



# Methacrylate-based polymer films useful in lithographic applications exhibit different glass transition temperature-confinement effects at high and low molecular weight



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## ABSTRACT

The effects of confinement on polymer films are important in applications related to photoresists. To optimize resolution, methacrylate polymers used in photoresists are often low molecular weight (MW). We use ellipsometry and fluorescence to study how the glass transition temperature ( $T_g$ ) is affected by confinement in silica-supported films of low and high MW poly(1-ethylcyclopentyl methacrylate) (PECPMA) and poly(methyl methacrylate) (PMMA). With decreasing nanoscale thickness,  $T_g$  is nearly invariant for high MW ( $M_n = 22.5, 188$  and  $297$  kg/mol) PECPMA but decreases for low MW PECPMA, with  $T_g - T_{g,bulk} = -7$  to  $8$  °C in a 27-nm-thick film ( $M_n = 4.1$  kg/mol) via ellipsometry and  $-15$  °C in a 17-nm-thick film ( $M_n = 4.9$  kg/mol) via fluorescence. Fluorescence studies using a 20-nm-thick dye-labeled layer in multilayer, bulk PECPMA films reveal a much greater perturbation to  $T_g$  in the free-surface layer for low MW PECPMA, which propagates tens of nanometers into the film. The effect of MW in single-layer monodisperse PMMA films is even more striking;  $T_g$  increases with confinement for high MW but decreases for low MW, with  $T_g - T_{g,bulk} = 9$  °C in a 12-nm-thick film (nominal MW = 509 kg/mol) and  $-16$  °C in a 17-nm-thick film (nominal MW = 3.3 kg/mol). The strong influence of MW on confinement effects in PECPMA and PMMA is in contrast to the previously reported invariance of the effect with MW in supported polystyrene films, reconfirmed here.

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## 1. Introduction

In 1994, Keddie et al. first reported that supported polystyrene (PS) and poly(methyl methacrylate) (PMMA) films confined at the nanoscale exhibited glass transition temperatures ( $T_g$ s) that deviated substantially from bulk  $T_g$  [1,2]. For films supported on silica,  $T_g$  decreased with decreasing thickness for PS [1] but increased for PMMA [2]. Since then, many studies have reported on the  $T_g$ -confinement effect for a variety of polymer systems [3–51], with the investigations of linear PS and PMMA chains generally in accord with Keddie et al.'s original observations. These studies have employed many (pseudo-) thermodynamic measurement techniques that typically report significant effects of confinement on the  $T_g$ s of polymer films [1–24,26–36,38–41,43,46–51], quasi-nanospheres [37], and nanocomposites [25,42,44,45]. These

techniques include ellipsometry [1–21], fluorescence spectroscopy [4,22–32], dielectric spectroscopy [33–37], x-ray and neutron reflectivity [38–40], and differential scanning calorimetry (DSC) [37,41–45], Raman spectroscopy [46,47], among others [48–51].

The  $T_g$ -confinement effect in films consisting of linear polymers has commonly been explained with the help of a simple model considering the effects of both the free surface (polymer–air interface) and the polymer–substrate interface in perturbing the  $T_g$  response [1–4,22,52]. With this model, in a sufficiently thin layer adjacent to a free surface,  $T_g$  decreases due to reduced requirements for cooperative segmental mobility, thereby enhancing mobility and decreasing  $T_g$ ; in the layer close to the substrate,  $T_g$  increases if the polymer has attractive interactions with the substrate, e.g., hydrogen bonds, which impede chain mobility. As measured in several studies employing multilayer films, these perturbations to  $T_g$  at surfaces and interfaces can propagate some tens of nanometers into the film interior [22,26,30,40]. When thickness decreases to the nanoscale and depending on the relative strength of the perturbations, the average  $T_g$  across a single-layer film can decrease (PS on silica) or increase (PMMA on silica). With films with that lack

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an attractive interaction with a substrate, a recent study [31] comparing eight different polymer systems has found that the fragility of the bulk polymer, which correlates with frustration in packing of the chain segments [53], is a key (but not the only) parameter in defining the magnitude of the  $T_g$ -confinement effect. That study also indicated that other factors beyond fragility may play a role in the effect and that fragility alone may be insufficient to explain confinement effects in some methacrylate-based polymers.

