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The Descent into Glass Formation in Polymer Fluids

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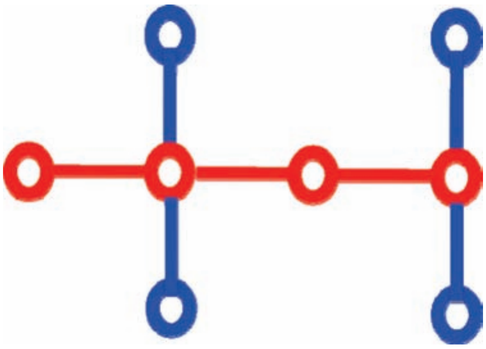

Glassy materials have been fundamental to technology since the dawn of civilization and remain so to this day: novel glassy systems are currently being developed for applications in energy storage, electronics, food, drugs, and more. Glass-forming fluids exhibit a universal set of transitions beginning at temperatures often in excess of twice the glass transition temperature T_g and extending down to T_g, below which relaxation becomes so slow that systems no longer equilibrate on experimental time scales. Despite the technological importance of glasses, no prior theory explains this universal behavior nor describes the huge variations in the properties of glass-forming fluids that result from differences in molecular structure. Not surprisingly, the glass transition is currently regarded by many as the deepest unsolved problem in solid state theory.

In this Account, we describe our recently developed theory of glass formation in polymer fluids. Our theory explains the origin of four universal characteristic temperatures of glass formation and their dependence on monomer−monomer van der Waals energies, conformational energies, and pressure and, perhaps most importantly, on molecular details, such as monomer structure, molecular weight, size of side groups, and so forth. The theory also provides a molecular explanation for fragility, a parameter that quantifies the rate of change with temperature of the viscosity and other dynamic mechanical properties at T_g. The fragility reflects the fluid's thermal sensitivity and determines the manner in which glass-formers can be processed, such as by extrusion, casting, or inkjet spotting.

Specifically, the theory describes the change in thermodynamic properties and fragility of polymer glasses with variations in the monomer structure, the rigidity of the backbone and side groups, the cohesive energy, and so forth. The dependence of the structural relaxation time at lower temperatures emerges from the theory as the Vogel−Fulcher equation, whereas pressure and concentration analogs of the Vogel−Fulcher expression follow naturally from the theory with no additional assumptions. The computed dependence of T_g and fragility on the length of the side group in poly(α-olefins) agrees quite well with observed trends, demonstrating that the theory can be utilized, for instance, to guide the tailoring of T_g and the fragility of glass-forming polymer fluids in the fabrication of new materials. Our calculations also elucidate the molecular characteristics of small-molecule diluents that promote antiplasticization, a lowering of T_g and a toughening of the material.

Introduction

Glass formation[1−4] has been central to fabrication technologies since the dawn of civilization. Glasses not only appear as window panes, insulation in homes, optical fibers supplying telephone, cable TV, and internet communication, and vessels for eating and drinking, but they also include a vast array of "plastic" polymeric materials in our environment. Many advanced glassy materials find applications in high resolution photoresists, electronics, nonlinear optics, nanoimprint patterning (for memory storage and device

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fabrication), organic photovoltaics and plastic crystals (for batteries), polymer films (as coatings and templates), as well as in energy storage, generation, and power conversion where molecular and/or polymeric glasses are structural entities. Because the impressively slow dynamics of cooled polymer systems is also characteristic of many biological materials, an understanding of polymer glass formation is also essential to designing technological processes aimed at preserving foods, drugs, and tissues.[5,6]

Despite the fundamental nature of glass formation and the regularities observed in this process, a generally accepted theoretical description of this ubiquitous and conceptually vexing form of matter remains elusive. Indeed, the Nobel laureate P. W. Anderson is quoted as saying "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition."[7] The well-known quip that "There are more theories of the glass transitions than there are theorists who propose them"[7] is also symptomatic of the enormity of the problem. Hence, a serious challenge confronts our goal of explaining the universal characteristics of glass formation and the dependence of the physical properties of polymer glass-formers on molecular structure, molecular weight, pressure, temperature, and so forth. An important component of this endeavor lies in elucidating the enigmatic molecular origins of fragility.

