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Robertson, C. G.; Hogan, T. E.; Rackaitis, M.; Puskas, Judit D.; and Wang, X., "Effect of Nanoscale Confinement on Glass Transition of Polystyrene Domains from Self-assembly of Block Copolymers" (2010). *Chemical and Biomolecular Engineering Faculty Research*. 26.
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THE JOURNAL OF CHEMICAL PHYSICS **132**, 104904 (2010)

Effect of nanoscale confinement on glass transition of polystyrene domains from self-assembly of block copolymers

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(Received 20 October 2009; accepted 8 February 2010; published online 9 March 2010)

The understanding of size-dependent properties is key to the implementation of nanotechnology. One controversial and unresolved topic is the influence of characteristic size on the glass transition temperature (T_g) for ultrathin films and other nanoscale geometries. We show that T_g does depend on size for polystyrene spherical domains with diameters from 20 to 70 nm which are formed from phase separation of diblock copolymers containing a poly(styrene-co-butadiene) soft block and a polystyrene hard block. A comparison of our data with published results on other block copolymer systems indicates that the size dependence of T_g is a consequence of diffuse interfaces and does not reflect an intrinsic size effect. This is supported by our measurements on 27 nm polystyrene domains in a styrene-isobutylene-styrene triblock copolymer which indicate only a small T_g depression (3 K) compared to bulk behavior. We expect no effect of size on T_g in the limit as the solubility parameters of the hard and soft blocks diverge from each other. This strongly segregated limiting behavior agrees with published data for dry and aqueous suspensions of small polystyrene spheres but is in sharp contrast to the strong influence of film thickness on T_g noted in the literature for free standing ultrathin polystyrene films. © *2010 American Institute of Physics*. [doi:10.1063/1.3337910]

I. INTRODUCTION

Interest in nanoscale size effects on the glass transition temperature of glass-forming materials has grown substantially since the pioneering work in this area by Jackson and McKenna.[1] When the characteristic size is decreased to less than 100 nm, the influences of surfaces and interfaces on properties can become significant.[2,3] This is in contrast to large size scales, and hence small surface area to volume (S/V) ratios, where bulk properties alone dominate. Size effects may come from these contributions of surfaces/interfaces with altered mobility or from confinement features wherein the smallest dimension of the sample approaches the cooperative domain size at T_g or the characteristic length of the glass transition which is considered to be in the range from 1 to 4 nm.[4–8] Polymer confinement issues can also play a role at nanoscale dimensions when the size of the sample becomes less than the unperturbed radius of gyration of the chains.[9] This chain confinement aspect is generally only relevant at very high molecular weights or extremely small sizes, however, and we are not concerned here with situations where this is a significant factor. Rather, the focus of this paper is investigating intrinsic size effects.

The manner by which size influences the glass transition temperature has been considered by studying the behavior of liquids in pores, polymers confined between clay layers in nanocomposites, supported and free standing ultrathin polymer films, surface properties of films, and other approaches. The many contributions to this area have been nicely summarized in a recent review article,[3] and it is clear from that survey of the literature that there is no general experimental consensus, and certainly no widely accepted physical description, of how size affects T_g. Similar lack of clarity exists in the literature concerning the effect of proximity to a rigid particle on the segmental dynamics and T_g of polymers.[10]

Block copolymers are of interest due to their ability to self-assemble into nanoscale morphologies which can be exploited for templating, drug delivery, and other areas of nanotechnology.[11–16] These systems also provide a unique method to probe the size dependence of T_g. For block copolymer materials, if the relative length of the minor block is increased at constant total molecular weight, then the type of morphology changes (e.g., from spheres to cylinders to lamellae).[17] Increasing the length of both blocks in proportion to maintain approximately the same relative volume fractions, however, can largely preserve the type of phase-separated structure while modifying the characteristic size. For example, morphologies characterized by polyisoprene spheres with diameters from 10 to 600 nm surrounded by a polystyrene (PS) matrix have been generated with poly(styrene-block-isoprene) diblock copolymers using this approach.[18] We employ a similar method to vary the size of phase-separated PS spherical domains formed from a diblock copolymer system which has a poly(styrene-co-butadiene) soft block and a PS hard block. A triblock copolymer with PS endblocks and a polyisobutylene midblock is also included in our study. Our goal is to study the influence of the PS domain size on T_g. To critically evaluate the existence of an intrinsic size dependence of T_g, we compare our findings

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with the results from studies on other block copolymer systems,[19–22] free standing ultrathin PS films,[23,24] and small PS spheres.[25,26] Roth and Torkelson[27] recently demonstrated that chain connectivity across the immiscible interface has very little impact on the glass transition of the domains formed from diblock copolymers compared to similar multilayer films; this supports the validity of the block copolymer approach taken herein.

