

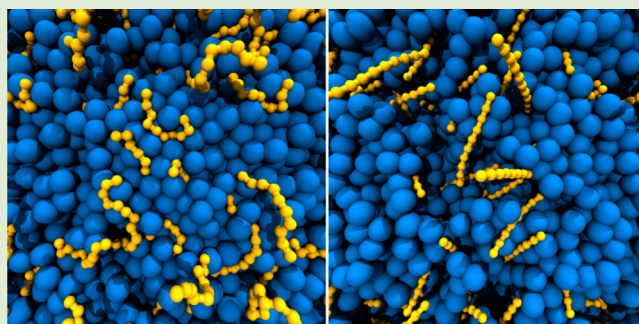
Tuning Polymer Glass Formation Behavior and Mechanical Properties with Oligomeric Diluents of Varying Stiffness

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Supporting Information

ABSTRACT: Small-molecule diluents are important tools in the control of polymers' glass formation, transport, and mechanical properties. While recent work has indicated that these diluents can impose a more diverse range of effects than previously appreciated, use of these additives to rationally control polymer properties requires a predictive understanding of their effects. Here we employ molecular dynamics simulations to show that diluent-induced changes in a polymer's glass transition temperature T_g can be predicted based on the diluent's Debye–Waller factor $\langle u^2 \rangle$, a measure of picosecond time scale rattle-space, via a functional form previously found to predict nanoconfinement-induced shifts in polymer T_g . Moreover, we show that diluent-induced alterations in polymer segmental relaxation time are related to changes in modulus and $\langle u^2 \rangle$ via the Generalized Localization Model of relaxation. These results provide new design principles for the use of oligomeric diluents in achieving independent, targeted control of structural relaxation and glassy moduli.



Introduction of a molecular diluent, a low-volume-fraction additive, is one of the longest-standing methods of modifying a polymer's properties without dramatically altering its chemistry. Diluents can improve a polymer's performance, inducing changes in its glass transition temperature T_g , structural relaxation time τ_w , moduli, and other related properties. Although diluents have traditionally been divided into two classes, plasticizers and antiplasticizers, recent evidence indicates that their array of possible effects is far richer than suggested by this binary classification scheme.^{1,2} For example, observed diluent effects include suppression of T_g and the high-frequency glassy modulus G_∞ (plasticizers), suppression of T_g coupled with low-temperature enhancement of G_∞ ^{3–7} (antiplasticizers), suppression of T_g with high-temperature enhancement of G_∞ ², and enhancement of T_g .⁸ These examples illustrate that diluents can independently tune low-frequency dynamics (as reflected in T_g) and high-frequency dynamics (as reflected in G_∞) in a temperature-dependent manner,^{1,3,6,9–11} suggesting new opportunities for diluent-based rational polymer design. Leveraging these opportunities will require a deeper understanding of diluent effects, accounting for potentially distinct, temperature-dependent impacts on high- and low-frequency dynamics.

Here we employ molecular dynamics simulations of polymer/diluent blends to guide selection of diluent molecular properties producing targeted alterations in polymer linear-regime dynamics. Inspired by recent predictions of the Generalized Entropy Theory (GET) of glass formation,^{1,12} which is based on an extension of the Adam–Gibbs theory of glass formation,¹³ we focus on the role of diluent molecular stiffness in determining these alterations. Simulation details are

provided in the Supporting Information (SI). In summary, we simulate a melt of attractive, unentangled bead–spring polymer chains,¹⁴ in which nonbonded beads interact via a 12–6 Lennard–Jones potential with characteristic energy ϵ and length scale σ , with both values equal to one for the polymer. In addition to a pure “reference” melt, we introduce 5% by volume of diluents ranging from single beads to stiff oligomers, with this volume fraction chosen because it corresponds to a concentration at which antiplasticizers often exhibit a maximum effect.¹⁵ Consistent with prior work on polymer/diluent blends, we focus on the case where σ for diluent beads is half of that for polymer beads, mimicking commonly “bulkier” chemical moieties in polymer chains as compared to small-molecule diluents.^{6,7,11,16} Glass formation is simulated via a quench-and-anneal procedure that is inspired by experimental glass formation and is widely used in the literature.^{6,10,11,17–19}

