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Why Enhanced Subnanosecond Relaxations Are Important for Toughness in Polymer Glasses

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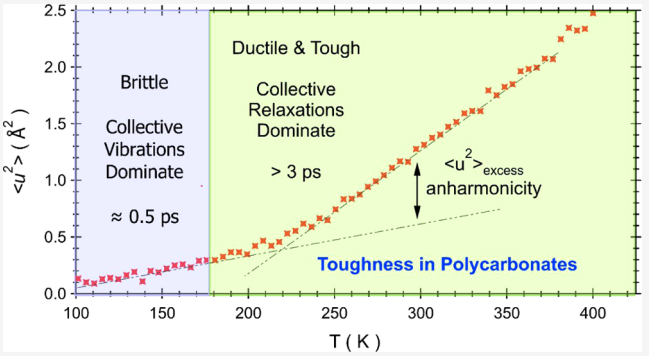
ABSTRACT: This manuscript explores the connection between the fast relaxation processes in an undeformed polymer glass and essential trends in the mechanical toughness, a nonlinear mechanical property that is of practical interest for engineering polymers with high impact strength. We quantify the time scale of the molecular relaxations in the subnanosecond regime for a quiescent polycarbonate glass using inelastic and quasi-elastic neutron scattering and then correlate these processes with the macroscopic brittle-to-ductile transition (BDT), which demarcates a change in the dominant mechanism of failure and a marked increase in the material toughness. We show that the macroscopic phenomenon of the BDT corresponds to a change in the dominant dynamical process at the nanoscale. The brittle regime is characterized by collective vibrational modes (the so-called Boson peak) with a characteristic time scale $\tau \approx 0.5-0.8$ ps, while slower collective relaxations with $\tau \approx 3$ ps become dominant above the BDT. We further establish that the onset of ductility coincides with the appearance of anharmonicity in the mean-square atomic displacement $\langle u^2 \rangle$ on a picosecond time scale, emphasizing that fast anharmonic molecular motions are important for energy dissipation. This builds upon our previous report correlating toughness with the amplitude of these anharmonic fluctuations across a wide range of polycarbonate glasses. Brillouin light scattering measurements are used to characterize the bulk and shear moduli of the material, revealing a concomitant upturn in Poisson's ratio in the region of the BDT, a phenomenon that has been reported in metallic and oxide glasses. The ratio of transverse acoustic mode velocity and the Boson peak frequency is used to estimate the length scale for these processes, indicating that the dynamic heterogeneities are collective across 100−1000s of atoms. These length scales are strikingly similar to the activation volume of yield derived from mechanical measurements, suggesting that these fast and collective relaxation processes may be related to the mechanisms of yield.



INTRODUCTION

Toughness is a desirable attribute in a polymeric glass. Tough polymers, such as polycarbonates (PCs), are renowned for their combination of optical clarity and high impact strength. This has led to their use in engineering applications such as safety glasses, aircraft windows and canopies, and even bulletproof windows. The exemplary toughness in PCs is, however, not a common trait shared by all polymer glasses. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are two examples of optically transparent polymer glasses that lack mechanical toughness. Toughness, defined as the amount of energy that a material can absorb per unit volume without catastrophic failure, is a complicated viscoplastic property. This energy can either be elastically stored in a deformed material, like a spring, or dissipated through internal relaxations or deformation mechanisms that do not lead to rupture. However, strength alone does not ensure toughness. In fact, toughness and strength are normally anticorrelated.[1] High strength materials can store significant levels of elastic strain energy but still exhibit brittle failure at low strains. Toughness is manifest when a material is able to dissipate energy through either internal relaxations or plastic deformation without catastrophic voiding, cracking, or failure. Tough polymers normally result from a tradeoff between strength and ductility. In PCs at ambient conditions, this balance stems from their propensity to undergo ductile deformation, via diffusive shear yielding, as opposed to highly localized crazing that leads to void formation and catastrophic cracking.[2−5] The combination of a low critical stress for shear yielding and a high stress for

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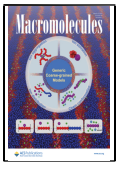