Universal Characteristics of Glass-Forming Fluids

Many fluids possess complex molecular structure and/or interact with complicated potentials. Consequently, when cooled, these fluids solidify into glasses rather than crystallize. During this process, the dynamics undergo drastic changes. Specifically, the fluid's viscosity η and structural relaxation time τ vary over 12−14 orders of magnitude as temperature decreases by a couple hundred degrees (see Figure 1[8]). The glass transition temperature T_g is generally identified as the temperature at which $\tau \sim 100$s or $\eta \sim 10^{13}$ P. Thus, below T_g, the relaxation becomes extremely sluggish, and the fluid no longer equilibrates on the time scale of most experiments. The rate of change (evaluated at T_g) of η, τ, and other dynamical mechanical properties with temperature is termed the "fragility",[8] which provides a measure of the fluid's thermal sensitivity, the temperature dependence of transport properties, and the broadness of the glass transition. The magnitude of the fragility determines whether the material can be processed by extrusion, casting, ink jet, and so forth. The ability to control the location of the glass transition temperature T_g and the fragility through molecular engineering is thus essential for rational design of glass materials with desired properties but requires a deep understanding of the relation between molecular characteristics and the properties (T_g and the fragility) of glass-formers that has hitherto been lacking, despite the plethora of theoretical "descriptions" of the glass transition.

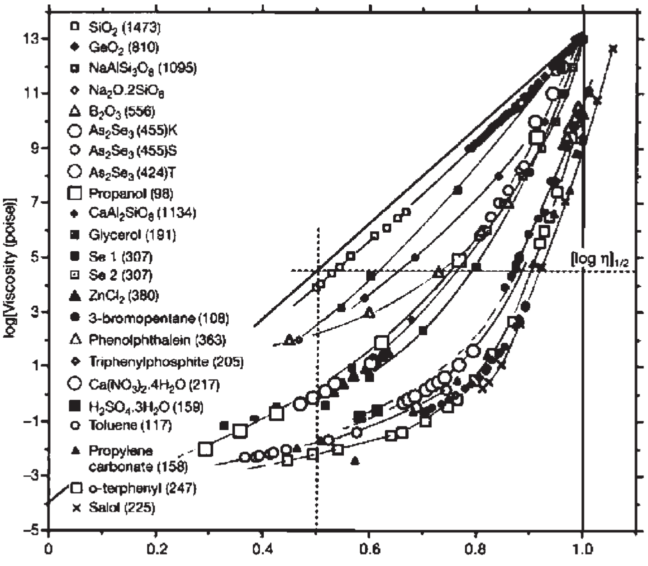

FIGURE 1. Angell plot of viscosity verses reduced temperature T/T_g for a variety of glass-formers. Reprinted with permission from Nature (http://www.nature.com/), ref 8. Copyright 2001 Nature Publishing Group. Curved lines imply the glass-formers are fragile.

The appearance of huge variations in viscosity, structural relaxation time, and so forth, and the existence of four characteristic temperatures are universal properties of glass formation that are common to both small molecule and polymeric glass-formers. However, theoretical studies of glass formation in these systems can benefit from recognizing special features of polymer systems.[9] First, varying the polymer's molecular weight and side chain length generates a family of chemically "identical" systems, whereas each small molecule fluid contains molecules with unique molar mass, size, and shape. Comparing theoretical predictions to experimental trends in variations of the properties of polymer glass-formers with, for instance, molecular weight provides a stringent test of theory that is unavailable to theories for glass formation in small molecule systems. Second, a polymer chain of N monomers interacts in the liquid state with $\sim N^{1/2}$ other polymer chains,[10] which implies that mean-field lattice theories can adequately represent the thermodynamics of polymer fluids but not of small molecule fluids.

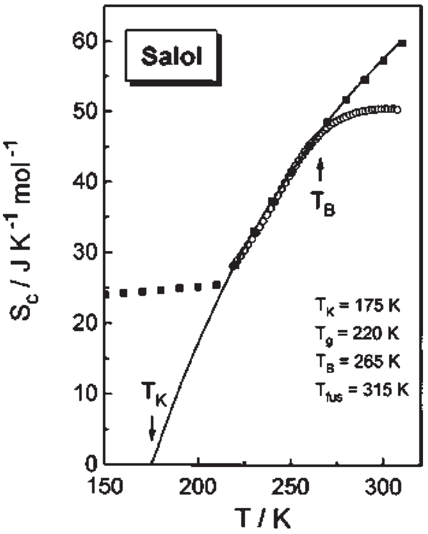

FIGURE 2. Excess entropy from heat capacity (squares) and as extracted from dielectric relaxation data using Adam–Gibbs model (circles). Reprinted with permission from ref 12. Copyright 1998 American Institute of Physics. Extrapolation of data for $T \gg T_g$ determines T_K.