II. EXPERIMENTAL DETAILS

Linear diblock copolymers consisting of a styrene-co-butadiene random copolymer (SB) block and a styrene (S) block were studied. These SB-S diblock copolymers were synthesized in an 8 liter batch reactor via standard anionic polymerization in hexane solvent using *n*-butyllithium as an initiator and with the addition of a polar modifier. The SB block was polymerized first from a mixture of 1,3-butadiene and styrene in hexane. A sample of the SB was taken from the reactor before the PS blocks were subsequently synthesized. The microstructure of each SB sample was analyzed using ^{1}H NMR (Varian Mercury 300 MHz NMR) with deuterated chloroform as solvent. All of the SB polymers considered in our investigation possessed essentially equivalent microstructures, with average values for styrene content equal to 13 ± 1 mol % (22 wt %) and vinyl content of 56 ± 2 mol %. The styrene content is the amount of styrene in the SB random copolymer, and the vinyl content is the extent of 1,2-addition for the 1,3-butadiene polymerization. This microstructure yields a glass transition temperature of -34 °C. The relative amount of PS repeat units which were clustered in microblocks was also evaluated by ^{1}H NMR and was found to be small ($<5\%$ of the total styrene). Gel permeation chromatography (GPC) was performed in tetrahydrofuran solvent using a Waters Model 150-C with a refractive index detector. GPC measurements were conducted relative to PS standards, and the results were then converted to absolute molecular weight information by applying the universal calibration approach using molecular weight dependence of intrinsic viscosity data. The molecular weight of the PS which was blocked onto the SB was calculated from the amount of styrene charged to the reactor following completion of the SB synthesis. GPC and NMR measurements confirmed these values. Molecular weight distributions were narrow for the SB precursors and SB-S final materials ($M_w/M_n<1.10$). The hexane solution containing the final SB-S copolymer was coagulated into an excess of isopropanol, and the polymer was then dried. Slab samples with thickness of 2.0 mm were formed from the SB-S diblock copolymers by compression molding at 433 K. Modulated differential scanning calorimetry (MDSC) was performed using a TA Instruments Modulated DSC (Model 2920). Samples for MDSC, which were cut from the slab using a razor blade, had approximate thicknesses of 0.3 mm and weights of 9 mg. The samples were cooled from 423 to 133 K at 5 K/min in the MDSC and then tested from 133 to 473 K using an underlying heating rate of 5 K/min with a superimposed temperature modulation having an amplitude of 0.5 K and a period of 40 s. To allow quantitative measurements of heat capacity (C_p) versus temperature (T) to be made, a sapphire sample was used to calibrate the instrument. Sample morphology was measured at room temperature using a Dimension 3100 (Veeco Metrology Group) atomic force microscope (AFM). Etched silicon tips with nominal force constant of 6 N/m were used for all measurements. Imaging was performed in light tapping mode where the amplitude setpoint value was approximately equal to 70% of the free oscillation amplitude. A flat polymer surface was prepared by trimming the bulk polymer slab with a microtome (Leica Ultracut UCT) at a temperature of 143 K. Average surface roughness measured with AFM was below 10 nm. After thresholding, statistical analysis of the phase image was performed using standard AFM software and MATHWORKS MATLAB routines to determine the average PS domain diameter. AFM and MDSC were also performed on a commercial sample of styrene-isobutylene-styrene (S-IB-S) triblock copolymer (Kaneka SIBSTAR 102 T) with 15 wt % styrene and a total molecular weight of 100 kg/mol as reported by the manufacturer.

