering experiments, the size of the cooperatively rearranging regions (typically 1 - 3 nm [3,5,8,9]) is generally not directly obtainable and involves model assumptions. In particular, the long awaited temperature-resolved description of the cooperation length is expected to provide vital microscopic information towards the ongoing mystery of the glass transition [3], and material property engineering deduced directly from the molecular design.

Here, we introduce a truly model independent spatial investigation of the molecular cooperativity of a polystyrene melt near its glass transition. This is possible due to recent developments of novel nanoscience tools [10,11]. The motivation of studying the glass forming process of polystyrene thin films is three-fold: (i) Polystyrene is a well-defined and widely studied model system, (ii) exhibiting a non-monotonous glass-transition profile in films of less than 100 nm thickness [12], which (iii) has recently been found to be crucial in the pursuit of a novel nano-electromechanical system (NEMS) (Millipede, IBM) that promises to circumvent the superparamagnetic limit associated with the electronic magnetic data storage [13].

2 EXPERIMENTAL

The samples atactic polystyrene (PS) (Polymer Source, Inc., $M_w = 96.5k$, $M_w/M_n = 1.04$), were spin cast from cyclohexanone (Mallinckrodt Baker, Inc.) solution onto silicon, and annealed at 160 °C for 4 hrs under vacuum. Friction force microscopy (FFM) was conducted under N_2 at ~7 % RH using a bar shaped silicon cantilever (Nanosensors, $k_N = 0.164$ N/m, $k_T \sim 80$ N/m). Friction force was determined from the hysteresis in the lateral deflection between forward and reverse scans [14, 15]. Scanning was performed over a 2 μm range with a 20 nm line-spacing. Isothermal friction-velocity curves were recorded over a velocity range of 0.01 - 20 μm/s, for temperatures between 377 - 403 K. The reported friction data were obtained with a constant zero applied load, under an average adhesive load of ~90 nN. Calorimetric glass transition values, T_g, were determined with shear-modulated force microscopy (SM-FM) [10]. SM-FM is a non-scanning nanorheological method that is well suited for surface rheological studies involving thermally activated transitions or relaxations. It has proven to be particularly successful in determining structural phase transitions, e.g., glass transitions of ultrathin films [12]. SM-FM involves a nanometer sharp SFM cantilever tip that is brought into contact with the sample surface, as sketched in Figure 1 [3, 10]. While a constant load of 5-100 nN is applied, the probing tip is laterally modulated with a "no-slip" nanometer amplitude, $A_{X,IN}$; i.e., a small enough amplitude that guarantees no relative probe-sample slippage. The modulation response, $A_{X,OUT}$, is analyzed using a two-channel lock-in amplifier, comparing the response signal to the input signal. The response amplitude is a measure of the contact stiffness.

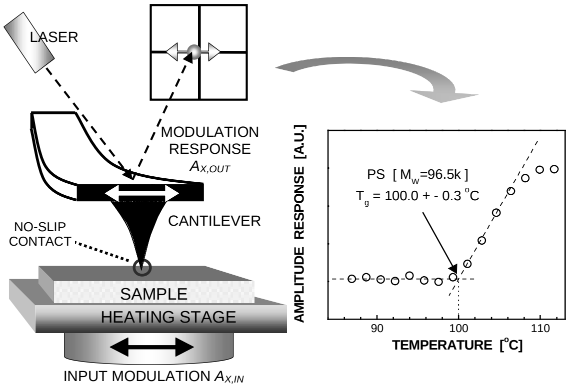

Figure 1: Working Principle of SM-FM.

3 RESULTS AND DISCUSSION

3.1 Molecular Cooperativity

A friction approach towards molecular mobility is justified, as a mesoscopic description of polymer dynamics involves, in general, only two parameters; an appropriate macromolecular length scale and an internal friction coefficient [16]. Figure 2 shows the superimposed friction $F_F(v)|_T$ results above T_g of a relatively thick PS film of 160 nm, from which an activation barrier energy E_a of 88 Kcal/mol can be deduced. This value corresponds to the 90 kcal/mol of the energy barrier for the α-relaxation process [17]. Two phases can be identified from the functional relationship of the α-peak intensity with temperature. Above 388 K the melt is fully developed. A heterogeneous phase is found below 388 K, exhibiting a cooperation length $\xi_\alpha(T)$ that increases from the monomer scale (0.4 nm) to astonishing 37 nm clusters towards the glass transition temperature, Fig. 3.

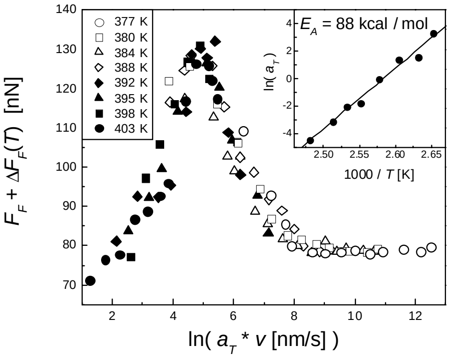

Figure 2: Friction-velocity-temperature analysis [18].