Relatively few theories of glass formation are developed on a *molecular* level. Mode-coupling theories[11] describe a mean-field approximation to the exact dynamics of a monatomic supercooled liquid, with a focus on the dynamical consequences of local caging of particles upon the dynamic structure factor, the structural relaxation time, and the translational diffusion coefficient of the fluid. Approximate solutions of this model indicate structural arrest at a particular critical temperature or concentration. However, mode-coupling theory fails to recover Arrhenius dynamics at high temperatures and thus fails to describe the observed activated transport even at high temperatures. The opposite pole of models of glass formation focuses on thermally activated structural relaxation and transport. Gibbs–DiMarzio theory[9] is an example that uses a standard lattice model description for the configurational entropy of a polymer melt. The theory treats only the ideal glass-transition temperature T_K as the temperature where the *extrapolated* configurational entropy vanishes (see Figure 2[12]) but cannot describe the other characteristic temperatures. Although both theories provide some highly nontrivial, experimentally confirmed predictions, they cannot describe the actual glass transition temperature T_g, and many of their predictions are quantitatively inaccurate.[13] Moreover, there is no reason to believe that mode-coupling theory predictions for a monatomic fluid bear any relevance for a fluid of complex molecules that possess conformational states whose relative populations vary greatly with temperature.

We have developed a systematic, predictive framework for calculating essential properties of glass-forming polymeric fluids as a function of their molecular architecture, bond stiffness, cohesive interaction energy, pressure, molar mass, concentration and structure of additives, and so forth.[14−18] The theory combines the lattice cluster theory (LCT)[19−22] for a polymer fluid composed of semiflexible polymers[13] with the Adam–Gibbs model (described below) for the structural relaxation time.[23,24] The LCT employs an extended lattice model in which monomers have internal structure reflecting their actual size, shape, and bonding patterns. While this type of molecular modeling involves a coarse grained picture of monomer structure, the LCT has proven valuable in modeling subtle thermodynamic properties for a plethora of condensed polymer systems, including homopolymer blends, diblock copolymer melts, random copolymer systems, and so forth.[22]

The combined Adam–Gibbs-LCT model is initially regarded as a physically plausible hypothesis that is tested before being integrated into the theory of glass formation. The tests involve comparing the calculated T_g and fragility for a wide range of molecular weights and chain stiffness with experimental data. The validated, combined LCT/Adam–Gibbs approach is then applied as a predictive tool to describe several polymer glass-forming liquids, as illustrated below.

Universal Properties of Glass Formers and Fragility

The enormous temperature sensitivity of liquid dynamics as the temperature approaches the glass transition temperature T_g is evident from an "Angell plot" of log η versus the reduced temperature T/T_g (Figure 1[8]). Some substances (called strong glasses) exhibit a linear Arrhenius behavior,

$$\eta = \eta_0 \exp(\Delta\mu/kT) \qquad (1)$$

over a wide temperature range, where $\Delta\mu$ is the temperature independent activation energy, but the majority of substances (called fragile glasses) exhibit a non-Arrhenius temperature dependence for η. Viscosity data for a range of temperatures above T_g are often fit to the empirical Vogel–Fulcher equation,

$$\eta = \eta_0 \exp\left[D/k(T - T_0)\right] \qquad (2)$$

where η_0 is a constant and $T_0 > 0$ is the Vogel temperature. *D* is a parameter characterizing fragility, with smaller *D* corresponding to more fragile systems.

The dynamics of fragile fluids generally undergo qualitative changes upon cooling, beginning first where Arrhenius behavior ceases to apply at the onset temperature T_A, which often exceeds $2T_g$, continuing at a crossover temperature $T_c \sim 1.2-1.4T_c$, where the temperature dependence of η and τ changes qualitatively, and finally passing through T_g in the descent to the Vogel temperature T_0 where a divergence appears in the *extrapolation* of the viscosity and other dynamical properties. This divergence and a similar vanishing of the extrapolated excess entropy (see below) have been studied extensively to determine whether a true thermodynamic or dynamic transition intervenes (somewhere in the temperature range $T_0 < T < T_g$) to prevent the physically unreasonable divergence from occurring. Because systems below T_g equilibrate too slowly to ever determine whether a true divergence occurs, our theoretical studies of glass formation concentrate on temperatures $T \geq T_g$ where fluids equilibrate on an experimentally convenient time scale. Nevertheless, the temperature T_0 is still meaningful as a characteristic parameter derived from fitting data for $T \geq T_g$.

Commonly used fragility parameters are the isobaric and isothermal fragility parameters,

$$m_P = \left(\frac{\partial \log \tau}{\partial (T_g/T)}\right)_{P,T=T_g}$$

$$m_T = \left(\frac{\partial \log \tau}{\partial (V_g/V)}\right)_{T,V=V_g}$$

respectively, that may be determined from the structural relaxation time τ (or η), with V being the specific volume. m_P is related to D of eq 2, while new information emerges from m_T which remains to be studied by our entropy theory.