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craze nucleation is a salient characteristic of tough polymers like PCs. However, even in PCs, this toughness is lost when the material is cooled below the brittle-to-ductile (BDT) transition temperature; at very low temperatures, highly localized deformation modes become dominant and result in brittle failure.[6]

This manuscript focuses on the mechanisms that dissipate energy and contribute to the toughness of PC glasses. For decades, it has been appreciated that relaxations in the glassy state are important for mechanical toughness in polymers.[7−10] However, this understanding has been built on a disparity between the time and length scales of the molecular mechanisms that dissipate energy and the characterization techniques that are used to quantify these relaxation processes. We recently initiated an effort to close this gap by reporting correlations between the level of anharmonicity in the atomic mean-square displacement, $\langle u^2 \rangle$, of undeformed polymer glasses as quantified by incoherent neutron scattering, and their impact strength.[11] Across a homologous series of PCs with large variations in toughness, we reported a strong correlation between $\langle u^2 \rangle_{\text{excess}}$ and impact strength. Our assertion was that the large "excess" mean-square atomic displacements measured in the tough PCs reflect collective motions of the molecules on a subnanosecond time scale that are the signature of incipient dissipative relaxations. However, these measurements, based on a Debye−Waller analysis of the elastic incoherent neutron scattering intensities, did not precisely resolve the time scale of the motions beyond ascertaining that they were faster than the approximately 1 ns resolution of the spectrometer. In this manuscript, we analyze the full energy spectra of the scattered neutrons to identify the dynamical processes and relevant time scales that underpin these observed motions in the quiescent glass and provide first-order estimates of the number of atoms that participate in these relaxations. This is performed as a function of temperature (T) from deep in the glassy state to well above room T, traversing the BDT of a tough PC glass. We find that the onset of anharmonic fluctuations as quantified by the excess contribution $\langle u^2 \rangle_{\text{excess}}$ is relative to the low T harmonic contribution to $\langle u^2 \rangle$ that scales linear in T. The increase in $\langle u^2 \rangle_{\text{excess}}$ with T coincides with the emergence of a relaxation process with a characteristic time scale, $\tau \approx 3$ ps. This is the typical order of magnitude of the fast β relaxation time.[12,13] The onset of this relaxation coincides with the BDT temperature, confirming that many-atom, collective relaxations underpin macroscopic toughness.

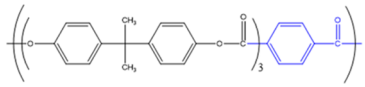
The time and length scales of these fast relaxations are quantified using inelastic and quasi-elastic neutron scattering (INS and QENS) methods at the NIST Center for Neutron Research (NCNR). As in our previous work, fixed window scans on the high flux backscattering spectrometer (HFBS) are used to quantify $\langle u^2 \rangle_{\text{excess}}$ as a function of temperature. These INS measurements are complimented here by QENS measurements on the disc chopper spectrometer (DCS) to characterize the time scale of these relaxational processes in the critical picoseconds to nanoseconds range. Our hypothesis is that this window is critical because it represents the first signs of when the fast-optical modes that are readily visible in Fourier transform infrared (FTIR) or Raman spectroscopy, reflecting local bond vibrations on the fs time scale, begin to couple and give rise to collective motions across several atoms and bonds. These fast and largely reversible collective motions become overdamped in a thermally activated fashion leading to slower relaxational processes ($\tau \geq \mu$s), which are readily accessible via solid-state nuclear magnetic resonance (ssNMR), dielectric relaxation spectroscopy (DRS), dynamic mechanical analysis (DMA), and other mechanical relaxation methods. Our assertion is that INS and QENS are well suited to bridge this gap between the high-frequency atomic vibrations and the much slower diffusive properties of polymer glasses. The use of INS and QENS to characterize polymer relaxations is not new; this is a mature field with several comprehensive texts on the topic.[14−16] The unique aspect of the present manuscript is that it leverages these techniques to understand the relationship between these fast relaxation processes and the macroscopic toughness of polymer glass, relating two measurements on vastly different time and length scales.