We begin by characterizing diluent-induced alterations in the polymer's low-frequency dynamics, as quantified by τ_w defined here as the time at which the self-part of the intermediate scattering function, calculated for the polymer segments only, decays to a value of 0.2. This yields results comparable to time-resolved incoherent neutron scattering. From this data, we determine T_g via two conventions to account for the gap between computationally accessible times and the time scale of the laboratory T_g : we obtain a “computational” dynamic T_g based on the temperature T_g^c at which simulations fall out of

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equilibrium on a time scale of $10^3 \tau_{LJ}$ (the LJ unit of time) and an “extrapolated” T_g at the temperature T_g^c at which a Vogel–Fulcher–Tammann^{20–22} fit to in-equilibrium τ_α data extrapolates to $10^{14} \tau_{LJ}$, corresponding to an ~ 100 s experimental T_g convention. We additionally compute computational time scale T_g^s via two pseudothermodynamic conventions: a calorimetric temperature T_g^{CP} at which the energy versus temperature curve changes slope and an analogous dilatometric temperature T_g^v . However, recent work has emphasized the insufficiency of T_g as a measure of low-frequency structural relaxation,^{9,23,24} because changes in the temperature-breath of the glass transition can decouple shifts in τ_α from shifts in T_g .^{1,3,6,9–11} These changes are commonly quantified via the kinetic fragility index $m = \partial \log \tau_\alpha / \partial (T_g/T)|_{T=T_g}$. m quantifies the T_g -normalized “abruptness” with which dynamics slow down upon approach to T_g and is generally suppressed by classical plasticizers and antiplasticizers.¹ m is relevant to polymer processing, which is impacted by the temperature-dependence of τ_α . As with T_g , we compute computational and extrapolated values of m (m^c and m^e , respectively) by applying its definition at T_g^c and T_g^e , respectively. As shown in Figure 1, results are qualitatively insensitive to the choice of T_g and m convention. Except where noted, throughout this paper, standard deviations on plotted data, as determined from four independent runs, are similar to or fall within the size of the points.

To isolate the effects of diluent chemical bulkiness, degree of polymerization, and stiffness, we perform a series of simulations building up to stiff oligomers in a stepwise fashion. First, we introduce a diluent consisting of individual beads of size $\sigma = 1$, equal to the chain monomers. As shown by Figure 1a,b, this diluent has little effect on polymer segmental dynamics at this volume fraction ϕ . Maintaining the same ϕ , we then reduce diluent size to $\sigma = 0.75$ and 0.5 , which reduces T_g and m , consistent with results in prior simulations.^{6,10,11} Given the weak alterations induced by the $\sigma = 1.0$ diluent (or upon reducing chain length from 20 to 10 in a pure melt, shown in Figure 1b), this suppression must emerge from alterations in molecular packing upon mixing moieties of different chemical bulkiness rather than from chain-end concentration effects. Indeed, the GET predicts a reduction in T_g and m upon introduction of small-molecule diluents driven by shifts in configurational entropy associated with alterations in molecular packing efficiency.¹ It also suggests that reductions in free volume generally correlate with suppression of fragility;²⁵ suppression of m with reducing bulkiness of a single-bead diluent can then be understood as emerging from densification upon mixing different size moieties. This connection to free volume theory is understood within the GET as emerging from a rough correlation between free volume and configurational entropy.^{12,26}

Next, to study the role of oligomeric diluents, we simulate systems in which the diluent beads are polymerized to form oligomers with several degrees of polymerization n . To prevent stiffness-driven aggregation, we render the oligomer–oligomer interaction purely repulsive by truncating the nonbonded potential at its minimum. Relative to the $\sigma = 0.5$ diluent, diluent polymerization substantially increases T_g while modestly enhancing m . These shifts reflect a net enhancement in τ_α at high temperature, but an incipient crossover to suppression of τ_α at low temperatures in the presence of the 10-bead additive, apparent from VFT extrapolations of the data (see SI).

