Nanoscopic Resolution of the Glass Transition within Spatially Inhomogeneous Polymer Mixtures

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Christie, Register, and Priestley report the first direct measurement of the glass transition temperature as a function of location within a bulk nanostructured polymer material.

Resistant to fundamental theory and ill-defined in experiment, yet central to so many processes and applications, the glass transition represents an enduring challenge in polymer science.1 Qualitatively, the glass transition occurs over the temperature range where substantial backbone motions cease on cooling. All plastics are therefore utilized at temperatures well below the nominal glass transition temperature, \( T_g \), whereas processing operations occur as far above \( T_g \) as practical. The temperature interval \( \Delta T = T - T_g \) exerts a profound influence on the rate of any dynamic process, be it the relaxation and diffusion of individual chain molecules or the mobility of small molecule penetrants, such as ions in battery separators and fuel cell membranes. Many emerging high-value-added applications of polymeric materials involve nanostructures, such as self-assembled block polymers or polymer-based nanocomposites, which contain substantial quantities of interfacial material and steep gradients in chemical composition. Therefore, understanding the compositional and spatial variation in \( T_g \) assumes paramount importance in designing new nanostructured polymeric materials.

The model system comprises nearly symmetric block copolymers of poly(methyl methacrylate) (PMMA) and poly(\( \pi \)-butyl methacrylate) (PBMA), which self-assemble into lamellae—a layered nanostructure with alternating domains and a total period of thickness \( d \approx 27 \text{ nm} \) (see Figure 1). As illustrated schematically in the figure, the end-to-end vector of each chain is aligned on average along the \( z \) coordinate, with the block junction tethered to an approximately 4 nm interfacial zone. The team prepared a series of 24 model block copolymers, in which the location of the fluorescent label was systematically varied along the chain. Self-consistent mean-field theory allows reliable calculation of the composition profile as a function of the total degree of polymerization, the volumetric composition, and a parameter based on the energy of interaction between the two blocks.3 In this way it is possible to compute the environment experienced by the fluorophore label for a given chain position and distance from the interface. The apparent \( T_g \) was determined for each label position and mapped onto a \( z \) coordinate within the lamellar period. The \( T_g \) varied by almost 90 °C across one-half period, with the major effect being a remarkable 40 °C drop over the 4 nm interfacial region. These results,

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Figure 1. Alternating layers of PMMA (blue) and PBMA (red), with wide interfacial zones (\( t \approx 4 \text{ nm} \)). The yellow “monomer” indicates a specific location of the fluorescent tag.

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while not surprising, have profound implications for understanding dynamics in block copolymer nanostructures. It is well established that the segmental relaxation time for a polymer can range over at least 12 orders of magnitude for $0 < \Delta T < 100$ °C, following a distinctly non-Arrhenius temperature dependence. Furthermore, both chain motions and transport of most small molecules depend on the segmental relaxation time. Thus, any equilibration process that requires chain motion, or movements of ions, will depend very sensitively on $\Delta T$ along the z coordinate. Note that this effect may be further complicated by thermodynamic barriers to motion, such as when the ion is much better solvated by one block than the other.

The authors interpret their data in the context of the self-concentration model (see Figure 2). This simple model was developed two decades ago, motivated by extensive measurements of component dynamics in miscible blends that revealed an interesting assortment of seemingly anomalous phenomena. It rationalized all of these phenomena at least qualitatively, and in many cases quantitatively. The two key ingredients of the model are (i) the assumption that a polymeric segment is sensitive to its environment primarily on the scale of the length $\lambda_K$ (the distance over which the chain can reverse course, typically $\sim$1 nm for most carbon-backbone polymers), and (ii) this local environment for a given monomer is inevitably enriched in the same species, due to chain connectivity. This local excess is termed the self-concentration and can achieve fractions as large as 0.5. Consequently, even in a macroscopically homogeneous miscible blend, the two monomers experience quite distinct average compositions. If the two components have very different $T_g$’s, then the effective $T_g$ for each component is a strong function of local composition. This model makes several illuminating predictions, the most remarkable of which is that one can observe two distinct component $T_g$’s in a miscible blend, which refutes the longstanding conventional wisdom that two $T_g$’s is a reliable diagnostic of phase separation. Most importantly, the model explains why segmental relaxation time of the two components can have very different dependences on temperature, leading to the well-known failures of the principle of time–temperature superposition in miscible blends. This model allows Christie et al. a way to interpret their observed spatial variation of $T_g$ based on the spatial variation in composition.

In recent years there has been tremendous interest in understanding the spatial variation of $T_g$ in thin films, and at surfaces. Typically a “hard” surface with attractive interactions increases the local $T_g$ whereas a free surface reduces it; however, there are exceptions to this synopsis, and the relatively large propagation length away from the sharp interface remains a topic of debate. The work of Christie, Register, and Priestley goes well beyond these studies in two important ways. First, their measurements can be applied within the bulk of a nanostructured material and are in no way constrained to thin films. Second, they address nanoscale variations in mean composition, an essential aspect of block polymer nanostructures, whereas the “thin film $T_g$” field has almost exclusively considered polymers consisting of only a single block. This work opens the door to a wide range of further studies, albeit significant synthetic effort is required. Fortunately, the polymer field has been blessed with many recent advances in controlled polymerization techniques, so this challenge is not nearly as daunting as it might have been 20 years ago. One example where this approach could be most illuminating is in the dynamics of block copolymer micelles. Escape of a single chain from a micelle requires surpassing a substantial thermodynamic barrier, as the core-forming block does not “like” the solvent. It is also likely that segmental relaxation time varies significantly with radial position within the core, due to possible penetration of solvent and an inevitable compositional gradient at the core/corona interface; as yet, however, there has been no quantification of this effect.

Figure 2. The self-concentration concept. A test monomer (teal sphere) senses the composition of the local environment to a radius of about the length $\lambda_K$. Due to chain connectivity alone, the environment is guaranteed to be enriched in teal monomers, compared to the bulk composition.

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Notes
The author declares no competing financial interest.

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