MATERIALS AND METHODS[17]

The synthesis and thermomechanical characterization of the B_3t PC copolymer, whose chemical structure is shown in Scheme 1, were

Scheme 1. Chemical Structure of the B_3t PC Copolymer

B_3t: Bisphenol-A Polycarbonate with a terephthalate (t) link every 3rd repeat unit



published previously.[2,3,17] Here, we focus on the protocols for the inelastic neutron scattering measurements. Samples were prepared by dissolving B_3t in dichloromethane, precipitating into acetone, and drying in vacuo. The solution-precipitated powder was then distributed into an aluminum foil packet (so as to achieve 95% neutron transmission to minimize multiple scattering), which was subsequently annealed at T_g + 20 K for 1 h under vacuum and quenched to room temperature. This thermal treatment reproduces the thermal history used for the mechanical property tests.

The incoherent neutron scattering experiments were performed at the NIST Center for Neutron Research on both high flux backscattering spectrometer (HFBS) located on the NG2 beamline and the disc chopper spectrometer (DCS) located on the NG6 beamline. For both instruments, the polymer foil packets were rolled into the annular sample cans for the instrument and measured under vacuum. The HFBS spectrometer utilizes cold neutrons with a wavelength of 6.271 Å and probes motions over a reciprocal-space range of 0.25 Å^{-1} < Q < 1.75 Å^{-1}, where Q is the magnitude of the momentum transfer vector, corresponding to real space length scales $2\pi/Q$, or approximately 3.6−25 Å. The HFBS spectrometer was operated in the "fixed window mode", where the elastic incoherent scattered intensity is measured as a function of Q and T. The 0.8 μeV full width at half-maximum (FWHM) energy resolution of HFBS spectrometer means that motions slower than approximately 200 MHz (approximately one nanosecond) appear as static and contribute to the elastic scattering. In this mode, the sample was ramped from approximately 50 K through T_g at 1 K/min. For elastic incoherent scattering, the Q-dependence of the elastic scattering at each T is often approximated with the Debye−Waller factor

$$I_{\text{inc,elastic}}(Q) \propto \exp\left(-\frac{1}{3}Q^2\langle u^2 \rangle\right) \quad (1)$$

Within this model, based on a harmonic oscillator, the slope of $\ln I_{\text{inc, elastic}}(Q)$ versus Q^2 is proportional to $\langle u^2 \rangle$. The details of these $\langle u^2 \rangle$ calculations, including the linearized fits, for B_3t are provided in the SI. It is important to realize that the magnitude of $\langle u^2 \rangle$ depends upon the Q range over which the fits are performed. Here, we report the linear fits from the low Q region (detectors 1−7, Q = 0.25−0.87

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Macromolecules 2021, 54, 2518−2528

Å^{-1}), which is consistent with our previous reports of $\langle u^2 \rangle$ on polycarbonate materials using the HFBS spectrometer.[11,18,19]

The DCS spectrometer was used to characterize the INS spectra as a function of temperature between 75 and 400 K in increments of approximately 30 K using an incident neutron wavelength of 4.8 Å. At each T, the spectra were collected for 12−24 h (depending on the T) to obtain reasonable statistics. To further improve the statistics, the resulting spectra were integrated over all Q from the spectrometer into a single spectrum for each T. The data from both spectrometers were normalized to a vanadium standard, and the spectra were fit using the DAVE software package.[20] The uncertainties reported in Figures 3 and 4 represent 1 standard deviation in the fitted values.

In situ Brillouin light scattering (BLS) was used to measure sound velocities in the temperature range from 93 to 413 K on a Linkam THMS600 sample stage by using a 532 nm Verdi V2 DPSS green laser light source. B_3t films were cast from dichloroethane onto a clean Si wafer, dried under ambient conditions, and then annealed at 453 K under vacuum for 1 h. After annealing, the film was peeled off the Si wafer and placed on a polished Pt disk for temperature-dependent measurements. The sample was cooled/heated at a rate of 50 K/min to reach a target temperature. Each BLS spectrum was collected in the emulated platelet geometry. Details of the experimental setup and the light scattering geometry can be found elsewhere.[21] Three spots were measured for each of the five samples at room temperature to estimate the error in measurements. Due to the long-time temperature-dependent measurements, we did not perform multiple measurements at each temperature, but the error bars should be similar to ambient conditions; once a sample was set up at room temperature, it was not touched during temperature-dependent measurements.

