

Glass Transition of Miscible Binary Polymer-Polymer Thin Films

Brian M. Besancon,¹ Christopher L. Soles,² and Peter F. Green^{3,*}

¹*Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, USA*

²*NIST Polymers Division, Gaithersburg, Maryland 20889-8541, USA*

³*Department of Materials Science and Engineering, Applied Physics, University of Michigan, Ann Arbor, Michigan, USA*

(Received 2 March 2006; published 31 July 2006)

The average glass transition temperatures, T_g , of thin homopolymer films exhibit a thickness dependence, $T_g(h)$, associated with a confinement effect and with polymer-segment–interface interactions. The T_g 's of completely miscible thin film blends of tetramethyl bisphenol-A polycarbonate (TMPC) and deuterated polystyrene (dPS), supported by SiO_x/Si , decrease with decreasing h for PS weight fractions $\phi > 0.1$. This dependence is similar to that of PS and opposite to that of TMPC thin films. Based on an assessment of $T_g(h, \phi)$, we suggest that the $T_g(h, \phi)$ of miscible blends should be rationalized, additionally, in terms of the notion of a self-concentration and associated heterogeneous component dynamics.

DOI: 10.1103/PhysRevLett.97.057801

PACS numbers: 61.41.+e, 68.15.+e, 68.60.–p

The physical properties of polymers confined to sufficiently small dimensions by external “walls” are generally difficult to predict because they manifest the influence of a confinement effect as well as the influence of interfacial interactions between the material (chemical) constituents and the external “walls.” For example, the glass transition T_g of thin, supported polymer films is influenced by the relative monomer-monomer and monomer-interface (substrate or free surface) interactions [1,2]. The T_g of freely standing films, and of films supported by weakly interacting substrates, such as polystyrene (PS) on oxidized silicon wafers, is known to decrease with decreasing film thickness h [3,4]. When the interactions between the chain segments and the substrate are particularly strong, such as tetramethyl bisphenol-A polycarbonate (TMPC) on oxidized silicon wafers, the glass transition increases with decreasing h [5]. Theories based on energy landscape (configurational entropy) models [6], packing densities [7], or dynamic percolation [8] yield predictions consistent with the foregoing.

With few exceptions, the vast majority of studies on the T_g of polymer thin films have been performed on homopolymers [1,2]. An important unanswered question is what factors determine the T_g of miscible thin film polymer-polymer mixtures? We show that while relative monomer-substrate, monomer-monomer, and monomer-free surface interactions determine the average T_g of a homopolymer film, the self-concentration, intrinsic to long-chain polymers, and the associated heterogeneous dynamics are additional factors that determine the T_g of miscible polymer-polymer systems.

We performed incoherent elastic neutron scattering (INS) measurements of completely miscible binary polymer-polymer blends of bulk and thin film samples of deuterated polystyrene (dPS) and TMPC, supported by SiO_x/Si substrates (oxidized silicon wafers). The INS

technique [9] measures the mean square atomic displacements of thermal motions in dPS/TMPC thin films while simultaneously providing the glass transition temperature. Since TMPC is the only hydrogenated species, we learn about its behavior within the blend (TMPC effectively determines the incoherent scattering). In these miscible systems, we see evidence of a separate glass transition, distinct from the average T_g of the film, measured by spectroscopic ellipsometry (SE) in an earlier study [4]. Specifically, the SE measurements revealed that for mixtures containing more than 90 wt% TMPC, $\Delta T_g > 0$, whereas for smaller TMPC concentrations, $\Delta T_g < 0$ [4,5]. The implications of these observations on the T_g of thin film mixtures is examined.

Thin film mixtures of TMPC ($M_w = 37\,900$ g/mol; $M_w/M_n = 2.75$ and $T_g = 220$ °C) obtained from Bayer, Corp., and fully deuterated polystyrene, (d_8 -PS, $M_w = 139\,900$ g/mol; $M_w/M_n = 1.06$, $T_g = 100$ °C) purchased from Polymer Source, Inc., were dissolved in toluene. These solutions were then spin cast onto cleaned (100) silicon wafers (Wafer World, Inc.; 75 mm diameter; ≈ 350 μm thick), which had a native oxide layer of 1.5 nm as determined by ellipsometry. Film thicknesses of 20, 30, 50, and 120 nm were prepared and subsequently annealed 30 K above their T_g 's for at least four hours.