The  $T_g$ -confinement effect in polymeric systems has major implications in a wide array of technologies, including tissue engineering [54,55], membranes for gas separation [56,57], and nanoelectronics [58,59]. Another critically important application of thin polymer films is as resists that are used for generating nanoscale circuits in the manufacture of microelectronics. Studies have shown that nanostructured features in thin PMMA films can significantly alter the  $T_g$  and other properties that are important in their functionality as resists [27,60–62]. In recent years, copolymers of alicyclic methacrylates have been used as photoresists in conjunction with 193-nm (ArF) immersion lithography [63–70]. Among the monomers incorporated in these copolymers include 1-ethyl cyclopentyl methacrylate (ECPMA), methyl adamantyl methacrylate (MAMA), hydroxyl adamantyl methacrylate (HAMA), and  $\alpha$ -gamma butyrolactone methacrylate (GBLMA). Each comonomer plays a specific role; for example, a photoacid-promoted deprotection of the ECPMA unit at high temperature leads to dissociation of a leaving group with an accompanying change in copolymer polarity and hence development contrast [71]. Such copolymers are often synthesized to have low molecular weight (MW) in order to achieve optimal lithographic resolution, for which high MW polymers are ill suited because of large coil dimensions and chain entanglements [63], and possibly reduced solubility [72].

Thus, studies of the  $T_g$ -confinement effect in low MW polymeric systems are of major importance. While some studies have examined the effect of confinement on  $T_g$  of low MW small-molecule (non-polymeric) glass formers, e.g., *o*-terphenyl, confined in nanopores [73–76], relatively little research has focused on low MW polymer films. The most comprehensive study [23] of the  $T_g$ -confinement effect as a function of polymer MW was done with PS films supported on silica. That study used fluorescence to demonstrate that there was little to no effect of MW on the  $T_g$ -confinement effect for PS with number-average molecular weight ( $M_n$ ) ranging from 5 to 3000 kg/mol and concluded that factors such as polymer coil radius of gyration, chain end segregation to the free surface, and chain entanglements did not play significant roles in the effect [23]. Other studies that investigated narrower ranges of PS MWs reported similar observations [3,13]. We note that Dutcher and co-workers have reported on the  $T_g$ -confinement effect in free-standing PS [6,7] and PMMA [8] films of various high MWs. However, all of the polymers had MW in excess of 100 kg/mol, making the interesting results, which reveal a significant MW dependence in high MW PS free-standing films, irrelevant for the current study.

Recently, Vogt and co-workers [5] reported an unexpected decrease in  $T_g$  upon confinement in silica-supported films of a commercial PMMA sample with  $M_n = 32$  kg/mol and dispersity = 2.6. After careful washing and precipitation to remove additives and the lowest MW fractions, they found that  $T_g$  decreased slightly from bulk  $T_g$  ( $T_{g,bulk}$ ) for thickness ( $h$ ) below 60 nm and increased for  $h < 20$  nm and suggested that the low MW components modified the behavior. Very recently, in a study of the effective viscosity of films of 2.7 kg/mol PMMA (dispersity = 1.09) supported on silica, Tsui and co-workers [77] reported as background results the effect of film thickness on  $T_g$ . At  $h = 20$  nm, they found that  $T_g/T_{g,bulk} = 1.01$ , in keeping with the report for high MW PMMA by Keddie et al. [2] but in opposition to the implications of

Vogt's study [5] that low MW PMMA should exhibit a decrease in  $T_g$  for sufficiently low  $h$ . Notably, a study focused on the  $T_g$ -confinement effect in low MW methacrylate-based polymers relevant for lithographic applications has yet to be reported.