RESULTS

This manuscript focuses on B_3t, a copolymer whose repeat unit consists of three consecutive bisphenol-A polycarbonate monomers (B_3) followed by a terephthalate linkage (t), as illustrated in Scheme 1 in the Experimental Section. As described in previous publications, inserting the t linkages into the PC backbone moderately increases the glass-transition temperature, $T_g \approx 444$ K, without compromising toughness.[17,22] Despite the sophisticated molecular structure, the behavior of B_3t is typical of a tough PC glass in all respects.

A few typical QENS spectra of B_3t are shown in Figure 1, where the Bose-scaled scattering intensity (described in the SI) is plotted as a function of neutron energy exchange. The intense peaks at zero energy correspond to elastically scattered neutrons that do not exchange energy with the sample. The ordinate has been scaled so that the peak of the elastic scattering is out of view; the ensuing discussion focuses on the lower-intensity inelastic and quasi-elastic modes. A fit of the elastic peak is shown (solid red curves), illustrating the energy resolution of this DCS configuration. The full width at half-maximum (FWHM) of the Gaussian elastic resolution function is approximately 0.044 meV, obtained by fitting the lowest T spectra at 75 K (see Figure S2). There are two additional features in the spectra collected above 75 K. The first is a broad, asymmetric peak near −1.4 meV. This feature is commonly referred to as the Boson peak (BP) and fits with an empirical, asymmetric log−normal distribution (solid blue curve). The BP is readily visible in the low T spectra deep in the glassy state. The second feature is the low-intensity, symmetric broadening around the base of the elastic peak (dashed purple), which quantifies the quasi-elastic scattering (QES). The QES is fit with a single Lorentzian with an FWHM of 0.25 meV. The sum of the elastic resolution peak, log−normal BP, and the Lorentzian QES functions are enough to parameterize the spectra at all Ts studied in the present work. Spectra of B_3t were collected in the glassy state from 75 to 400 K in increments of 30 K. While the individual components for each of these fits are reported in Figure S2, Figure 1c summarizes the total fits as a function of T and shows a smooth transition from BP-dominated spectra near 100 K to QES-dominated spectra near 400 K. As T increases, the BP frequency shifts to lower energies (softens), while the amplitude of the QES increases. We explore these important trends in greater detail below.