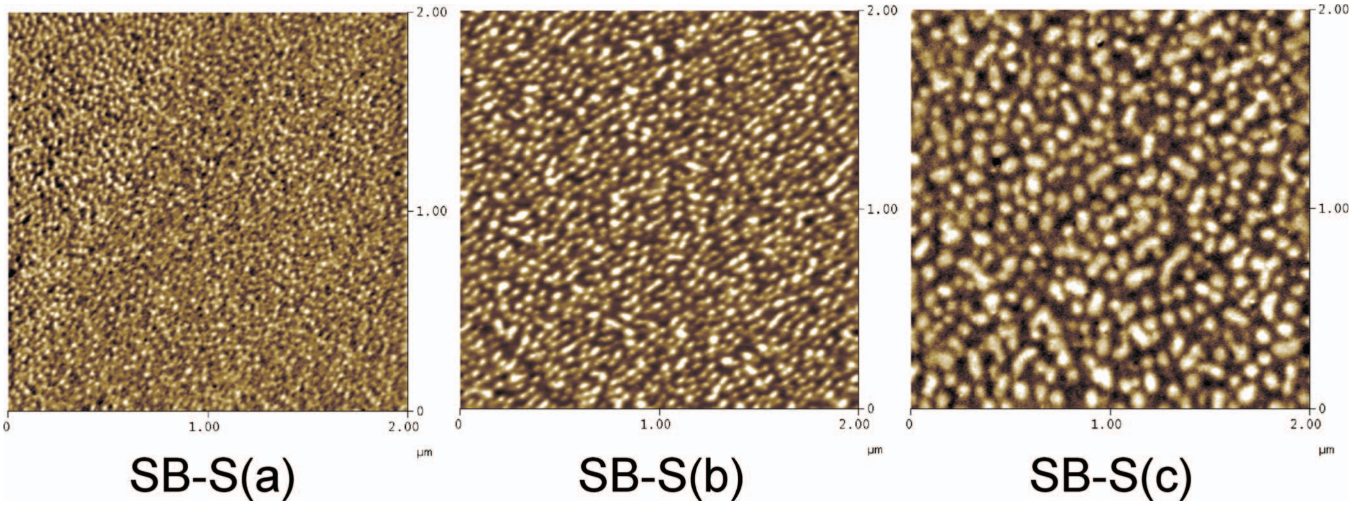

FIG. 1. AFM phase contrast images of the SB-S block copolymers. The harder regions appear lighter in color. The scans are 2×2 μm^2.

TABLE I. Properties of SB-S diblock copolymers.

	SB-S(a)	SB-S(b)	SB-S(c)
M_n of SB block (kg/mol)	91.5	183.6	255.6
M_n of S block (kg/mol)	10.0	20.0	30.0
Additional SB added	No	No	Yes[a]
Volume fraction of S block in sample[b]	0.09	0.09	0.09[a]
Diameter of PS domains by AFM (nm)	23 ± 6	34 ± 9	69 ± 22
T_g of PS domains by MDSC (K)	318 ± 3	343 ± 4	355 ± 3
T_g of bulk PS at M_n of S block[c] (K)	356	365	367
ΔT_g (K)	38	22	12

[a] Small amount of 260 kg/mol SB (without S block) was added to reduce S block volume fraction from 0.095 to 0.09 (blend contained 94 wt % SB-S and 6 wt % SB).

[b] Calculated using density values of 1.04 g/cc and 0.93 g/cc for S and SB blocks, respectively (Ref. 30).

[c] Determined from Eq. (1).

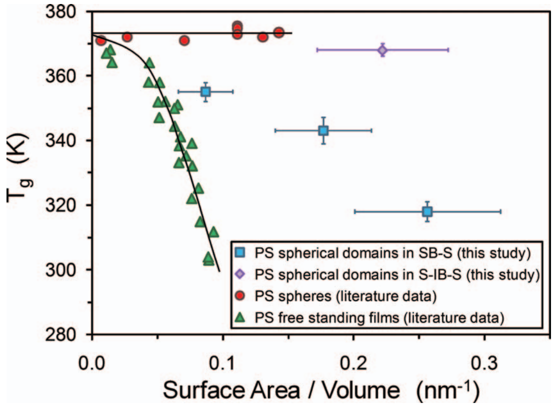

FIG. 3. Effect of S/V ratio on glass transition temperature of PS, including literature results for free standing films (Refs. 23 and 24) and spheres (Refs. 25 and 26). The lines are included only to guide the eye.