Figure 2[12] depicts the typical temperature dependence of the excess entropy S_{ex} of the supercooled fluid (over that of the crystal) as determined from specific heat data. The excess entropy is crashing near T_g, and the extrapolation of experimental data for $T \geq T_g$ yields a Kauzmann temperature $T_K \approx T_0$ below which the *extrapolated* excess entropy unphysically becomes negative. (The entropy of an equilibrated fluid cannot be less than that of the crystal at the same temperature.) The experimental excess entropy below T_g in Figure 2 behaves quite differently because the systems for $T < T_g$ are no longer equilibrated.

In summary, the universal characteristics of glass-forming fluids are described in terms of four characteristic temperatures,[15] the onset temperature T_A, the crossover temperature T_c, the glass transition temperature T_g, and the Kauzmann/Vogel temperature $T_K \approx T_0$ (where $T_A > T_c > T_g > T_K \approx T_0$). Mode-coupling theory deals with the two highest temperatures T_A and T_c, while Gibbs–DiMarzio theory effectively treats only the ideal glass transition temperature $T_K \approx T_0$. No other prior theory enables evaluating all four characteristic temperatures or explains the molecular basis for fragility.

The generalized entropy theory of glass formation fills the gap in the statistical mechanical theory of glass formation in polymer fluids by describing the dependence of the four characteristic temperatures and the fragility on the polymer's molecular structure.[14−18,25,26] We begin by briefly reviewing basic assumptions underlying the theory and comparing its prediction with general behavior observed experimentally. Special attention is devoted in this comparison to the influence of the length of the side groups in poly(α-olefins) on the magnitude of the glass transition temperature T_g and the fragility parameter. The discussion concludes with predictions of the molecular characteristics for diluents to promote antiplasticization (a toughening of the material) and with a description of new combining rules for estimating T_g of a blend/diluent system in terms of the T_g of the components.

Lattice Model Used in LCT for Polymer Glass Formation

The polymers are represented by chains of chemically connected monomers that are packed onto a cubic lattice. Each structured monomer is composed of several united atom groups that are linked by internal chemical bonds and that occupy individual lattice sites, as illustrated in Figure 3 for several polyolefin fragments where the united atom groups are simply CH_n groups (n = 0, 1, 2, or 3). Nearest neighbor united atom groups are assumed to interact with an attractive energy ε that is proportional to the cohesive energy of the polymer melt. Chain semiflexibility plays an essential role in glass formation and is modeled by designating a pair of consecutive collinear bonds as a "trans" conformation, while two orthogonal consecutive bonds are assigned as "gauche" and incur a gauche penalty of E_{bend}. The energy E_{bend} generally differs for backbone and side group bonds. While introducing this difference substantially increases the algebraic complexity of the LCT, its inclusion into the model is necessary because the disparities in E_{bend}

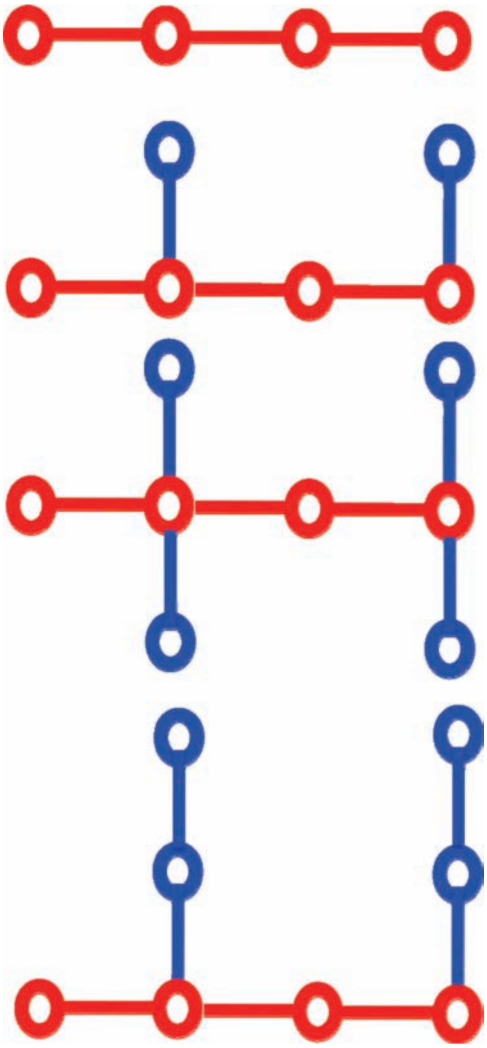

FIGURE 3. Cartoons of pairs of monomers for polyethylene, polypropylene, polyisobutylene, and polyethylethylene (top to bottom). Backbone and side group unit atom groups are depicted in red and blue, respectively.

between the backbone and side group are found empirically[27] to strongly affect fragility. The structured monomer model of the LCT[19−22] represents a significant extension of the traditional lattice model for polymers (where monomers are structureless entities) by including the bonding constraints, chain semiflexibility, and interactions, crucial factors responsible for the presence of correlations and nonrandom mixing the these systems. Classic Flory−Huggins (FH) mean-field theory[28] neglects these correlations and, therefore, cannot distinguish between the various structures in Figure 3. The ability to estimate the configurational entropy for *semiflexible* polymer fluids renders the LCT suitable for studying glass formation in polymers and especially its molecular basis.