Approximately 13 wafers of each film thickness were broken into strips and placed in a cylindrical, thin-walled aluminum cell, which was mounted on the high flux back-scattering spectrometer (HFBS) [10] on the NG2 beam line at the NIST Center for Neutron Research and cooled to 50 K under vacuum. The spectrometer operated in the fixed window mode (stationary Doppler drive) with the elastic intensities recorded over a Q range of 0.25 to 1.75 \AA^{-1} . The sample temperature T was increased to $T = 525$ K at rates of 0.6 K/min (120 nm films) to 0.3 K/min (30 nm films). The elastic intensities were summed over intervals

of 1.5 to 3 K. Since the HFBS energy resolution is $0.8 \mu\text{eV}$ (FWHM), the dynamics on a time scale of 200 MHz (approximately a nanosecond) or slower contributed to elastic scattering; faster processes contributed to inelastic scattering and a subsequent reduction of the elastic intensity. In this system of TMPC ($\text{C}_{20}\text{H}_{22}\text{O}_2$) and d_8 -PS, only the TMPC dynamics are measured, since the scattering is dominated by the incoherent scattering cross section of hydrogen, which is approximately 20 times greater than that of C, O, or ^2H (deuterium). Dynamics due to the silicon are transparent.

The incoherent elastic scattered intensity, $I(Q)$, summed over $0.36 \text{ \AA}^{-1} \leq Q \leq 1.75 \text{ \AA}^{-1}$, is plotted in Fig. 1 as a function of temperature for three samples containing 50 wt % TMPC. At temperatures $T < 200$ K, the scattered intensity is well approximated by the Gaussian approximation

$$I(Q) \propto \exp(-\frac{1}{3}Q^2\langle u^2 \rangle), \quad (1)$$

where $\langle u^2 \rangle$ is the mean square atomic displacement. The deviation from linearity of the data near $T = 200$ K for each curve is a sub- T_g relaxation that was attributed to a carbon-carbon torsional motion [11]. Since methyl rotation is typically observed below 100 K [12], the relaxation near 200 K could be induced by phenyl ring motions that would enable larger amplitude motions of the methyl groups.

The intensity in Fig. 1 drops less rapidly with temperature in the thinner films, which is associated with the fact that the mean square displacements $\langle u^2 \rangle$ decreased with decreasing film thickness. This suggests that the motions in thin polymer films possibly become faster and more localized due to a reduction and a shift to higher frequency of the density of states [9,13]. A reduction in the density of states with no shift in frequency would also suppress [14].

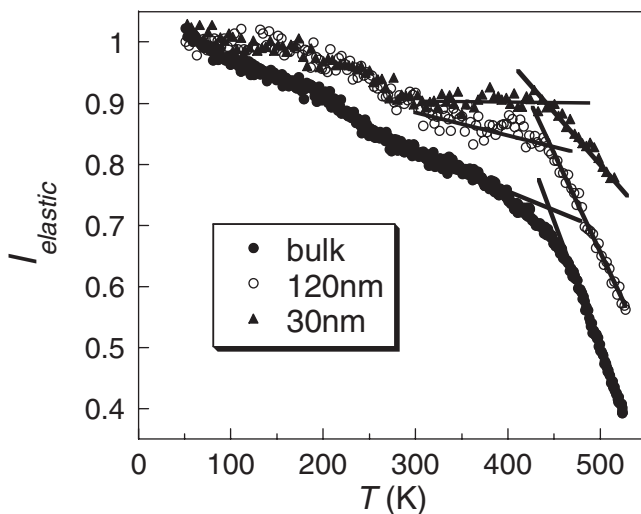


FIG. 1. The elastic scattered intensity plotted as a function of temperature for the 50 wt % TMPC/dPS samples.