III. RESULTS AND DISCUSSION

Three SB-S diblock copolymers were produced with the S block as a minor component. In this series of block copolymers, the lengths of SB and S blocks were increased in near proportion to yield phase separated morphologies featuring PS spheres with average diameters varying from 20 to 70 nm surrounded by an elastomeric poly(styrene-co-butadiene) matrix. The AFM phase images which show these morphological features are given in Fig. 1, and the domain sizes and other details of the block copolymers are reported in Table I. These PS domain diameters were also confirmed using scanning transmission electron microscopy (results not shown here). The volume fraction of the PS phase was 0.09 for these materials. As is indicated in Table I, it was necessary to blend a small amount of poly(styrene-co-butadiene) with the highest molecular weight SB-S block copolymer in order to achieve this volume fraction.

The PS domains have a weak yet detectable glass transition response by MDSC. The first derivative of the C_p versus T data clearly shows the T_g behavior for the phase separated S blocks in the three SB-S diblock copolymers. This is demonstrated in Fig. 2. The glass transition is observed to substantially decrease in temperature and broaden as the size of the PS domains decreases. However, the size of the PS domains is proportional to the molecular weight, and the molecular weight dependence of T_g for polymers is well known. The concentration of mobile chain ends appears to be the controlling factor in the variation in segmental relaxation and T_g with molecular weight for polymers.[28] In order to see if the size of the block copolymer domains causes T_g to be depressed relative to bulk PS, we need to determine the bulk T_g at the respective molecular weights according to the Fox–Flory expression for atactic PS (Ref. 29)

$$T_g(\mathrm{K}) = 373 - [170/M_n(\mathrm{kg/mol})]. \tag{1}$$

The results are shown in Table I. Compared to the bulk T_g of PS, values for the reduction in T_g (ΔT_g) of 38, 22, and 12 K were found for SB-S(a), SB-S(b), and SB-S(c) diblock copolymers which correspond to average PS domain diameters of 23, 34, and 69 nm, respectively. The ΔT_g increases as the domain size of the PS phase is reduced for this block copolymer system.

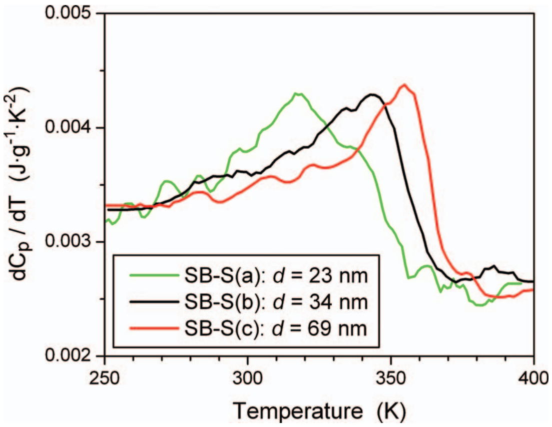

FIG. 2. Plot of dC_p/dT vs temperature from MDSC for the SB-S block copolymers.

It is useful to compare our findings with literature studies on the glass transition of PS at nanoscale dimensions. We can use the S/V to allow comparisons of different geometries. The S/V for a sphere is $6/d$, where d is the diameter. Due to the large aspect ratios of thin films and narrow cylinders, the surface contributions of edges and ends are neg-

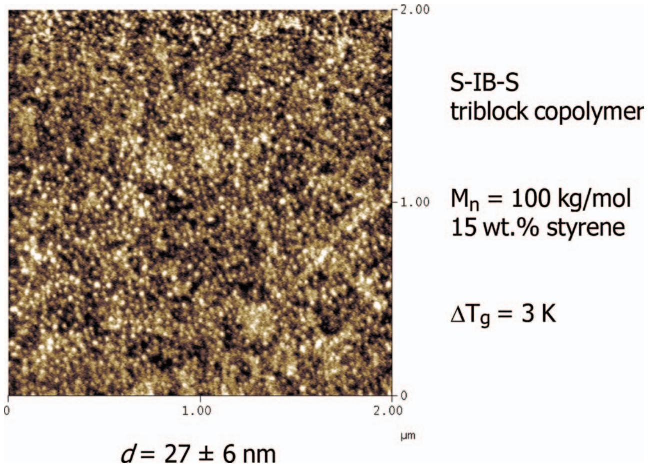

FIG. 4. AFM phase contrast image of the S-IB-S triblock copolymer. The harder regions appear lighter in color. The scan size is 2×2 µm^2. The T_g depression (ΔT_g) from MDSC is also given in this figure.

