Macromolecules
Article
Cite This: Macromolecules 2018, 51, 4694–4698

The α and Johari–Goldstein Relaxations in 1,4-Polybutadiene: Breakdown of Isochronal Superpositioning

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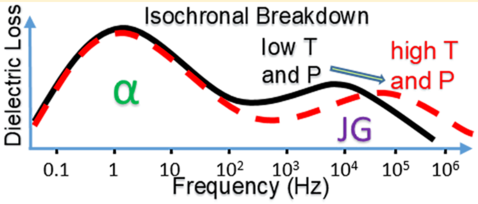

ABSTRACT: Dielectric spectra were measured for 1,4-polybutadiene (PBD) at various temperatures and pressures corresponding to a constant value of the relaxation time, τ_α, for the local segmental dynamics (α-process). Given the relationship of the Johari–Goldstein secondary relaxation to the α-process, it is of interest to determine whether the frequency separation of the Johari–Goldstein secondary relaxation and the α relaxation remains essentially constant under isochronal conditions. We find for PBD this is not the case; the JG relaxation peak moves systematically to higher frequencies at constant τ_α with increasing temperature and pressure. We show using molecular dynamics simulations that the behavior of PBD, which differs from that reported previously for molecular liquids, is a consequence of the torsional inflexibility of the polymer backbone. This accentuates the effect of constraints from local intermolecular barriers, with consequent deviation in the response of the JG and α relaxations due to their different dynamic length scales. Thus, although the Johari–Goldstein relaxation is related to and may even evolve into the structural relaxation associated with the glass transition, its response is not universal but rather depends to some extent on the chemical structure.

■ INTRODUCTION

The idea has emerged from numerous studies that the Johari–Goldstein (JG) secondary motion, involving all atoms of the molecule or polymer repeat unit, is the shorter time, less cooperative component of the structural relaxation process, culminating in the α relaxation that defines the glass transition temperature, T_g. Observations of the JG relaxation and its relationship to structural relaxation have been made both on molecular glass formers and polymers.[1−3] At T_g the behavior of the JG relaxation changes, as it begins to "sense" the α relaxation; these property changes include the T- and P-dependences of τ_{JG} and the T-dependence of the dielectric strength, $\Delta\varepsilon_{JG}$. Together with the correlation of the α and JG properties, this suggests that the JG process functions as the precursor to structural relaxation. An example of such a property correlation is the empirical relation for the activation energy, E_{JG}, below T_g:[4]

$$E_{JG} = 24RT_g \tag{1}$$

A nearly equivalent equation drawn from the coupling model[2] expresses the JG activation energy as a function of parameters describing the α relaxation function[5,6]

$$E_{JG} \approx 2.303\beta_K \log(\tau_\alpha)RT - (1 - \beta_K)11.7 - \log(\tau_\infty) \tag{2}$$

Here β_K is the stretch exponent of the Kohlrausch function

$$\varepsilon_\alpha^*(\omega) = \Delta\varepsilon_\alpha \int_0^\infty e^{-i\omega t} \frac{d}{dt} \exp[-(t/\tau_\alpha)^{\beta_K}]\, dt \tag{3}$$

describing the breadth of the α peak, with $\Delta\varepsilon_\alpha$ the dielectric strength and τ_∞ the pre-exponential factor of the Arrhenius equation for the JG process. Above T_g the separation of the JG and α peaks in the dielectric spectrum has also been related to the magnitude of the stretch exponent[6,7]

$$\log \tau_\alpha - \log \tau_{JG} \approx (1 - \beta_K)(\log \tau_\alpha - 11.7) \tag{4}$$

According to the model, for conditions for which the α relaxation time is constant (which means β_K is also constant[8,9]), the variation of τ_{JG} will not be "too different in order of magnitude".[7]

An issue with studies of the JG relaxation is assurance that an observed secondary dispersion is not due to trivial motion of side groups (that does not alleviate stress), rather than the JG dynamics, which involves all atoms in the molecule or repeat unit. The JG relaxation is distinguished from the α relaxation by the former being faster and typically having a smaller amplitude. The material studied herein was 1,4-polybutadiene (PBD). Since the only pendant moiety is hydrogen atoms, the prominent secondary relaxation observed in the spectrum of PBD must be the Johari–Goldstein process. There are two other very weak peaks at lower temperatures: at ca. 75 K below T_g, rotation of the backbone vinyl carbons produces a dispersion in dielectric,[10,11] Brillouin,[12] and depolarized light scattering[13] spectra, and at temperatures approaching absolute zero, oscillation of small groups of atoms gives rise to a temperature-insensitive dielectric peak.[10,11] Neither of these low-temperature processes is of interest in the present study.