The glass transition of the mixtures is now discussed. As shown in Fig. 1, the glass transition temperature, at $T = 445$ K, is identified by the midpoint of the kink in the curve. The T_g may, alternatively, be determined from changes in the slope of the mean square displacement, $\langle u^2 \rangle(T)$ versus T [using Eq. (1)]; such values of T_g agree with those determined from the I versus T data [9]. The T_g 's obtained from the INS and SE [and differential scanning calorimetry (DSC) for the bulk samples] measurements are plotted in Figs. 2(a)–2(c) as a function of composition for the 30 nm, 120 nm, and bulk samples. The values of T_g determined using these techniques are different. SE and DSC measure mixture average values of T_g , whereas INS intensities reflect the dynamics of the TMPC component only.

The implications of the distinct T_g 's measured by these techniques in completely miscible blends are rationalized below. Dynamics in binary, miscible, polymer-polymer mixtures are known to be heterogeneous [15–18]. Distinct dynamical signatures associated with each component, temperature-dependent distributions of relaxation times, and distinct component T_g 's within the blend are evidence of this dynamic heterogeneity.

The underlying reasons for the heterogeneity in the dynamics have been examined by a number of authors [16–20]. Chain connectivity [17,18] necessarily implies that a monomer on the A chain (B chain) will have an intrinsically higher concentration of A monomers (B monomers), locally, than the average concentration. This is often referred to as a self-concentration ϕ_s . The effective local concentration ϕ_{eff} , based on the Lodge-McLeish model [18], is determined by ϕ_s such that

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi. \quad (2)$$

The model assumes that the length scale of the local region of enriched concentration around a given monomer is the Kuhn length and is independent of temperature, in relation to our data [18]. Concentration fluctuations are believed to play an additional role and suggest a diverging length scale (beyond the Kuhn length) or a cooperative volume (Adam and Gibbs) to define the relevant local region near T_g [16,19,20]. However, there appears to be some consensus that the natural length scale over which the dynamics are affected is a dimension on the order of the Kuhn segment length.

According to the Lodge-McLeish model, component A of the mixture actually senses a different effective T_g determined by

$$T_g^{\text{eff}}(\phi) = T_g(\phi)|_{\phi=\phi_{\text{eff}}}. \quad (3)$$

The SE determined (average) T_g values in Figs. 2(a) and 2(b) were fit to the virial equation [21,22],