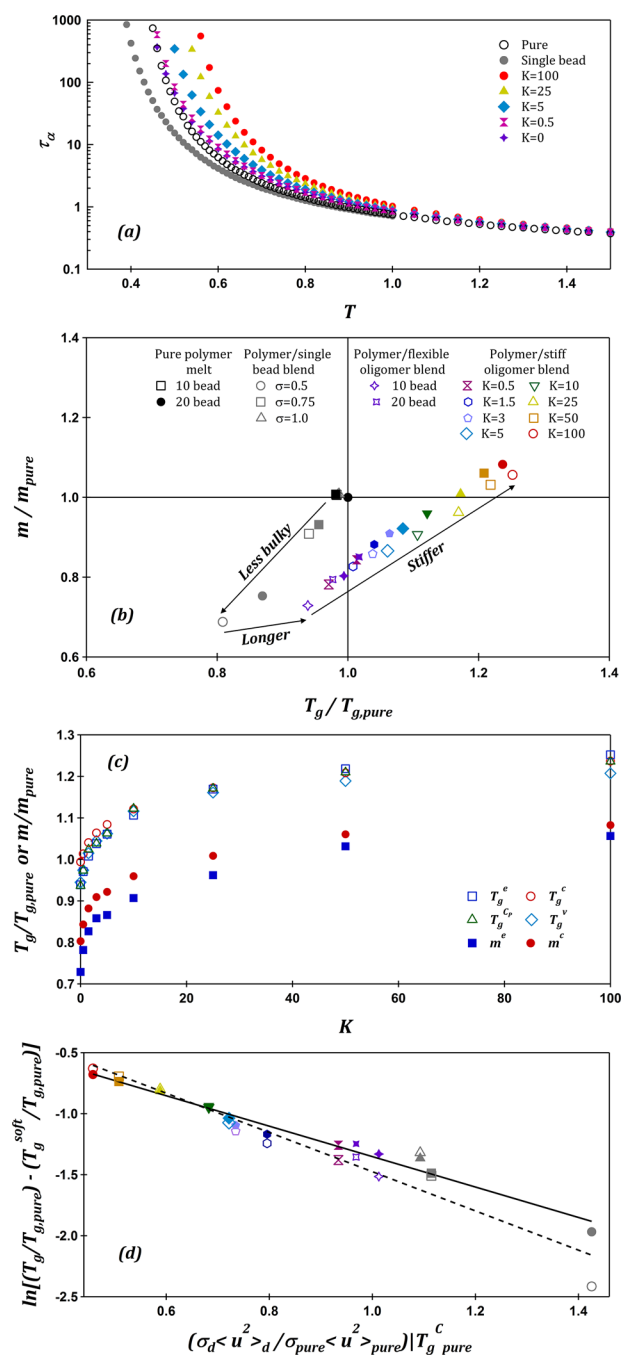


Figure 1. (a) Monomer τ_α vs temperature for systems shown in legend; (b) Diluent-induced shifts in m vs T_g for systems shown in legend, with filled and open symbols denoting values obtained by extrapolated and computational dynamic conventions, respectively; (c) Scaled T_g and m as calculated via conventions described in the text as a function of oligomer stiffness; (d) Test of eq 2 for all systems in this study, with symbols having the same meaning as in part (b). Average uncertainty on x -axis of part (d) is 0.03.

Finally, to probe the effect of diluent stiffness, we begin with this flexible oligomer with $n = 10$ and subject it to a cosine bending potential ($E_{bend} = K[1 + \cos(\theta)]$), with spring constant K ranging, in LJ units, from 0 (flexible) to 100 (nearly rod-like). As shown in Figure 1a–c, introducing diluent stiffness enhances polymer τ_α leading to a disappearance of the crossover in τ_α and an increase in both T_g and m . A crossover to enhancement of T_g is observed prior to a crossover to enhancement of m ,

such that by selecting an appropriate stiffness it is possible to suppress both relative to the pure polymer, increase T_g , but decrease m , or increase both. T_g and m for polymer/oligomer blends exhibit a rough linear correlation (Figure 1c) that is observed in a wide range of weakly interacting polymeric systems.²⁷ However, this does not include the pure polymer system or the single bead systems with $\sigma \neq 0.5$. Again, this can be rationalized based upon the GET, which predicts that reductions in free volume generally correlate with a fragility reduction, but can correlate with either suppressed or enhanced T_g .²⁵ Alterations in molecular packing efficiency can therefore decouple T_g and m .