The focus of this work is on the relaxation times for the α and JG processes, specifically how τ_α and τ_{JG} are affected by changes in thermodynamic variables. A relationship between

Received: March 28, 2018
Revised: May 31, 2018
Published: June 14, 2018

ACS Publications

DOI: 10.1021/acs.macromol.8b00664

the two relaxations implies that τ_{JG} may be a function of τ_α, but experimental results to date are equivocal. Measurements on molecular liquids suggest that τ_{JG} is constant for constant τ_α,[14,15] whereas for poly(methyl methacrylate) τ_{JG} decreases for isochronal τ_α and increasing T or P.[16]

One way to characterize the effects of temperature, T, and density, ρ, on relaxation times is from the density scaling property[3,17]

$$\tau = f(T/\rho^\gamma) \tag{5}$$

with f a function and γ a material constant; similar expressions apply for the viscosity and diffusion constant. This relation has been demonstrated to be applicable to a very large number of liquids and polymers,[3,17] with deviations observed only for hydrogen bonded materials.[18] If τ_{JG} is a function of τ_α, the α and JG relaxation times would have the same scaling exponent, γ, or stated differently, the relationship between τ_α and τ_{JG} would be independent of thermodynamic state point. Prior assessments of density scaling of the two processes were based on a comparison of the collapse of τ_α and τ_{JG} as a function of $T\rho^{-\gamma}$ for a common value of γ;[14−16] however, this approach requires an accurate equation of state in order to convert measured $\tau(T,P)$ to $\tau(T,\rho)$.

We avoid this problem by comparing spectra of PBD obtained at different thermodynamic conditions for which τ_α, that is, the α peak frequency, is the same (which corresponds to variation of T and P at constant $T\rho^{-\gamma}$). Under such isochronal conditions, the ratio τ_{JG}/τ_α would be constant if the two relaxations have the same density scaling relation, including the same scaling exponent γ. However, we find that the dielectric spectra are not invariant for constant τ_α; there is a systematic increase in the separation of the two peaks with increasing T and P. This means that the respective scaling exponents cannot be the same. This experimental result is consistent with an earlier study in which slowing down of the α process in PBD through the addition of antiplasticizer (high-T_g diluent) did not lead to any change in τ_{JG} (although the JG relaxation times were only measured in the glassy state).[19] Measurements of secondary relaxations in binary mixtures of glasses suggest behavior at odds with eqs 2 and 4,[20,21] although interpretation of the experimental results has been questioned.[22] We also report herein molecular dynamics (MD) simulations that reveal how subtle changes in chemical structure, specifically the conformational potential of the repeat units, underlie the effect of temperature and density on the relative magnitude of the α and JG relaxation times. Since our work addresses polymer dynamics, the results may not be generally applicable to glass-forming materials near or below T_g. For example, it is known that deep in the glassy state differences become evident between the JG dynamics of polymers and molecular liquids.[23] Nevertheless, a firm conclusion is that for PBD, as for PMMA,[16] the ratio τ_{JG}/τ_α decreases with increasing P and T; thus, there is no universal connection between the time scales of the α and JG processes.

■ EXPERIMENTAL SECTION

The monodisperse 1,4-polybutadiene (Bridgestone Americas) had a weight-average molecular weight = 138 kg/mol; details of the material can be found elsewhere.[24] The dielectric response is dominated by the cis units, with a negligible contribution from the ~9% vinyl content. Dielectric spectra were measured with a Novocontrol Alpha Analyzer on films having a thickness in the range 0.07−0.12 mm. Spectra were collected from 210 to 142 K at 0.1 MPa and from 252 to 197 K at pressures up to 795 MPa.