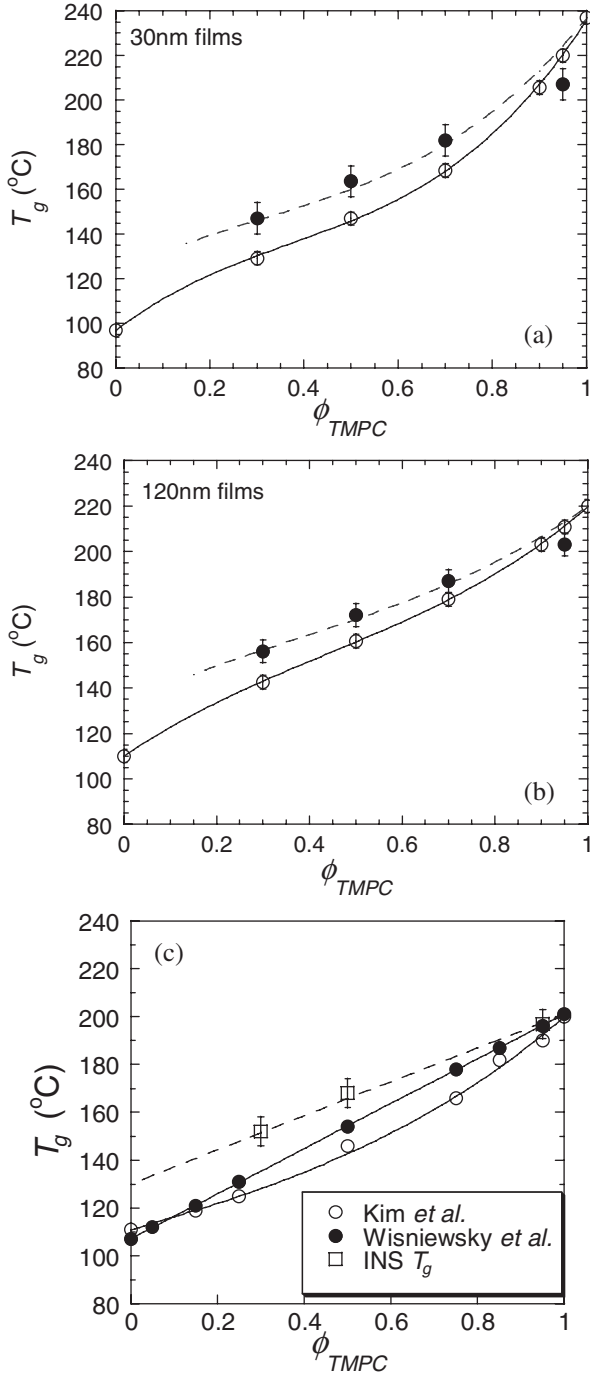


FIG. 2. The glass transition temperatures from ellipsometry (solid line and open symbols) are plotted along with the TMPC effective component T_g values measured from INS (closed symbols). The fit of the Lodge-McLeish model is also shown (dotted line) for the (a) 30 nm thick films, (b) 120 nm thick films, and (c) the bulk samples.

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 - K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2w_{2c}^3. \quad (4)$$

In this equation, T_g is the value of the mixture, T_{gi} are the

T_g 's of the individual components, K_1 and K_2 are constants, $w_{2c} = Kw_2/(w_1 + Kw_2)$, $K = T_{g1}/T_{g2}$, and w_i is the fraction of component i . The self-concentration was determined through a least squares fit to the data using Eq. (4) evaluated at ϕ_{eff} ; ϕ_s was the only adjustable parameter. We also estimated the bulk self-concentration from our INS measurements and the DSC T_g values reported by Wisniewsky *et al.* [23] to be $\phi_{s,\text{bulk}} = 0.24$. A similar analysis of the DSC T_g data of Kim *et al.* [24] yielded a value of $\phi_{s,\text{bulk}} = 0.44$. However, an analysis of the temperature-dependent friction factor data of Kim *et al.* [24], by He *et al.* [25], using the Lodge-McLeish model, determined a single, temperature-independent value of $\phi_{s,\text{bulk}} = 0.25$. The calculated values of the self-concentration are plotted in Fig. 3 as a function of film thickness. The self-concentration increases slightly as the thickness decreases, suggesting that TMPC monomers experience an environment slightly richer in TMPC than they do in the bulk.

To this end, we comment on recent findings [26,27] in relation to our data in Fig. 3. It has been shown that interactions between monomers on a chain are not screened on length scales beyond the excluded volume screening length, ξ , in contrast to the classical theory of Flory. In the absence of the long-ranged interactions, the classical theory would indicate a composition gradient at a "wall" that would fall off on the order of ξ (~ 1 nm). However, with the long-ranged interactions, the gradient should be larger and on the order of $\xi \log(N/\xi^2)$ [27]. Nevertheless, the effect is still small and should not be an issue with regard to our conclusions. We, in fact, measured the profiles using neutron reflectivity, and near the substrate, the gradient falls off at approximately 6 nm; near the free surface, it is smaller, 4 nm.

The data in Fig. 3 indicate that the self-concentration of the thinnest film is the largest. Chains with a center of mass close to an interface (comparable to the screening length)

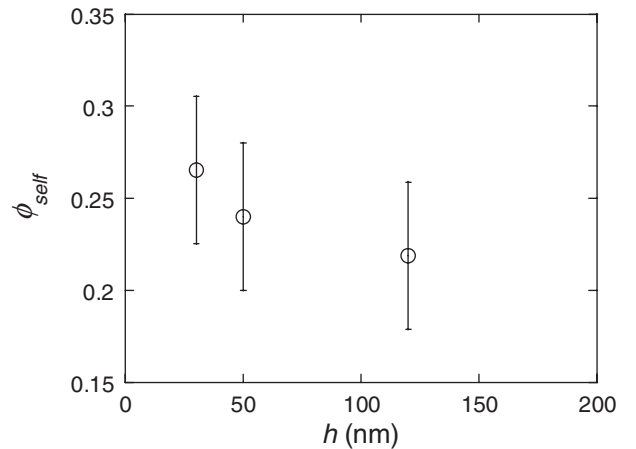


FIG. 3. The calculated values of the TMPC self-concentration shown to increase with decreasing h .

will increase in dimensions parallel to the interface, and because of the long-ranged interactions, they will exclude unlike chains on length scales larger than ξ ; the chain will fold back on itself and squeeze out neighboring chains [27]. This would increase the local concentration surrounding a given TMPC segment, as segments from neighboring chains would be excluded.