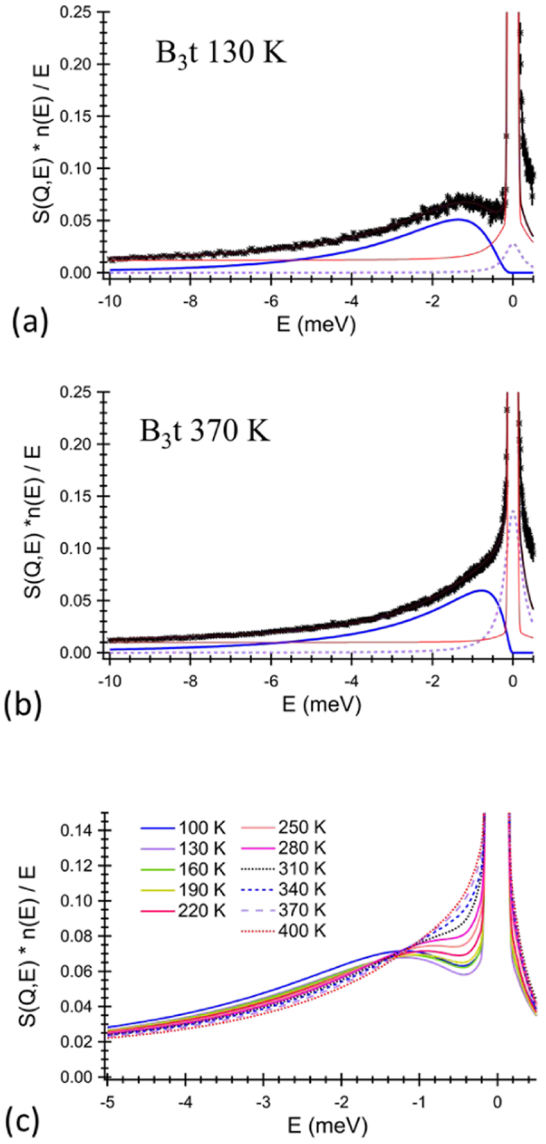

Figure 1. Representative plots of the Bose-scaled neutron scattering intensity scans ($S(Q,E)$) versus scattering energy E. A few examples of the fitted inelastic neutron scattering spectrum of B_3t PC at 130 K (a) and 370 K (b). The black points are the experimental data points, while the solid black line represents the fits. The fits consist of the sum of the elastic resolution function (solid red line), a broader Lorentzian reflecting the quasi-elastic scattering QES (purple dashed line), and a log−normal peak near −1 meV that represents the Boson peak BP (solid blue line). In part (c), the fits at each of the Ts studied here are compared; the contributions from the individual components at each T are provided in the SI. These fits show that as T increases, the BP peak softens to lower vibrational energies, while the intensity of the QES contribution increases.

The BP is a common feature in the INS spectra of amorphous materials deep in the glassy state; its amplitude and

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Macromolecules 2021, 54, 2518−2528

peak position vary from material to material, but it is generally observable in all glassy materials at cryogenic temperatures. The location of the BP at finite energy distinct from the QES is indicative of a collection of vibrational modes. The BP represents collective, quasi-localized vibrational modes arising from the intrinsic asymmetry of the intermolecular interactions of glassy materials at low temperatures, in combination with the intrinsic granularity of matter on a molecular scale. It is an acoustic-like vibration mode in character, having many similarities with the transverse acoustic mode phonons familiar from crystalline materials.[23−27] The peak energy for the BP in B_3t softens from approximately −1.4 to 0.8 meV upon heating from 100 to 400 K, as shown in Figure 2b, corresponding to time scales of $\tau \approx 0.5-0.8$ ps. This is in line with previous observations indicating that the Boson peak time is roughly a factor of 10 shorter than the fast relaxation time.[12,28] In contrast, the peak amplitude of the BP is essentially independent of T, as plotted in Figure 3a. This suggests that while the mode softens with T, the magnitude of the mode does not significantly change. We return to these points in the later discussion below.

The similarities of the BP to a transverse acoustic phonon mode inspired us to perform Brillouin light scattering (BLS) measurements as a function of T to accurately characterize both the longitudinal acoustic (LA) and transverse acoustic (TA) modes. Figure 2a displays the BLS spectra over a similar T range, where the LA and TA modes are visible. Peaks 1 and 2 correspond to the compressive LA modes in the back-scattering and emulated platelet geometries,[21] respectively, while peak 3 corresponds to the shear TA mode in the emulated platelet geometry. We use the frequency shifts of modes 2 and 3 to calculate the acoustic velocities V_{LA} and V_{TA}, respectively, as a function of T (Figure 2b). The thermal softening of the acoustic modes is immediately evident. V_{LA} softens from approximately 2900 to 2100 m/s, while the V_{TA} softens from approximately 1300 to 800 m/s. Figure 2b also shows that the thermal softening of the BP peak energies in meV (right axis), extracted from fits in Figure 1, tracks the softening V_{TA}. This is entirely consistent with previous reports that the BP shares many similarities with the transverse acoustic modes.[23−27] This is an important observation because it bolsters our confidence in the fits to the QENS spectra, particularly at high T where the BP is obscured by the intense QES (Figure 1b, for example). As shown in Figure 2a, BLS does not suffer this limitation; peaks 2 and 3 are well resolved at all T.