Molecular dynamic simulations (MDs) were carried out in the NPT ensemble, using the RUMD software[25] modified to incorporate a Berendsen barostat. 2000 Lennard-Jones particles were simulated (20 polymer chains × 100 segments). Nonbonded segments interact through a Lennard-Jones potential with the interparticle distance parameter and the potential well depth both set to unity. All MDs results are given in dimensionless Lennard-Jones units. Bond lengths were kept approximately constant (within 1%) using stiff harmonic bonds with a force constant 10^5. Bond angles were equal to 120°, kept essentially constant (within a few degrees) by means of a stiff harmonic bond angle potential, with the spring constant = 1000. Two model polymers were simulated: (a) *freely rotating chains*, with bond length of 0.48; (b) *semiflexible chains*, with bond length of 0.35. For the latter, a torsional potential was used, corresponding to that for the alkyl dihedrals in an atomistic model of polybutadiene,[26] and reduced to 40% of its original value in order to bring the JG relaxation time into the accessible time scale.[27]

■ RESULTS

Dielectric Spectroscopy. Measurements were carried out over a range of T and P (Figure 1). At lower temperatures and higher pressures the JG peak emerges toward higher frequencies from partial overlap with the α-relaxation. Figure 2 displays spectra obtained at three state points chosen so that the α peak frequency is the same for each. To superimpose the α peak maxima, the spectra in Figure 2 were scaled vertically

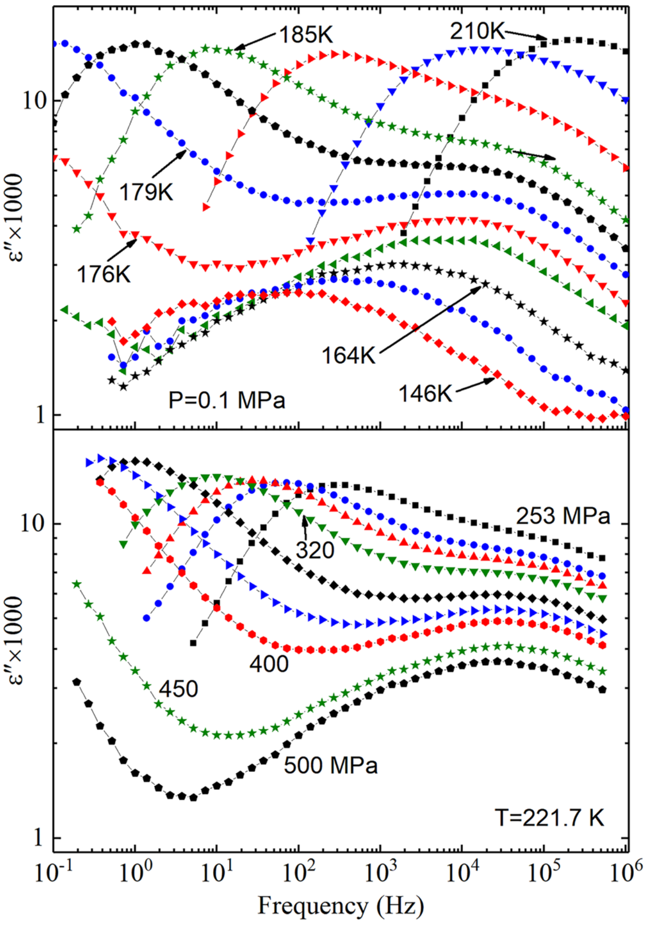

Figure 1. (a) Spectra of PBD at 0.1 MPa and varying temperatures. (b) Spectra at 221.7 K and varying pressures. At the highest pressures another secondary relaxation emerges.[9,10]

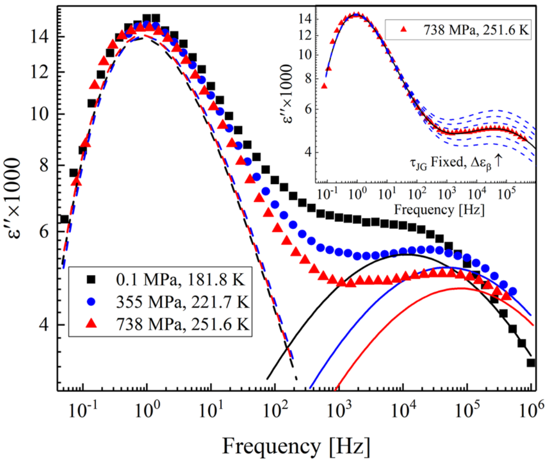

Figure 2. Dielectric spectra at the indicated T and P, corresponding to a nearly constant τ_α = 0.2 s. Dashed lines are eq 3, with the JG contributions from eq 7 shown as solid lines. Spectra shifted vertically (≤10%) to superimpose the α peaks; spectrum at 251.6 K also shifted horizontally by a factor of 1.1. (inset) Dielectric spectra at indicated T and P. Solid line is the fit of eq 1; dashed lines are fits using same τ_{JG} but varying $\Delta\varepsilon_{JG}$ by as much as 20%.