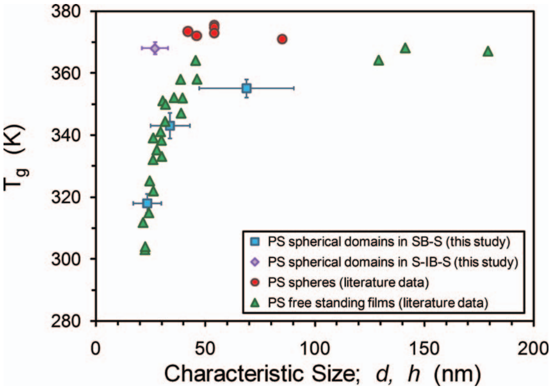

FIG. 5. Effect of characteristic size on glass transition temperature of PS, including literature results for free standing films (Refs. 23 and 24) and spheres (Refs. 25 and 26). For the characteristic size, the diameter (d) is used for the spheres and spherical block copolymer domains and the film thickness (h) is used for the films.

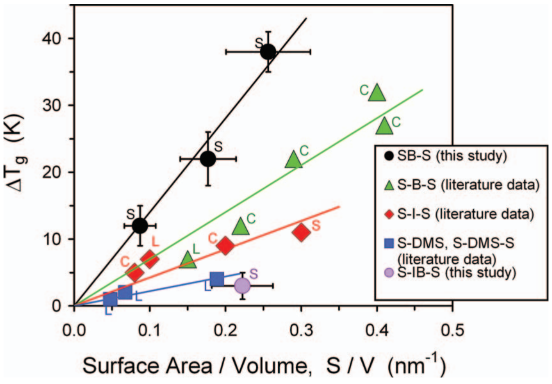

FIG. 6. T_g reductions relative to bulk PS as a function of surface area to volume ratio, S/V, for the indicated block copolymer systems [new results and literature data (Refs. 19–22)]. The solid lines are linear fits to the data with the intercepts fixed at zero. The letters near the symbols refer to the morphology of the PS phase: S=spheres, C=cylinders, and L=lamellae.

ligible. Therefore, S/V is well approximated by $2/h$ and $4/d$, respectively, for films or lamellae of thickness h and for cylinders of diameter d. Free standing ultrathin PS films display a remarkable influence of S/V on T_g.[23,24] On the other hand, small PS spheres, both dry[25] and in aqueous suspensions,[26] do not show any size dependence of T_g within the same range of surface area to volume ratio. Our results on the PS phase of the SB-S block copolymers are intermediate to these two dependences of T_g on S/V as illustrated in Fig. 3. We also evaluated one S-IB-S triblock copolymer sample, and the T_g depression is very small (3 K) despite 27 nm domain size (Fig. 4), in near agreement with the published data on PS spheres. These T_g comparisons between our block copolymer domains and literature results for PS films and small spheres are also shown versus characteristic size (h or d) in Fig. 5.

We can contrast the size dependence of T_g for our SB-S and S-IB-S block copolymer materials with published data[19–22] for diblock and triblock copolymers containing styrene (S) blocks and soft blocks of either isoprene (I), butadiene (B), or dimethylsiloxane (DMS). Analysis of literature data for these block copolymer systems, wherein PS is the hard phase with a spherical, cylindrical, or lamellar domain morphology, reveals that the T_g versus S/V relationship is weaker when the difference between the solubility parameters for the two phases becomes larger (see Table II and Figs. 6 and 7). For typical polymer systems which do not have specific interactions between components, the interfacial thickness in immiscible polymer blends and phase separated block copolymers is inversely proportional to $(\delta_A - \delta_B)^2$ where δ_A and δ_B are the solubility parameters for phase A and phase B.[31,32] This strongly suggests that the effect of S/V on T_g for our SB-S block copolymer system is related to diffuse interfaces with some degree of intermixing of phases and has nothing to do with an intrinsic size effect. This conclusion is further substantiated in Fig. 2 by the apparent increase in the glass transition breadth as the PS domain size is reduced for the series of SB-S block copolymers.