We now shift our attention to the Lorentzian component of the fits, i.e., the QES broadening around the elastic resolution of the spectrometer. The presence of QES is indicative of a process that is slower than the motions reflected in the BP and is thought to represent a cooperative many-atom relaxation (vide infra). The 0.25 meV FWHM of the QES Lorentzian corresponds to a time scale of approximately 3 ps, slower than the 0.5−0.8 ps time scales associated with the BP. We also note that the FWHM of the QES component does not vary with T; a single FWHM fits all of the B_3t spectra below T_g. As suggested in reference to Figure 1, we see interesting variations in the relative amplitudes of the BP and QES scattering as a function of T. At the lowest temperatures, deep in the glassy state, the QENS spectra are dominated by the BP. Closer to T_g, the QES dominates and obscures the BP. This is quantified in Figure 3a (left axis) where the peak amplitudes of BP and QES components are plotted as a function of T. These peaks

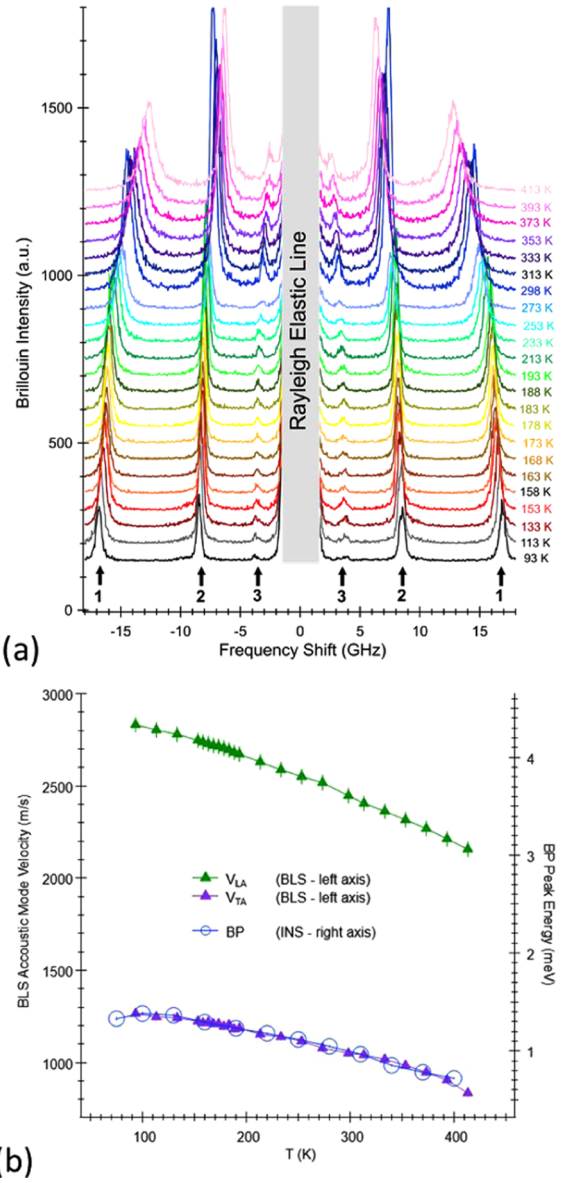

Figure 2. Part (a) shows the Brillouin light scattering (BLS) spectra as a function of T for B_3t PC. Peaks 1 and 2 correspond to the longitudinal/compressive modes (in different geometries), while peak 3 corresponds to the transverse/shear mode. The frequency shifts of peaks 2 and 3 (both from the emulated platelet geometry) are used to calculate the T-dependence of the longitudinal and transverse acoustic velocities, V_{LA} and V_{TA}, respectively, as shown in part (b). Part (b) shows that the thermal softening of the Boson peaks from the fits to the QENS data in Figure 1 tracks the softening of the transverse acoustic mode; the right axis has been scaled to illustrate the overlap. Error bars on the acoustic modes represent 1 standard deviation from repeating one measurement at room T 10 separate times.

are the maximum values of the fitting functions at their respective peak positions and should not be confused with the integrated area beneath the fit function. At low T, the 0.5−0.8 ps quasi-localized vibrations associated with the BP dominate the dynamics. As T is increased, these quasi-localized modes are overcome by the emergence and growth of 3 ps collective relaxations (QES). This transition occurs near 175 K, as illustrated in Figure 3a, which we show is consequential for the emergence of mechanical toughness.