10% or less to account for small variations of the dielectric strength. As known for many materials,[8,9] the peak shape is isochronally invariant; that is, β_K is constant for constant τ_α. Notwithstanding the constancy of the α peak, the JG peak shifts toward higher frequency with increasing T and P. This implies that τ_{JG} does not depend on τ_α. To verify that these apparent changes are not due to changes in JG peak intensity, the strength parameter Δ_{JG} was varied by as much as ±20% at fixed τ_{JG}. This was found to have a negligible effect on the position of the JG peak (Figure 2, inset). Thus, the shift of the JG peak at constant τ_α is not an artifact of a changing dielectric strength.

This conclusion, which is the main point of this work, is independent of any model or assumptions. Nevertheless, to proceed further we extracted values for the relaxation times by fitting the spectra using either of two assumptions: (i) independent motion of the α and JG processes, corresponding to additivity in the frequency domain

$$\varepsilon^*(\omega) = \varepsilon_\alpha^*(\omega) + \frac{\Delta\varepsilon_{JG}}{1 + (i\omega\tau_{JG})^a} + \varepsilon_\infty \tag{6}$$

or (ii) contemporaneous α and JG processes[28]

$$\varepsilon^*(\omega) = \int_0^\infty e^{-i\omega t}\frac{d}{dt}[\Delta\varepsilon_\alpha\varepsilon_\alpha(t) + (1 - \Delta\varepsilon_\alpha)\varepsilon_\alpha(t)\varepsilon_{JG}(t)]\, dt \tag{7}$$

in which $\varepsilon_{JG}(t)$ is the Cole−Cole equation in the time domain. Initially all fit parameters were allowed to vary freely, with the two shape parameters determined to be temperature and pressure independent, β_K = 0.43 ± 0.01 and a = 0.30 ± 0.01; this is in agreement with prior results for PBD.[29] The spectra were then refit using these values of β_K and a, with the strength parameters and relaxation times adjusted to obtain a best-fit of the spectra. Equations 6 and 7 yielded nearly identical results for the relaxation times, except for those spectra in which the peaks substantially overlapped. The average τ's for the two methods are plotted in Figure 3, with the almost negligible error bars (not larger than the symbol size) representing the difference in the relaxation times calculated by the two equations.

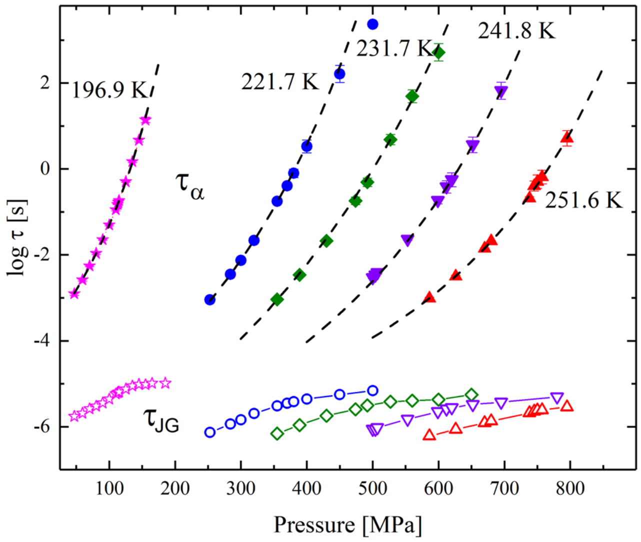

Figure 3. Johari−Goldstein (open symbols) and local segmental (filled symbols) relaxation times, determined as the mean of eqs 6 and 7.

Note that the pressure sensitivity of the segmental dynamics of PBD is weak in comparison to other polymers. Defining the glass transition temperature as the temperature at which τ_α = 100 s, we obtain the pressure dependence of T_g (Figure 4). In the limit of low pressure dT_g/dP = 116 ± 6 K/GPa, among the lowest found for polymers.[3,17] This is a consequence of a low fragility and small activation volume (=110 ± 6 and <70 mL/mol, respectively, in the low pressure limit).