In conclusion, the relative monomer-substrate, monomer-monomer, and monomer-free surface interactions determine the average T_g of a homopolymer film. In the case of miscible polymer-polymer mixtures, the additional consequences of a self-concentration (a natural consequence of chain connectivity) and the associated heterogeneous dynamics are responsible for the glass transition.

This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672, and was funded by the National Science Foundation (No. DMR-0601890) and the Robert A. Welch Foundation. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron facilities used in this work. B. M. B. thanks Eugene Mamontov and Victoria Garcia-Sakai for their help with the HFBS instrument. Finally, we would like to thank Marcus Müller for a helpful discussion regarding the latter aspects of this Letter.

*Electronic address: pfgreen@umich.edu-correspondence

- [1] M. Alcoutlabi and G.B. McKenna, *J. Phys. Condens. Matter* **17**, R461 (2005).

- [2] J. Baschnagel and F. Varnik, *J. Phys. Condens. Matter* **17**, R851 (2005).
[3] J.A. Forrest and K. Dalnoki-Veress, *Adv. Colloid Interface Sci.* **94**, 167 (2001).
[4] J.Q. Pham and P.F. Green, *Macromolecules* **36**, 1665 (2003).
[5] J.Q. Pham and P.F. Green, *J. Chem. Phys.* **116**, 5801 (2002).
[6] J. Mittal *et al.*, *J. Phys. Chem. B* **108**, 19769 (2004).
[7] J.D. McCoy and J.G. Curro, *J. Chem. Phys.* **116**, 9154 (2002).
[8] D. Long and F. Lequeux, *Eur. Phys. J. E* **4**, 371 (2001).
[9] C.L. Soles *et al.*, *Phys. Rev. Lett.* **88**, 037401 (2002).
[10] A. Meyer *et al.*, *Rev. Sci. Instrum.* **74**, 2759 (2003).
[11] J. Colmenero and A. Arbe, *Phys. Rev. B* **57**, 13508 (1998).
[12] B. Frick and L.J. Fetters, *Macromolecules* **27**, 974 (1994).
[13] C.L. Soles *et al.*, *Macromolecules* **37**, 2890 (2004).
[14] R. Inoue *et al.*, *Phys. Rev. Lett.* **95**, 056102 (2005).
[15] R.H. Colby, *Polymer* **30**, 1275 (1989).
[16] A. Zetsche and E. W. Fischer, *Acta Polym.* **45**, 168 (1994).
[17] G.C. Chung *et al.*, *Macromolecules* **27**, 964 (1994).
[18] T.P. Lodge and T.C.B. McLeish, *Macromolecules* **33**, 5278 (2000).
[19] S.K. Kumar *et al.*, *J. Chem. Phys.* **105**, 3777 (1996).
[20] R. Kant *et al.*, *Macromolecules* **36**, 10087 (2003).
[21] M.J. Brekner *et al.*, *Polymer* **29**, 78 (1988).
[22] H.A. Schneider and E.A. Di Marzio, *Polymer* **33**, 3453 (1992).
[23] C. Wisniewsky *et al.*, *Eur. Polym. J.* **20**, 691 (1984).
[24] E. Kim *et al.*, *Macromolecules* **28**, 1979 (1995).
[25] Y. He *et al.*, *J. Chem. Phys.* **119**, 9956 (2003).
[26] A.N. Semenov and A. Johner, *Eur. Phys. J. E* **12**, 469 (2003).
[27] A. Cavallo *et al.*, *J. Phys. Condens. Matter* **17**, S1697 (2005).