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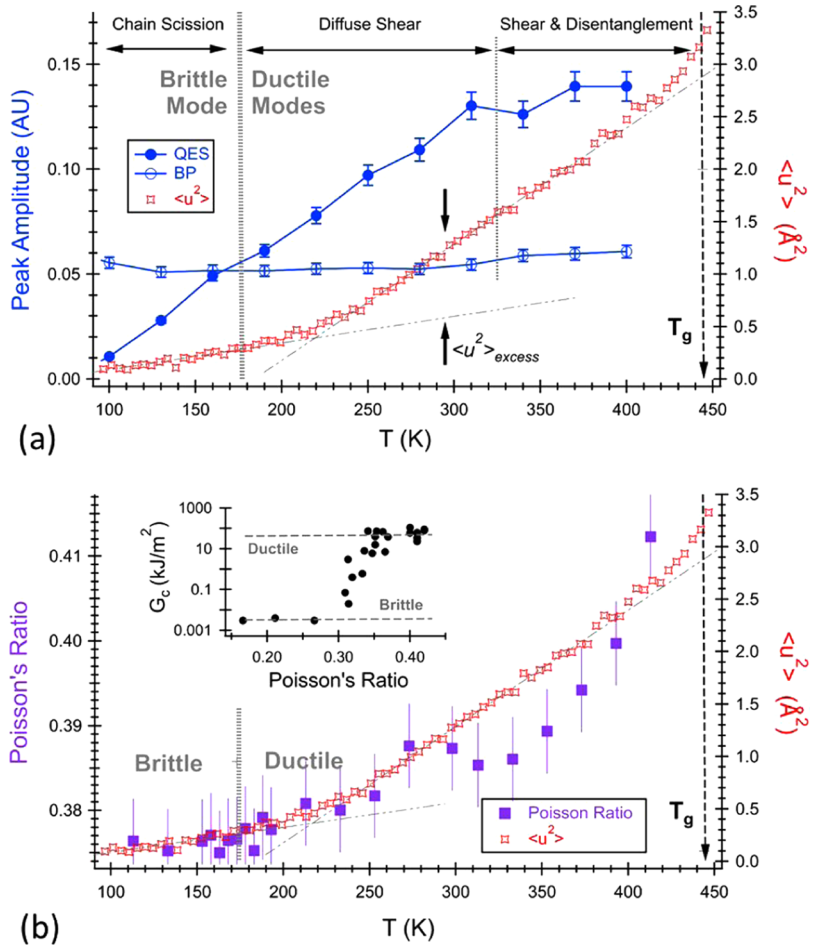

Figure 3. Peak amplitude of both the BP and the quasi-elastic scattering (QES) components is plotted in part (a) as a function of T (left axis). The amplitude of the BP does not change significantly, while the intensity of the QES mode increases almost linearly with T. Superimposed over the data is the evolution of $\langle u^2 \rangle$ (right axis) as a function of T, showing that the onset of anharmonicity, as defined by $\langle u^2 \rangle_{excess}$, nominally corresponds to the cross-over where the QES relaxations overtake the BP vibrations. The dashed vertical line at 175 K corresponds to the brittle-to-ductile transition for this B_3t PC as published previously.[6] In part (b), the thermal evolution of Poisson's ratio (left axis) from Brillouin light scattering (BLS) measurements is compared with the same $\langle u^2 \rangle$ data (right axis) presented in part (a). This comparison shows that Poisson's ratio also goes through an upturn in the vicinity of the brittle-to-ductile transition. The inset of part (b) plots the fracture toughness G_c as a function of Poisson's ratio for a series of metallic and oxide glasses,[29] illustrating the robust correlations between Poisson's ratio and the brittle-to-ductile transition.