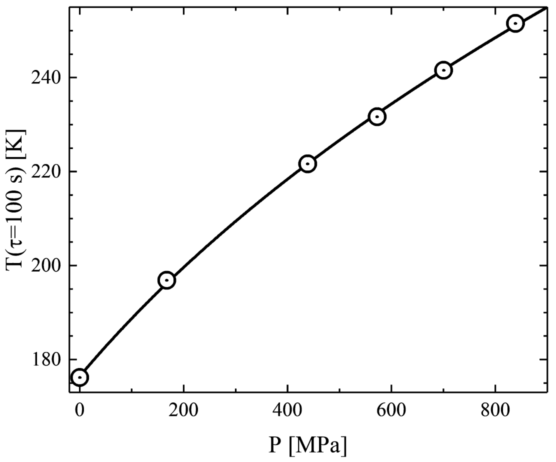

Figure 4. Glass transition temperature of 1,4-polybutadiene as a function of pressure. In the ambient pressure limit, dT_g/dP = 116 ± 6 K/GPa.

Displayed in Figure 5 is τ_{JG} as a function of τ_α. The variation of the JG relaxation time at constant τ_α is systematic and substantial, τ_{JG} changing by as much as an order of magnitude. This different sensitivity of the two relaxation times to changes in state point is evident as well in the inset showing the temperature variation of τ_{JG} at various fixed values of τ_α. The unambiguous conclusion is that τ_{JG} is not a function of τ_α; rather, the separation of the α and JG peaks at fixed τ_α increases significantly with increasing T and P (as also apparent in Figure 3). We note that the coupling model predicts approximate constancy of the quantity τ_{JG}/τ_α (e.g., eq 4).[6,7] However, without specifying the magnitude of the variance of τ_{JG} at

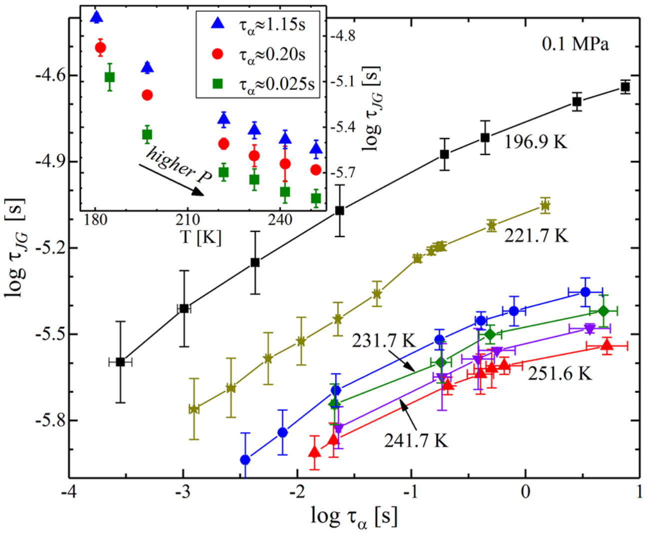

Figure 5. JG relaxation time as a function of τ_α for variation of T and constant ambient pressure and variation of P at various fixed temperatures. (inset) Variation of τ_{JG} with temperature at the indicated constant values of τ_α; error bars represent the difference between values calculated using eqs 6 and 7.

constant τ_α, this prediction of the model is not amenable to experimental verification.

Molecular Dynamics Simulations. For molecular liquids isochronal superpositioning of the JG and α relaxation times appears valid,[14,15] whereas for PMMA[16] and PBD the ratio τ_{JG}/τ_α varies with the thermodynamic state point. To understand the origin of this behavior, MDs were carried out for two polymers that exhibit secondary relaxations identifiable as JG processes.[30] The two chains differ in backbone flexibility: a freely rotating chain and a semiflexible chain. A shorter bond length is used for the latter in order to achieve a similar separation of α and JG time scales for the two model polymers, but the results do not qualitatively depend on bond length. For both, the translational and rotational correlation functions decay in three steps, corresponding to vibrations, the JG relaxation, and the α relaxation. These three processes can be seen in the susceptibility corresponding to the first-order bond rotational correlation function, shown in Figure 6 for state points selected to have the same τ_α. Relaxation times were determined by fitting the susceptibility spectra using eqs 6 and 7, which yielded identical results. Figure 7 shows JG relaxation times for several state points having the same τ_α. Choosing a different measure of the dynamics, such as the intermediate scattering function or the torsional autocorrelation function, would yield different relaxation times and spectral shapes, but the results are qualitatively the same.