The LCT has successfully been applied to a wide range of polymer systems and has explained subtle features of their thermodynamics.[22] For example, LCT predictions that block copolymers could order *on heating*[29] and that copolymers of weakly interacting polymers (like polyolefins) could exhibit closed loop phase diagrams[29] have subsequently been confirmed experimentally.[30,31] The ability to estimate the configurational entropy for *semiflexible* polymer fluids renders the LCT valuable for studying glass-formation in polymers and especially its molecular basis.

The Adam−Gibbs model posits that the dramatic slowdown in relaxation observed for supercooled liquids arises because relaxation becomes cooperative below T_A. The central quantity $z^*(T)$ of the model is the number of cooperatively rearranging groups and is defined such that $z^* = 1$ for $T > T_A$ and z^* grows as temperature is diminished. While this first postulate is physically plausible, the second assumption that $z^*(T)$ is inversely proportional to the configurational entropy $S_c(T)$ is much deeper. Clearly, $z^*(T)$ and $S_c(T)$ vary in opposite directions [as T decreases, $z^*(T)$ increases, while $S_c(T)$ decreases], but the inverse scaling remains to be verified. Consequently, the Adam−Gibbs model is taken tentatively as a hypothesis that is tested by comparison with experiments, just as grand theories (e.g., classical and quantum mechanics) have been tested in the past. According to the Adam−Gibbs model, the structural relaxation time τ is given by

$$\tau = \tau_\infty \exp[z^*(T)\Delta\mu/\mathrm{k}T] \tag{3a}$$

$$z^*(T) = S_c^*/S_c(T) \tag{3b}$$

where $\Delta\mu$ is the high temperature activation energy, τ_∞ is a constant, and S_c^* is the high temperature limit of the configurational entropy density [$S(T = T_A)$]. Above T_A, the relaxation is Arrhenius but may depart from this behavior at lower temperatures. The Adam−Gibbs model bears qualitative resemblance to transition state theory in the sense that both theories relate a dynamic quantity (the reaction rate in transition state theory and the structural relaxation time in the Adam−Gibbs model) to equilibrium information.

Substituting the configurational entropy evaluated from the LCT into the Adam−Gibbs expression 3a for τ enables the first explicit calculations of T_g and τ for polymers with varying molecular structure. However, the literature contains conflicting beliefs concerning the consistency of the Adam−Gibbs model, conflicts that have arisen due to the existence of two choices of normalization for S_c. The entropy S_c can be expressed either as a specific entropy per mole (or unit mass) or as an entropy density (per unit volume). Studies questioning the AG model are based on the use of the specific entropy,[12] but as depicted in Figure 4 only the

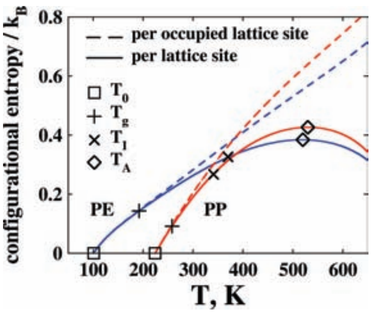

FIGURE 4. LCT calculations of configurational entropy and characteristic temperatures for PE and PP.

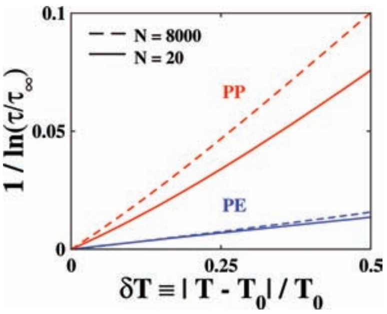

FIGURE 5. LCT calculations of $[\ln(\tau/\tau_\infty)]^{-1}$ verses δT_0 for PE and PP with different polymerization indices *N*.

entropy density is consistent with the Adam–Gibbs model. The specific entropy is a nondecreasing function of temperature and, hence, cannot exhibit a maximum, as required by the Adam–Gibbs model. On the other hand, the temperature dependence of the configurational entropy density $S_c(T)$ in Figure 4 enables defining three of the four characteristic temperatures of glass formation: (i) the onset temperature T_A where $S_c(T)$ is maximum, (ii) the crossover temperature T_c where $TS_c(T)$ has an inflection point, and (iii) the Kauzmann temperature T_K where the extrapolated $S_c(T)$ vanishes. The remaining characteristic temperature, T_g, is commonly defined as the temperature at which $\tau = 100$ s. Thus, the combined LCT/Adam–Gibbs theory enables evaluating both τ and all four characteristic temperatures of glass formation for polymer fluids.