In Figure 3, similar to Grosch [19] and Ludema and Tabor [20], who combined the velocity at the friction peak with the frequency for the maximum viscoelastic loss to deduce a dissipative length scale, we relate our friction-velocity results to dielectric spectroscopy data [21] for PS of comparable molecular weight (M_w = 90.0k, M_w/M_n = 1.06), with

$$\xi_\alpha(T) = v_o(T) \cdot \tau_\alpha(T) \,. \qquad (1)$$

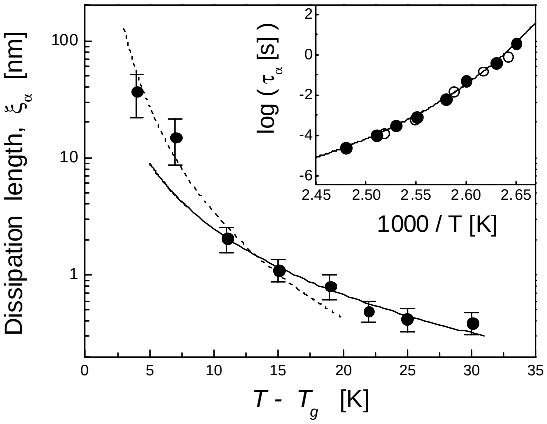

Figure 3: Length of CRRs towards T_g [18].
Inset: α-relaxation times, τ_α .

The thermal behavior of $\xi_\alpha(T) \approx (T\text{-}T_g)^{-\phi}$ confirms recent predictions based on molecular dynamics (MD) simulations ($\phi = 1.87 \pm 0.15$) for the spatial correlation of segmental displacements above the critical temperature of the mode coupling theory [22]. In essence, the dissipation length may be considered as the size of cooperatively rearranging regions (CRRs), or regions in space where the motion of individual chain segments is contingent upon the orchestrated motion of an ensemble of surrounding segments. On closer approach to T_g (T < 388 K), we find a strong deviation from the above power law behavior. CRRs with sizes up to 37 nm occur. Recent MD simulations incorporating angular and torsional potentials, suggest that intramolecular interactions effectively slow down the cooperative dynamics near T_g [23]. The MD simulation predicts an amplified power-law behavior with an exponent ϕ of 2.9 [23]. A power law fit to $\xi_\alpha(T)$ below 388 K (Fig. 3) reveals an exponent ϕ of 3.0 ± 0.2. Based on this MD simulation, 388 K could be interpreted as a critical temperature below which intramolecular interactions alter the dynamics of the CRRs, and thus, the relaxation behavior and the nature of the dissipation process. In context of the observed power law behavior, $\xi_\alpha \approx (T\text{-}T_g)^{-\phi}$, $\xi_\alpha(T)$ represents the degree of molecular coordination. The exponent ϕ captures the growth dynamics of the CRRs when approaching T_g, which acts as a thermal asymptote to a diverging $\xi_\alpha(T)$.

The large size of the CRRs deserves particular attention. Based on our study, the size of the CRRs in PS near the glass transition grows from single molecular segments to domains of tens of nanometers in diameter. Compared to structures in modern device technologies, e.g. ultrathin films and nanocomposites involving sub-100 nm dimensions, one can expect a competition between material and device length scales. Consequently, material properties in dimensionally constrained systems are likely to be modified from their original bulk values.

3.2 Glass Transition in Ultrathin Films

Near surface glass transition temperatures were acquired using SM-SFM on spin cast PS films. Bulk-deviating values were found at a film thickness δ below ~100 nm. The non-monotonic $T_g(\delta)$ profiles in Figure 4 can be interpreted considering two competing processes that affect the relaxation process [12]: (a) Shear induced structuring, which creates an interfacial region where the spin casting shear stresses induce polymer stretching and/or disentanglement and molecular alignment along the substrate surface and (b) interdiffusion between the entropically cooled interfacial region and the unperturbed bulk phase. The location of the maximum in the non-monotonous T_g profile was found to be controllable in lateral and normal plot direction by an appropriate choice of the molecular weight (Fig. 4) and the crosslinking density,[1] respectively [12].