For the freely rotating chain, τ_{JG} is approximately constant at constant τ_α, in agreement with the results of Bedrov et al.,[31] although there is a very small (but consistent) increase in τ_{JG} with increasing temperature at constant τ_α. For the semiflexible chain, the JG relaxation becomes significantly faster with increasing temperature and pressure at constant τ_α. The slope of the $\tau_{JG}(T)$ curve in Figure 7 is a measure of the deviation from the prediction of constant τ_{JG}. This slope decreases with increasing temperature/pressure (isochronal τ_α). Evidently, the intramolecular potentials (which remain the same) exert a smaller constraint on the dynamics with increasing thermal energy, thus bringing the behavior closer to that of the freely rotating chain. The same behavior is observed for polybutadiene in the inset to Figure 5.

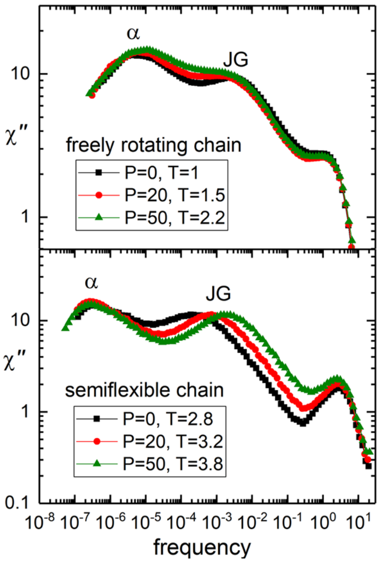

Figure 6. Imaginary part of the susceptibility corresponding to the first-order bond rotational correlation function, for the freely rotating and semiflexible chains at the indicated state points. State points were chosen to have approximately the same α relaxation time. The density change from $P = 0$ to $P = 20$ and $P = 50$ is approximately 5% and 10%, respectively, for both systems.

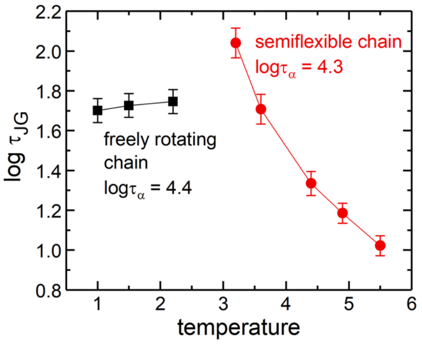

Figure 7. JG relaxation times from MD simulations at state points having the indicated constant value of the α relaxation time.

We further modified the semiflexible chain model to more closely approximate polybutadiene, first taking into account double bonds and corresponding cis−trans isomers and then adding 9% vinyl monomers, using the potentials of ref 26. (The dihedral potentials, except for the double bonds, were kept reduced at 40% of their original value in order that the JG process be observable.) The qualitative behavior of the α and JG relaxations was not affected by these changes (results not shown), suggesting that the operative difference between the freely rotating chain and real polybutadiene is the torsional potential.

CONCLUSIONS

The main result of this work is the determination that the time constant for the JG relaxation in PBD is not a function of τ_α. The analysis leading to this conclusion avoids the ambiguity of identifying the JG among sundry secondary relaxations, since polybutadiene has no pendant groups. Moreover, the behavior reported herein is directly evident in the isochronal spectra, obviating the need to extract relaxation times by fitting the dielectric spectra. The results are consistent with an increasing separation in time scales of the JG and α processes upon addition of antiplasticizer to PBD.[19] An implication of our finding is that if both relaxations exhibit density scaling, their respective scaling exponents will differ. These experiments are supported by MDs, which indicate that the origin of the breakdown of a strict relationship between τ_{JG} and τ_α is the limited flexibility of the PBD backbone. More flexible polymers, and presumably molecular liquids as well, have simpler dynamics because of their capacity to avert intermolecular constraints on local motions. Thus, while a common γ for structural and secondary dynamics can be observed in some materials, such behavior is not universal.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the Office of Naval Research, in part by the Naval Materials Division (R.G. Barsoum, Code 332). We thank T. E. Hogan of Bridgestone Americas for synthesizing the polybutadiene. T.R. acknowledges an American Society for Engineering Education postdoctoral fellowship.

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DOI: 10.1021/acs.macromol.8b00664