As shown by Figure 1c, the effects of diluent stiffness on T_g and m saturate for high K , with a dependence that does not obey any simple functional form. To understand the nature of this dependence, we draw inspiration from a recent study of the effect of a confining interface on a polymer's glass transition.²⁸ That study identified a relationship between nanoconfinement-induced T_g shifts and the stiffness of the confining material, as measured by its Debye–Waller factor $\langle u^2 \rangle$, which is a measure of segmental rattle volume on a ps time scale and exhibits an inverse proportionality with the high frequency modulus, $G_\infty \propto kT/\sigma\langle u^2 \rangle$.^{11,29–31} Specifically, it found that

$$\frac{T_g}{T_g^{\text{bulk}}} = \frac{T_g^{\text{fs}}}{T_g^{\text{bulk}}} + B \exp\left(-C \frac{\langle u^2 \rangle_{\text{confining}}}{\langle u^2 \rangle_{\text{bulk}}}\right) \Bigg|_{T_g^{\text{pure}}} \quad (1)$$

where $\langle u^2 \rangle$ is defined as mean square displacement at $1\tau_{LJ}$ (roughly 1 ps), T_g^{fs} is the T_g of the polymer in contact with a completely soft interface (i.e. $\langle u^2 \rangle \rightarrow \infty$), such as a free surface, B and C are fitting parameters, and subscripts “confining” and “bulk” denote values for the confining material and bulk polymer, respectively.

Equation 1 is consistent with the intuition that contact with harder confining surfaces, as defined by the high-frequency modulus, should more severely restrict relaxation. It is reasonable that an analogous form could describe blends of polymers with diluents of varying stiffness: a stiff diluent molecule, as defined by a low relative $\langle u^2 \rangle$ or high G_∞ , imposes an internal constraint impeding segmental relaxation. There is also a phenomenological basis for seeking parallels between these systems: prior studies have noted parallels between glass formation under nanoconfinement and in nanocomposites,^{32,33} nanocomposites, in turn, share phenomenology with polymer/diluent blends. Consistent with this view, several prior studies have indicated the presence of strong interactions between nanoconfinement effects and diluent effects on the glass transition,^{10,15,34,35} suggesting possible overlap in their mechanistic origins. We therefore test whether a form equivalent to eq 1 also describes the variation of blend T_g with diluent stiffness, making several modifications for applicability to this new system. First, in the context of diluent/polymer blends, the logical equivalent of T_g^{fs} is a term quantifying the extrapolation T_g^{soft} of T_g in the limit of an infinitely soft diluent (i.e., a hypothetical diluent with $G_\infty = 0$ or $\langle u^2 \rangle \rightarrow \infty$). For a thin film, this is realized in a freestanding film geometry; in polymer/diluent blends, it is an extrapolation. Second, because these simulations consider beads of distinct sizes, we include the factor σ in the inverse proportionality between G_∞ and $\langle u^2 \rangle$, leading to the equation

$$\frac{T_g}{T_{g,\text{pure}}} = \frac{T_g^{\text{soft}}}{T_{g,\text{pure}}} + B \exp\left(-C \frac{\sigma_d \langle u^2 \rangle_d}{\sigma_{\text{pure}} \langle u^2 \rangle_{\text{pure}}}\right) \Bigg|_{T_{g,\text{pure}}} \quad (2)$$

where subscripts “pure” and “d” denote properties for the pure polymer and diluent, respectively. As shown by Figure 1c, this form describes T_g data for all systems included in this study (R^2 is 0.98 for T_g^c or 0.92 for T_g^E). This remarkably general result implicates $\langle u^2 \rangle$ and G_∞ as fundamental properties determining glass-formation behavior, conceptually consistent with the elastically cooperative activated barrier hopping theory,^{36,37} which predicts that the glassy modulus plays a key role in determining activation barriers in supercooled liquids. While this study does not examine the role of polymer/diluent interaction strength, the original development of eq 2 suggests that its parameter B is proportional to the strength of these interactions.

The above analysis indicates that the high-frequency dynamics of a diluent mediate its impact on polymer glass formation. We continue by assessing the impact of diluent stiffness on the high-frequency dynamics and mechanics of the polymer itself. These effects are most commonly quantified by alterations in the glassy modulus. As shown by Figure 2a, the