Comparison with Experiment: General Phenomena

We begin by analyzing the structural relaxation time τ, which is calculated from eq 3 by setting $\tau_\infty = 10^{-13}$ s and by estimating the high temperature activation energy $\Delta\mu$ from the empirical relation,

$$\Delta\mu = 6k_BT_c \tag{4}$$

where the crossover temperature T_c is computed from the entropy theory. Figure 5 presents calculations of $[\ln(\tau/\tau_\infty)]^{-1}$ verses the reduced temperature $\delta T_0 = (T - T_0)/T_0$ for polypropylene (PP) and polyethylene (PE) melts using the van der Waals energy and cell volume from fits to the equation-of-state of polypropylene and trans–gauche "bending" energies from fits to the T_g of PP and PE, respectively. The curves in Figure 5 are fairly linear, whereupon the low temperature dependence of $\tau(T)$ *approximately* fits the Vogel–Fulcher eq 2. As a consequence of eq 2, the slope of the curves in Figure 5 is the reciprocal of the fragility parameter *D*. Since smaller *D* corresponds to higher fragility, polyethylene is predicted to be less fragile than polypropylene in accord with experiments. The greater slope for the high molecular weight PE and PP than for the lower molar mass PE and PP implies that fragility is enhanced by elevating molecular weight, a computed trend again agreeing with observations. When the data of Figure 5 are replotted as $[\ln(\tau/\tau_\infty)]^{-1}/kT_0$ versus δT_0, the scaling of $[\ln(\tau/\tau_\infty)]^{-1}$ by $1/kT_0$ almost entirely eliminates the dependence of the slope on molecular weight as found empirically.

Molecular Basis for Fragility and T_g

Numerous empirical correlations have been proposed between individual molecular properties and fragility, but these correlations suffer from the fact that several molecular parameters (monomer size, shape, polymer chain flexibility, interaction energies, etc.) change simultaneously as the chemical species varies, thus complicating the analysis of correlations. Our theory, in contrast, enables determining how fragility changes when only a single parameter is varied. Calculations for model "poly(*n*-α-olefin)" melts (where a single parameter is varied) show that fragility increases with chain stiffness, pressure, and polymer molar mass but decreases when the cohesive energy or side group length grow. Combining these findings with those discussed below for model polymers having varying ratios of backbone and side group flexibilities enables deducing the pattern that fragility arises due to the frustration in packing of molecules (or particles) with large stiff portions and/or irregular local structure. The frustration in packing often elevates free volumes and, hence, leads to greater temperature sensitivity, also known as fragility, of thermodynamic and transport properties. Increasing molecular weight also diminishes packing efficiency and thus enhances fragility while *diminishing* free volume.

Sokolov et al.[33] have applied and extended these ideas to explain their experimental data, and more generally these concepts can be helpful in engineering materials with desired fragility. Our interpretation of fragility is also supported by experiments of Weitz and co-workers[34] for model soft colloidal particle systems (where altering the particle rigidity changes the packing efficiency and controls the fragility) and by experiments by McKenna, Roland, and their respective co-workers[27] who note that the relative flexibility of the backbone and side groups strongly correlates with fragility. The most easily packed polymer chains consisting of flexible backbones and flexible side groups (labeled as FF) are least fragile, those with flexible backbones and stiff side groups (FS) pack less easily and thus are moderately fragile, while chains having stiff backbones and flexible groups (SF) pack least favorably and hence are found to be very fragile.[27] Typical examples include polyisobutylene (FF), polystyrene (FS), and polycarbonate (SF). In summary, the packing efficiency in the glassy state constitutes a general determinant of fragility.

