

# Determination of the Glass Transition Temperature of Freestanding and Supported Azo-Polymer Thin Films by Thermal Assisted Atomic Force Microscopy

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**Abstract.** In this paper we introduce and apply the method for determination of the glass transition temperature of the sub-100 nm thick freestanding and supported polymer films based on thermally assisted atomic force microscopy (AFM). In proposed approach changes of the phase of an oscillating AFM cantilever are used to determine glass transition temperature. An anomalous decrease of the glass transition temperature for both free-standing and supported azobenzene-functionalized polymer thin films is shown.

## 1 Introduction

Azobenzene-functionalized polymers are one of the most promising materials in polymer photonics and organic electronics. Due to *trans-to-cis* photoisomerization, azo-chromophores found applications in formation of surface relief gratings and study of nonlinear optical effects.<sup>1-4</sup> These effects are widely used in practice, for example for optical switching and storage,<sup>5-6</sup> light filtering<sup>7-10</sup> and frequency conversion.<sup>11</sup> In particular, bottlenecks of optical near-field memory based on azo-polymers are cycling endurance, data retention, and thermal stability. Photoinduced alignment of the azo-dyes in glassy polymers is affected by the thickness of a polymer thin film, since the glass transition temperature  $T_g$  critically drops when the film thickness decreases.<sup>12</sup> In addition,  $T_g$  is influenced by the interface interaction and, therefore, type of a substrate plays role as well.<sup>13,14</sup>

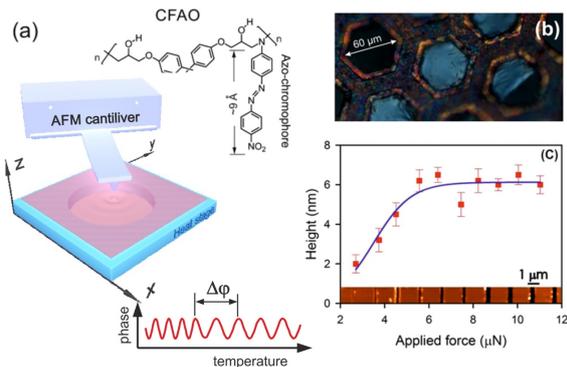
The integrity and thermal stability of the oriented state of polymer thin films are greatly sensitive to the glass transition temperature, at which an intrinsic structure of the polymer changes from a hard disordered solid to a rubber-like bulk. In turn, this influences on the increased mobility of a surface layer that underlies the most observable photo-induced effects in the azo-polymers. The determination of the glass transition temperature has been the subject of through studies over last 50 years. Nowadays, there are many methods for determining the glass transition temperature of bulk amorphous and liquid crystalline polymers such as differential scanning calorimetry<sup>15</sup>, dynamic mechanical analysis<sup>16</sup>, Raman scattering<sup>17</sup>, Brillouin scattering<sup>18</sup> and others. However, most of these methods have a low sensitivity to the sub-100 nm thick polymer films. Atomic force microscopy is a promising technique,

which provides information about glass transitions through a mechanical behavior of the AFM cantilever. In this paper, we determine the glass transition temperature of freestanding and supported azo-polymer films using thermal assisted atomic force microscopy.

## 2 Experimental section

Herein, we study thin films of epoxy-based oligomers containing hydroxyl groups with covalently attached nitroazobenzene chromophores, further it is referred to as CFAO. A chemical structure of this molecule is given in Fig. 1(a). The solution was prepared by dissolving 5 wt. % CFAO compound in 1 ml cyclohexanone. Polymer films with different thicknesses in the range of 5-500 nm were fabricated. The thin films were produced by spin coating 1  $\mu$ l CFAO solution onto a glass substrate at a rotation rate of 10 000 rpm for 2 min. Freestanding films were prepared by centrifugation on a KBr substrate. Then substrate was dissolved in distilled water and after that thin polymer films were picked up with a mesh copper grids as shown in Fig. 1(b). The film thickness was determined by atomic force microscopy in contact mode. In order to minimize errors in determining the film thickness, we have built the dependence of the depth of lithographically produced "grooves" on applied force of the AFM cantilever. The film thickness was defined as a value that meets a plateau on this curve (see Fig.1(c)).