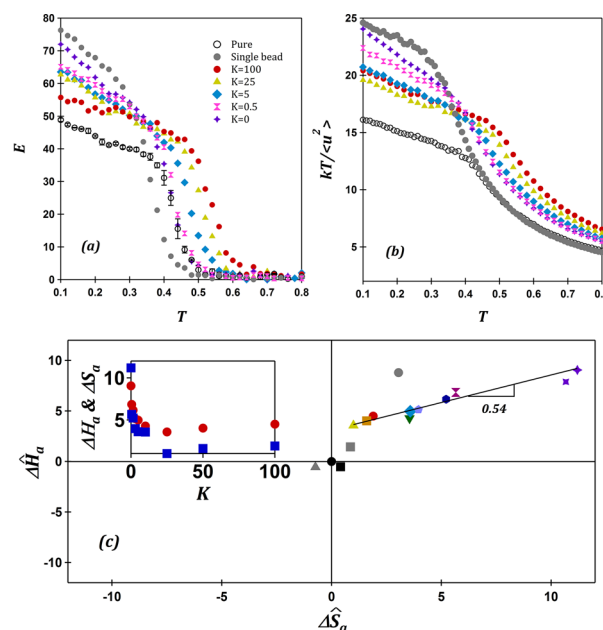


Figure 2. (a) Apparent Young's modulus and (b) $kT/\langle u^2 \rangle$ for polymer beads vs temperature; (c) diluent-induced shift in apparent high frequency activation enthalpy vs entropy determined from eq 4, with symbols denoting the same systems as Figure 1b; inset shows ΔH_a (red circles) and ΔS_a (blue squares) vs oligomer stiffness. In part (a), error bars shown for pure polymer are qualitatively characteristic of uncertainties in all systems shown.

glassy Young's Modulus of these systems, as measured within the linear regime of a uniaxial deformation simulation at a rate of $10^{-4} \sigma/\tau_{LJ}$ (where σ is the LJ unit of distance), is enhanced upon addition of all oligomeric additives. As shown by Figure 2b, $kT/\langle u^2 \rangle$, which, as described above, is proportional to G_∞ , exhibits qualitatively equivalent trends. Notably, the oligomer stiffness yielding the greatest modulus-enhancement is observed to change upon cooling the system through a temperature modestly below T_g : at high temperature, a stiff

oligomer yields the most stiffening; at low temperature, the most flexible oligomer yields the most stiffening.

This observation seems counterintuitive: one might expect a molecularly stiff diluent to yield, at all temperatures, a higher modulus than a flexible additive. To understand this observation, we make use of a body of theory³⁸ treating $\langle u^2 \rangle$ as an effective free-energy activation barrier for local relaxation. The simplest such theory is that of Hall and Wolynes,³⁹ which suggests that

$$\frac{G_a}{kT} \propto \frac{u_0^2}{\langle u^2 \rangle} \quad (3)$$

where G_a is the activation free energy for relaxation and u_0 is interpreted as a critical distance a segment must travel to escape its local minimum. This can be rewritten as

$$\frac{kT}{\langle u^2 \rangle} = \frac{H_a}{u_0^2} - \frac{S_a}{u_0^2} T \equiv \hat{H}_a - \hat{S}_a T \quad (4)$$

where H_a and S_a are the activation enthalpy and entropy of local relaxation.

The slope and intercept of the glassy modulus in Figure 2a or $kT/\langle u^2 \rangle$ in Figure 2b can be interpreted as relating to an entropy and enthalpy, respectively, for local relaxation, similar to an approach for quantification of diluent effects on the dielectric β relaxation time.² As shown in Figure 2c, \hat{H}_a and \hat{S}_a , as computed from $kT/\langle u^2 \rangle$, track together as oligomer stiffness is varied. This effect, known as entropy–enthalpy compensation,^{2,3} explains the above trend in glassy modulus as a function of diluent stiffness: lower stiffness yields a higher favorable ΔS_a for high-frequency relaxation than a stiff additive, consistent with weaker constraints imposed by its more flexible backbone; these weaker constraints allow better molecular packing (see SI), which yields a higher ΔH_a . The outcome of this trade-off is a higher modulus at low temperature but a lower modulus at high temperature. At an intermediate “compensation temperature” of ~ 0.54 , given by the slope of the line in Figure 2c, the modulus of these systems nearly intersects. Identification of this temperature is essential to design of polymer/diluent blends, since in its vicinity modulus may be insensitive to diluent molecular stiffness. The pure polymer and blends involving single-bead diluents do not fall into this trend, likely for the same packing-related reasons that these systems do not exhibit the same proportionality of T_g and m as the oligomeric additives.

Consistent with the literature, the above results indicate that diluents’ effects on low- and high-frequency dynamics do not always track with one another; enhancement of modulus can accompany either enhancement or suppression of τ_α and T_g . How are we to understand the relationship between these effects?