TABLE II. Solubility parameters and glass transitions of polymers.

Polymer	δ ($MPa^{1/2}$)[a]	T_g (K)
Polystyrene (PS)	19.1	375[b]
Poly(styrene-co-butadiene) (SBR), 25wt % styrene	17.3	239[c]
Polybutadiene (PBD), (predominantly 1,4)	17.1	173[b]
Polyisoprene (PI), (predominantly 1,4)	16.8	200[b]
Polyisobutylene (PIB)	16.1	201[b]
Poly(dimethylsiloxane) (PDMS)	15.0	146[d]

[a] All solubility parameters are from Shvarts (Ref. 37).
[b] T_g values from Böhmer *et al.* (Ref. 38).
[c] T_g for SBR from this study [SBR with 22 wt % styrene and 56% vinyl (1,2)].
[d] T_g for PDMS from Qin and McKenna (Ref. 39).

Attributing the broadening and reduction of T_g for nanosized PS domains to interfacial mixing implies that the difference in bulk glass transitions for the PS block and the soft block for the phase-separated block copolymers should play an important role in the extent of apparent T_g reduction. This is difficult to confirm with the present results. In addition to the flexibility and steric effects of chain backbones and pendant groups which are important to segmental dynamics and T_g,[33,34] the polarity of a polymer is a significant factor in the glass transition temperature, with more polar polymers (higher δ) typically having higher values of T_g.[35,36] This is the general trend for the data reported in Table II. Therefore, for the series of block copolymer systems we studied, the

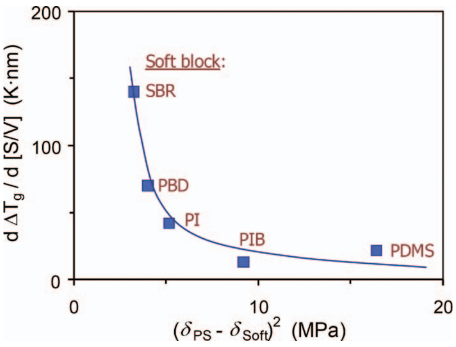

FIG. 7. Dependence of T_g depression on S/V ratio vs the square of the solubility parameter difference for the hard PS block and the soft block. The curved line is intended only to guide the eye.

interfacial thickness diminishes as the glass transition difference between PS and the soft block polymer increases such that the impact of the latter cannot be determined.

IV. FINAL COMMENTS

We expect that strongly segregated block copolymer phases with divergent solubility parameters for the soft and hard blocks will show no variation in T_g for the PS hard block due to nanoscale domain size. This limiting behavior agrees with the literature data for nanosized PS spheres (dry and in aqueous suspensions) but is in clear disagreement with published results for free standing PS ultrathin films. The reason for the unique strong size dependence of T_g for the PS films is not known. Experimental artifacts as well as film preparation factors and related metastability may contribute to the apparent variation in T_g at these very small thicknesses, as suggested by others.[40–43] Work by Bodiguel and Fretigny[44,45] and Lu *et al.*[46] showed that relaxed ultrathin PS films floating on liquid surfaces exhibited glass transitions which were close to the bulk polymer T_g.

There are certainly studies which provide supporting evidence for the pronounced influence of h on T_g for PS films. The film thickness dependence of T_g for PS reported by Forrest *et al.*[23,24] was confirmed by O'Connell *et al.*[47,48] using a microbubble inflation technique, but they also found an unexpected dramatic stiffening of the films with decreasing thickness. Further support was provided by dielectric spectroscopy results which showed enhanced segmental mobility with decreasing h for PS (Refs. 49–51) and by testing using a fluorescence method which showed reduced T_g as PS film thickness was decreased.[52]

Given all of the above, it is quite possible that other effects (surface tension, nonequilibrium chain orientation and packing, etc.) are responsible for the observed T_g variation with thickness for PS films, rather than $T_g = f(h)$ reflecting an intrinsic size dependence of the glass transition or reflecting a significantly enhanced polymer mobility at a free surface. PS may be a special case, because we note that ultrathin films of poly(methyl methacrylate),[53] poly(vinyl acetate),[47] and poly(2,6-dimethyl-1,4-phenylene oxide),[54] as well as microtome-sliced epoxy specimens[55] do not show the same strong dependence of film thickness on T_g.

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