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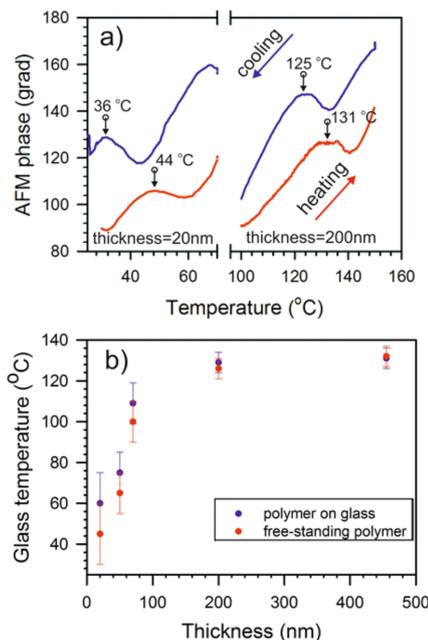
**Fig. 1.** a) experimental setup and chemical formula of CFAO; b) optical image of the freestanding CFAO film; c) plot of the groove depth on applied contact force.

The phase measurements were performed with an atomic force microscope Ntegra Prima (NT-MDT) in tapping mode. We used silicon AFM cantilever with the curvature radius of 10 nm, the resonant frequency of 150 kHz and the force constant of 5 N/m (NSG01, NT-MDT). Polymer films were heated with the thermo stage (SU045NTF, NT-MDT) with an accuracy of 0.05 °C within the range from room temperature to 150 °C. A schematic drawing of the experiment is given in Fig. 1(a). In our approach, the atomic force microscope was used as a dynamic mechanical analyzer of the AFM cantilever phase shift during *in-situ* heating/cooling at a rate of 5 °C/min (Fig. 1(a)).

### 3 Results and discussion

Due to the fact that the phase of the cantilever oscillations is sensitive to the surface properties, we can use this parameter to monitor the glass transition of polymer films. It is known that cantilever phase shift  $\phi$  is determined by energy dissipated during tip-sample interaction:  $\sin \phi \sim E_{\text{dis}}$ , where  $E_{\text{dis}}$  is energy dissipated during one period of oscillation.<sup>19</sup>

The phase of the cantilever oscillations is influenced by viscoelasticity, friction, adhesion etc. which leads to energy dissipation. This can be attributed to the loss of energy of the cantilever, which is associated with a change in the Gibbs free energy of the polymer:  $\Delta G = \Delta H - T \Delta S$ . At the glass transition temperature, changes in enthalpy  $\Delta H$  and entropy  $\Delta S$  of the CFAO thin films are changed and it can lead to reversible jumps of the AFM phase during heating (red curve) and cooling (blue curve).<sup>20</sup> For stable and reliable AFM measurements with *in-situ* heating/cooling, we heat or cool the polymer step-by-step by a value of 20 °C at a linear thermal rate of 5 °C/min. This stepwise regime permits the sample to be in a near-equilibrium state. Using this approach,  $T_g$  can be defined as the temperature at which the jump on phase curve occurs during heating/cooling, as shown in Fig. 2(a).



**Fig. 2.** A plot of the AFM phase vs. temperature of the CFAO thin film with thickness of 20 nm and 200 nm (a), a dependence of the glass transition temperature on the thickness of freestanding and supported CFAO films.

This figure shows results of measurements of the glass transition temperature for both 20 nm and 200 nm thick CFAO films. The  $T_g$  value for the bulk film coincides with the results obtained with other methods and is equal to ~130 °C. For a thinner CFAO film we observe the decrease of  $T_g$  down to roughly 40 °C. The depression of the glass transition temperature with the decrease of film thickness was shown in numerous studies.<sup>13,17,21</sup> Thus, our results are in agreement with earlier published ones. Fig. 2(b) demonstrates the influence of thickness on  $T_g$  for both free-standing and supported CFAO thin films. As follows from this figure, the  $T_g$  behaviours for both freestanding and supported CFAO thin films are close to each other. It means that a role of the substrate in our case is negligible. This was experimentally confirmed by a poor wettability of the CFAO film. Indeed, very thin films with the thickness of less than 7 nm exhibit a ragged structure on the substrate surface.

### 4 Conclusions

The glass transition temperature of CFAO thin films can be determined by using thermal assisted atomic force microscopy in tapping mode. The applied method is based on high sensitivity of the oscillating cantilever phase to changes of the surface properties. This method gives reliable and robust estimations for the glass transition temperature for very thin films with the thickness of less than 20 nm.

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