To answer this question, we turn again to the body of literature,³⁸ of which the Hall-Wolynes theory is a seminal example,³⁹ attempting to understand glass formation in terms of relationships between τ_α and high-frequency dynamic properties such as G_∞ and $\langle u^2 \rangle$. We focus on the “Generalized Localization Model” (GLM) for supercooled liquid relaxation,^{16,40} which has been found to describe a number of systems^{16,41–43} based on the following relationship between τ_α and $\langle u^2 \rangle$:

$$\tau_\alpha = \tau_A \exp[(u_A^2/\langle u^2 \rangle)^{\alpha/2} - 1] \quad (5)$$

where α is interpreted, based on the free volume model underlying this equation, as being a measure of the anisotropy of local caging volume, with $\alpha = 3$ denoting isotropic free volume and $\alpha > 3$ denoting anisotropic free volume, and where τ_A and $\langle u_A^2 \rangle$ are the values of τ_α and $\langle u^2 \rangle$ at the onset temperature T_A of glass formation (see SI).

As shown by Figure 3, eq 5 leads to a collapse of τ_α vs $\langle u^2 \rangle$ data for all systems in this study despite use of only one

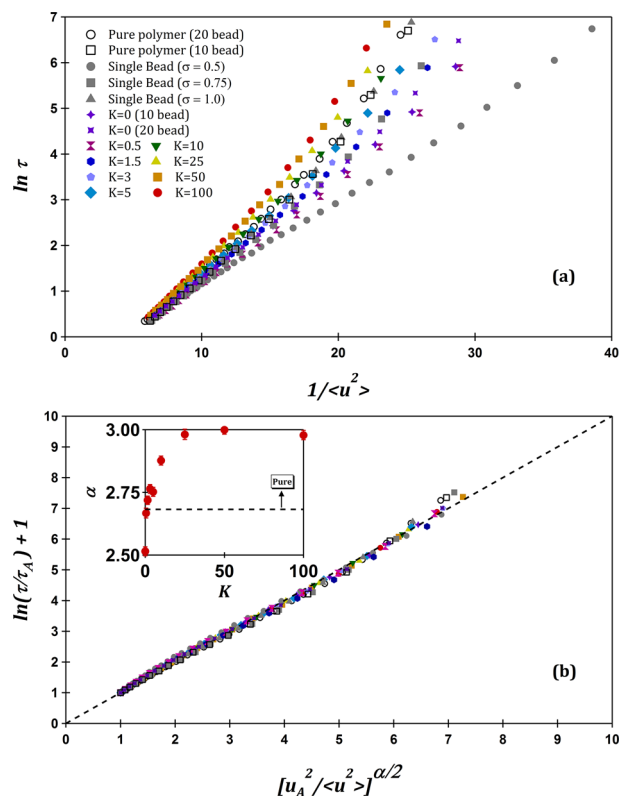


Figure 3. (a) $\ln \tau_A$ vs $1/\langle u^2 \rangle$ for chain monomers; (b) GLM collapse of this data via eq 5; (b inset) α from the GLM vs oligomer stiffness, with error bars corresponding to 95% confidence intervals on fit values.

adjustable parameter. Within the GLM, shifts in α observed with varying diluent stiffness (see Figure 3b, inset) suggest that these diluents decouple high- and low-frequency dynamics by altering the local anisotropy of free volume. However, the observation of α generally less than 3 is inconsistent with the scaling model underlying this interpretation. Instead, this functional form can be rationalized based on an elastic localization framework such as the Hall-Wolynes theory, in which case values of α greater than 2 can be interpreted as indicating anharmonic particle caging. The exact relationship of the variation in α with oligomer stiffness or other molecular properties remains an open question that should be a focus of future research.

In summary, our simulations indicate that oligomeric diluents of varying molecular stiffness can induce diverse alterations in polymer dynamics and mechanical properties. The dependence of T_g on diluent stiffness is found to obey the same functional form describing the T_g -dependence of nanoconfined polymers on the stiffness of a confining interface, suggesting that interface and diluent effects on T_g may be mechanistically related. This implicates diluent $\langle u^2 \rangle$ and G_∞ as key parameters controlling

polymer T_g , with eq 2 providing a design rule for diluent selection. Success of the GLM in describing the relationship between diluent effects on low- and high-frequency dynamics suggests that diluents decouple these regimes by modifying the local anisotropy or anharmonicity of picosecond-time scale segmental rattling. Several observed trends in these systems also qualitatively accord with predictions of the GET. These successes, together with evidence suggesting that the GET and GLM are compatible,⁴⁰ suggest that these models can play an important role in design of diluents with targeted effects on polymer dynamics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00635.

Simulation and analysis methodology (PDF).
Supplementary data tables (XLSX).

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Notes

The authors declare no competing financial interest.

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