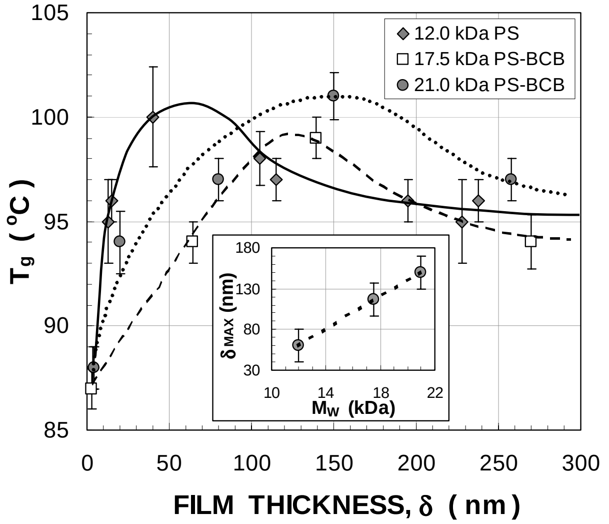

Figure 4: $T_g(\delta)$ profiles of PS. *Inset*: Linear relationship between maximum T_g value and molecular weight, M_w [12].

Thus, tailored relaxation properties and enhanced conformational stability may be achieved in finite size limited systems, such as ultrathin films, through matching conventional control parameters, such as the molecular weight and the crosslinking density, to anisotropic relaxation properties within the constrained regime of the polymer system. In this regard, glass transition profile characterizations of thin films become increasingly important for nanotechnological applications. An example, in which tailored relaxation on the nanoscale is crucial is provided below, with a recently introduced NEMS application of ultrahigh (terabit) density recording scheme.

3.3 Impact on NEMS Storage Application

Ultrahigh density thermomechanical data storage (TDS) is a novel NEMS recording scheme intended to circumvent the superparamagnetic limit associated with magnetic storage [13]. TDS relies on writing, reading, and erasing nanometer sized data bits in thin polymer films using thousands of SFM-like cantilever probes in parallel. In essence, TDS recording is a high speed (MHz), elastic-viscoplastic indentation process. The polymer storage media must be designed to achieve the narrow range of physiochemical properties necessary for high data density, fast data rates, high durability, long shelf life, and low power consumption. The ideal polymer should be easily deformable for bit writing; however, the written bits must be stable against thermal degradation and wear.

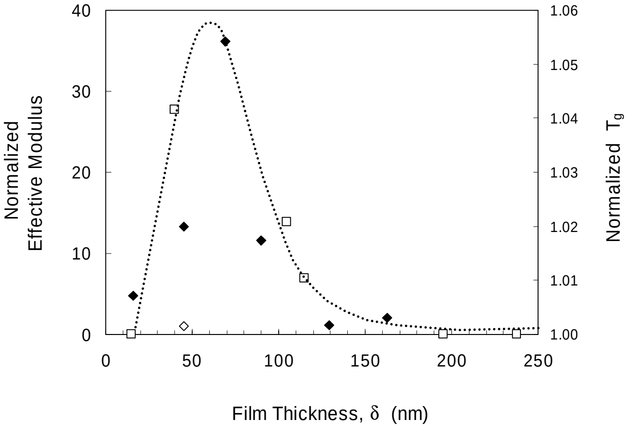

Figure 5: $T_g(\delta)$ profile and non-monotoneous effective modulus in ultrahigh density TDS NEMS application [24].

If we superimpose the effective modulus that a single NEMS tip experiences during a pulsed writing process with the non-monotonous T_g-profile of PS, introduced above, a strong resemblance is noticeable as shown in Figure 5. It can be concluded that the anisotropic transition properties within the constrained thin film region strongly impact the mechanical deformation mechanics, which in the case of thermomechanical recording, are used to optimize the shape of the indentation. For instance, a restraint over the growth

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[1] Crosslinking was achieved on application of heat for polystyrene-benzocyclobutene (PS-BCB) co-polymers with the crosslinking agent BCB [12].

of the indentation rim is achieved by controlling the mobility in the subsurface material. Low rims, which are preferable for this NEMS application, can be expected for a decreasing modulus gradient in the subsurface material, and vice versa. As discussed above, the T_g-profile, can be controlled with the appropriate crosslinking density and molecular weight, and thus, the modulus gradient tailored, and consequently, the NEMS application optimized.

4 SUMMARY

Our study on heterogeneous dynamics during the glass forming process provided access to the intrinsic relaxation energy, and temperature resolved cooperation lengths. In the vicinity of T_g, cluster sizes close to 40 nm were observed – a length scale that is considered to impact the glass transition value for ultrathin polymer films with a thickness on the order of 100 nm and less. The reported cooperation lengths and their qualitative thermal dependence compared well with predictions based on MD simulations. Considering that many of today's ultrathin film applications deal with film thicknesses on the sub-100 nanometer scale, the finding of such large clusters provides a new and exciting opportunity to shape materials on the nanometer scale towards modern nanotechnological applications. Bulk deviating relaxation properties were found in ultrathin films in form of a non-monotoneous, T_g–profile. It was suggested that by engineering an appropriate T_g-profile using conventional parameters, such as the molecular weight and the crosslinking density, process parameters relevant to nanotechnological applications could be optimized. The potential of this idea was documented on a recently introduced NEMS application for ultrahigh density recording.

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