The glass transition temperature T_g is another basic property of polymer glasses that generally trends opposite to free volume. Calculations of T_g have been performed for model FF, FS, and SF polymers that have the molecular structures of poly(*n*-α-olefins) chains, but different pairs of bending energies are chosen for their backbone and side group bonds. More specifically, the rigidity of the backbone and side groups of the SF class of polymers is specified by the empirically determined bending energies $E_{\text{bend,PP}}$ and $E_{\text{bend,PE}}$ of polypropylene and polyethylene, respectively, while the bending energy of the quite flexible polyethylene is used to model all semiflexible bonds in the FF class. Finally, FS chains have $E_{\text{bend,PP}}$ and $E_{\text{bend,PE}}$ assigned to the backbone and side groups, respectively. Since end groups of polymers accumulate more excess free volume than equivalent backbone units within the chain, the total excess free volume diminishes as the length (*n*) of the side group chain is increased and the overall molecular weight is held constant. Consequently, T_g is expected to increase in accord with the old empirical argument that diminished free volume implies higher T_g. Figure 6 presents the calculated T_g as a function of *n* for the FF, FS, and SF model polymer melts. The least fragile FF system yields a slowly increasing T_g for small *n* that levels off for larger *n*, and the same trend is observed for the more fragile FS system but with greater sensitivity of T_g to *n*. Finally, T_g of the SF polymers *decreases* with increasing *n*, which is at first counterintuitive until it is realized that the flexible side groups of the SF chain act as a plasticizer for the stiff backbones and, hence, T_g must drop. In fact, this behavior is observed for poly(*n*-α-olefins) and for poly(*n*-alkyl methacrylates), while the trends exhibited in Figure 6 for FS polymers are consistent with experimental data for the relative T_g of polystyrene and poly(2-vinyl naphthalene). The general decrease in the calculated free volume fraction with growing *n* suggests a common tendency toward reduced fragility as *n* exceeds 3, a suggestion supported by experiments for poly(*n*-alkyl methacrylate) polymers, which exhibit diminished fragility with increasing side group size. In summary, stiffer and longer side groups for fixed cohesive energy lead to larger T_g, while the addition of side groups that are more flexible than the chain backbone can cause T_g to decrease. The generalized entropy theory successfully predicts these experimentally established trends in the variation of T_g with molecular structure, trends indicating that controlling side group structure provides a powerful means of regulating T_g and the fragility of glass-forming polymers.

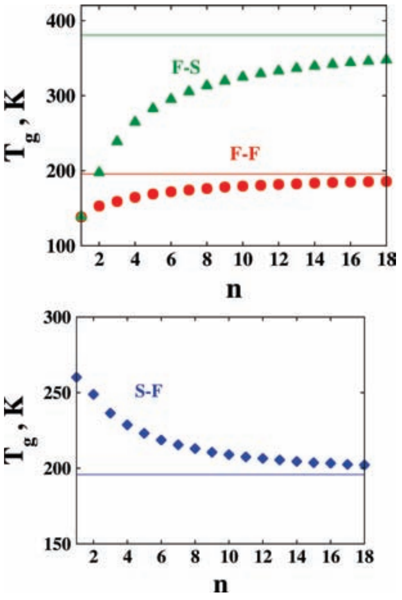

FIGURE 6. Calculated glass transition temperature T_g as a function of the length *n* of the side groups for FF, FS, and SF models of polymers.

Quantitative Comparison with Experiment: Poly(*n*-α-olefins)

The comparisons with experiment described above all concern general trends rather than properties of particular systems. Quantitative comparisons between theory and experiment require introducing into the theory a plethora of adjustable parameters especially when describing complicated chemical systems where, for instance, different united atom groups interact with differing van der Waals energies ε_i. Thus, we focus here on the simplest case of

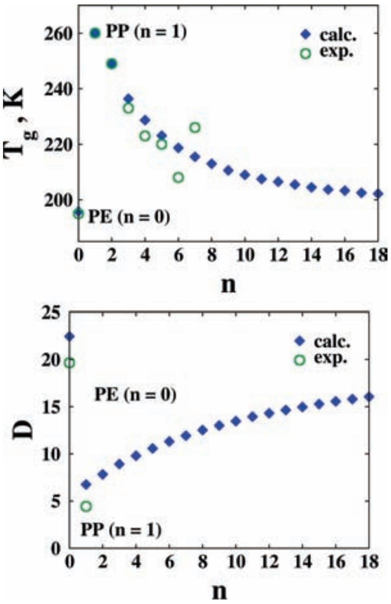

FIGURE 7. Glass transition temperature T_g and fragility parameter D of poly(n-a olefins) as a function of side group length n. Adapted with permission from ref 25. Copyright 2009 American Institute of Physics.

poly(α-olefins) glass formers because a realistic model for these systems requires only two distinct bending energies (one each for the backbone and side groups), a single energy ε (since the CH$_n$ groups are treated as energetically equivalent), and the cell volume. The latter two parameters are determined from fits to equation-of-state data for polypropylene, while $\{E_{\text{bend}}\}$ values for the backbone and side groups are obtained from fits to the observed T_g of polypropylene and polyethylene, respectively. Figure 7 illustrates our calculations of T_g for a series of poly(n-α-olefins) with variable side chain length n and fixed pressure $P = 1$ atm.[25] The agreement between theory and experiments is quite good.