Here, we investigate the  $T_g$ -confinement effect in silica-supported films of low and high MW PMMA and poly(1-ethyl cyclopentyl methacrylate) (PECPMA), the latter serving as a model polymer for the copolymers of alicyclic methacrylates used in photoresist production via 193 nm immersion lithography. A control study with low and high MW PS films is also reported. Ellipsometry yields the thickness dependence of  $T_g$ , glass transition breadth, and thermal expansion coefficients in both the glassy ( $\alpha_{glassy}$ ) and rubbery ( $\alpha_{rubbery}$ ) states. These studies clearly demonstrate that PMMA and PECPMA exhibit qualitatively and quantitatively different  $T_g$ -confinement effects at low and high MW while the effect for PS is independent of MW. Complementary fluorescence studies exhibit a MW dependence of  $T_g$ -confinement effect in single-layer films of PMMA and PECPMA similar to that shown by ellipsometry. Bilayer and trilayer PECPMA films characterized by fluorescence demonstrate that it is the perturbation to  $T_g$  caused by the free surface that is the origin of much of the MW dependence of the  $T_g$ -confinement effect, with a 20-nm thick free-surface layer in a bulk film exhibiting a much larger  $T_g$  reduction relative to  $T_{g,bulk}$  with low MW PECPMA than with high MW PECPMA.

## 2. Experimental

### 2.1. Materials and synthesis

Monodisperse PS [nominal MW = 4.0 kg/mol (dispersity  $\leq 1.06$ ), nominal MW = 170 kg/mol (dispersity  $\leq 1.06$ )] and PMMA [(nominal MW = 2.0 kg/mol (dispersity  $\leq 1.1$ ), 3.3 kg/mol (dispersity  $\leq 1.09$ ), and 1300 kg/mol (dispersity  $\leq 1.09$ )] (Pressure Chemical) were used as received. The ECPMA monomer was supplied by The Dow Chemical Company and used as received.

The PECPMA samples (unlabeled and labeled) were synthesized by free radical polymerization. Synthesis was done either in bulk monomer or dimethylformamide (DMF, Macron) to target different MWs. Details of initiator species and content, DMF content, and reaction temperatures are given in Table 1. The pyrene-labeled PECPMA (Py-PECPMA) samples were synthesized by adding trace levels of 1-pyrenylbutyl methacrylate to ECPMA monomer before synthesis and following procedures in Refs. [22,29]. After synthesis, polymers were purified by dissolving in tetrahydrofuran (THF) and precipitating in methanol three times for unlabeled polymers and seven times for labeled polymers. As measured by gel permeation chromatography (GPC) relative to PS standards in THF, unlabeled PECPMA samples were synthesized with a range of  $M_n$  values: 4.1, 4.7, 7.0, 22.5, 188, and 283 kg/mol. The two Py-PECPMA samples had

**Table 1**  
Conditions for PECPMA synthesis.

Material	Initiator (mmol)	Monomer (mol)	Solvent <sup>b</sup> (mol)	$T_{\text{synthesis}}$ (°C)	$M_n^c$ (kg/mol)	$M_w/M_n$
PECPMA	4.38 (AIBN)	0.021	0.040	80	4.1	1.79
PECPMA	3.65 (AIBN)	0.021	0.052	80	4.7	1.61
Py-PECPMA <sup>a</sup>	3.65 (AIBN)	0.021	0.052	80	4.9	1.53
PECPMA	1.21 (AIBN)	0.021	0.017	80	7.0	2.07
PECPMA	0.30 (AIBN)	0.021	0.017	80	22.5	1.85
PECPMA	0.041 (AIBN)	0.021	–	80	188	1.84
PECPMA	0.10 (BPO)	0.026	–	70	283	1.62
Py-PECPMA <sup>a</sup>	0.060 (BPO)	0.016	–	70	297	1.58

<sup>a</sup> Pyrene-labeled PECPMA.

<sup>b</sup> Dimethylformamide.

<sup>c</sup> Molecular weights were evaluated by GPC relative to PS standards in THF.

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