The LCT[25] predicts the structural relaxation time $\tau(P,T =$ const) to vary with pressure in the spirit of eq 2 with P and $P_0(T)$ replacing $1/T$ and $1/T_0(P)$, a prediction consistent with experimental observations. The computed dT_g/dP for polypropylene is in error by a factor of between 2 and 3 (see Figure 8). Our calculations[25,26] indicate that fragility decreases with pressure, but the computed derivative dD/dP is smaller than experiment data by a factor of $\sim 2-3$.[32,35] Both quantitative errors are probably due to using the FH approximation for the translational entropy.

Diluents

A small molecule diluent added to a polymer fluid usually acts as a plasticizer that depresses $T_{g,\text{mix}}$ of the mixture from that $T_{g,\text{p}}$ of the pure polymer melt. Generally, the depression of $T_{g,\text{mix}}$ induced by adding small molecule diluents grows as $T_{g,\text{d}}$ of the diluent diminishes relative to $T_{g,\text{p}}$ of the host polymer, and considerable recent interest has centered about determining $T_{g,\text{mix}}$ in terms of $T_{g,\text{p}}$ and $T_{g,\text{d}}$. In contrast to molecular plasticizers, which decrease the stiffness of the glassy polymer, some diluents act as antiplasticizers that *increase* the stiffness (i.e., the shear or bulk modulus) of glassy polymeric materials while also depressing $T_{g,\text{mix}}$. Antiplasticizers with higher material stiffness find numerous applications in preservation of foods, tissues, and drugs, enhancing the scratch resistance of polymer films, controlling the brittleness and other nonlinear mechanical properties of polymer materials, and so forth. Examples of antiplasticizer/polymer pairs include tricresyl phosphate in polysulfonate and dibutylphthalate in polycarbonate. Because the empirical search for antiplasticizers for a given polymer requires tedious, time-consuming trial and error, the generalized entropy theory of glass formation enables deducing the molecular characteristics of the diluent that promote antiplasticization or plasticization.

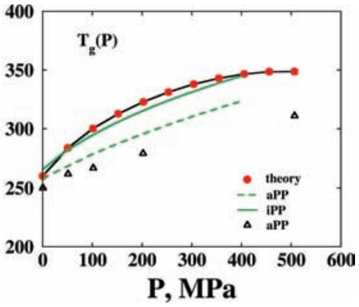

FIGURE 8. Comparison of computed pressure dependence of the glass transition temperature with experiment for PP. Green lines from ref 32 and triangles from ref 35.

First, the theory enables calculating the isothermal compressibility κ of the equilibrated fluid, which provides a good measure of antiplastization because κ scales inversely with the bulk modulus of the glass. Second, the analytical nature of the generalized entropy theory permits computations where only one of the diluent's molecular parameters is varied while the remaining parameters are fixed. Calculations for small oligomeric diluents consider several variable parameters, including the monomer structure, the polymerization index N, the van der Waals energy ε_{dd} of the diluent, and its bending energies. We find[26] that antiplasticization is promoted by diluents whose cohesive energies ε_{dd} exceed the cohesive energy ε_{pp} of the host polymer, while diluents with smaller ε_{dd} promote the opposite phenomenon, plasticization. Smaller and/or more flexible diluents generally depress T_g more than larger ones, and the larger diluents enhance fragility due to their less favorable packing.

Glass formation can arise as the concentration of a diluent is varied at constant temperature and pressure. Our calculations[26] indicate that the structural relaxation time τ of the polymer/diluent system has approximately a Vogel–Fulcher form in which T and T_0 of eq 2 are replaced by concentration c (in units of volume fraction) of the diluent and the "Vogel concentration" $c_0(T,P)$, respectively.

Our theories also enable deducing analytical expressions describing $T_{g,mix}$ for the mixture as a function of the diluent parameters (ε_{dd}, N_d, and the diluent concentration c). The results are then used to derive a new combining rule for $T_{g,mix}$ in terms of $T_{g,p}$ and $T_{g,d}$,

$$T_{g,\,mix} = T_{g,\,p}{}^{1-c}\,T_{g,\,d}{}^{c} \tag{5}$$

that should be helpful in designing systems with desired properties.

Discussion

The generalized entropy theory of glass formation opens up new avenues for probing the molecular factors affecting the glass transition temperature, fragility, and structural relaxation time and, hence, for the rational design of new materials for diverse applications. The theory agrees qualitatively with observations for a diverse array of subtle variations with molecular details, and quantitative tests for poly(α-olefins) are very encouraging. As an equilibrium theory (that produces dynamical information by virtue of the Adam–Gibbs model), the theory cannot describe either the dynamical heterogeneity of supercooled fluids or the nature of the cooperatively rearranging groups. Hopefully, information extracted from the generalized entropy theory can be combined with dynamical theories to address these fundamental issues.

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BIOGRAPHICAL INFORMATION

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