In a previous publication,[6] we used the thin film deformation technique developed by Lauterwiser and Kramer to map out the deformation modes of B_3t as a function of temperature, which includes the region around the low-temperature BDT. In these studies, the polymer film was glued to a ductile copper grid and deformed under uniaxial tension. The onset strain for deformation/crack onset was used to assess the ductility of the film. Once deformation was initiated, small sections of the copper grid were removed and imaged in a transmission electron microscope to identify the deformation mechanism. Below the BDT, the favored deformation mechanism was the localized chain scission crazing, which is consistent with a brittle response. Above the BDT, there was a change to either diffuse shear banding or a mixed mode deformation that combines shear banding with widespread chain disentanglement crazing. These delocalized mechanisms mean that B_3t can dissipate the applied strain energy, consistent with the emergence of toughness above the BDT. The location of the BDT in B_3t ($T \approx 175$ K) from our previous publication[6] is indicated in Figure 3a with a thick dashed vertical line. We have also annotated the plot with the regions where the different deformation mechanisms mentioned above (chain scission, diffuse shear, shear and disentanglement) are active. The mechanical BDT shows excellent agreement with the temperature at which the QES relaxations first overtake the BP vibrations. This finding provides a direct correlation between nanoscopic dynamics and macroscopic deformation mechanisms, with profound implications for toughness.

Our most recent publication connected the amplitude of anharmonic fluctuations, as quantified by $\langle u^2 \rangle_{excess}$, to the Izod impact strength across a wide range of PC glasses.[11] We defined $\langle u^2 \rangle_{excess}$ as the excess atomic mean-square displacement above that of a simple harmonic oscillator, i.e., an energetic particle rattling inside a single, symmetric potential energy minimum. The harmonic model is appropriate for polymer materials in the cryogenic regime, where $\langle u^2 \rangle$ grows linearly with increasing T, as in the case for crystalline solids at low temperatures. Deviations from this linearity are interpreted, again as in the case of heated crystals, in terms of the onset of anharmonic molecular motions. However, this measurement did not allow us to quantify the time scale of these motions beyond the elastic resolution of the HFBS spectrometer that is <1 ns. These previous measurements were repeated on B_3t, as shown in Figure 3b, where we plot $\langle u^2 \rangle$

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Macromolecules 2021, 54, 2518−2528

(right axis) as a function of T. From this representation, we see that the onset of $\langle u^2 \rangle_{excess}$ coincides with both the cross-over between the BP- and QES-dominated regimes of the full QENS spectra and the onset of ductility and toughness above the BDT. This is consistent with our previous assertion that $\langle u^2 \rangle_{excess}$ is important for impact strength. In B_3t, we see that when toughness is lost below the BDT, $\langle u^2 \rangle_{excess}$ tends toward zero. Thus, in accordance with our prior work, we conclude that the $\langle u^2 \rangle_{excess}$ is a critical, nanoscale indicator of macroscopic toughness. Crucially, this work shows that the anharmonic motions, which give rise to $\langle u^2 \rangle_{excess}$ and the concomitant toughness in B_3t, are the 3 ps relaxations captured by the QES. The fast, quasi-localized vibrations of the BP that occur on the 0.5−0.8 ps time scale are active below the BDT but do not evolve into cooperative relaxational processes, which dissipate energy and engender toughness. Toughness appears to be rooted in fast collective vibrations deep in the glassy state that successfully evolve into relaxational processes upon heating. These are seminal insights into the origins of toughness in polymer glasses.

To better understand the correlation between collective relaxations and toughness, we return to the discussion on the competition between brittle craze formation, where nanoscale voids nucleate and localize in the material under a triaxial stress state, and diffuse shear yielding, where the stresses are delocalized under nondilatative shear stresses. The propensity for a material to resolve stress by changing volume (tension or compression) or shape (nondilatative shear) is described by Poisson's ratio, ν, defined (see below) by the ratio of the bulk modulus, B, to shear modulus, G. There are general correlations between Poisson's ratio and toughness, as summarized in a recent review.[30] Materials that tend to be softer in shear relative to tension or compression also tend to be tougher and have a larger ν. Lewandowski and co-workers correlated the BDT and fracture toughness, G_c, in series of metallic and oxide glasses with an increase in ν;[29] their data are reproduced in the inset of Figure 3b for inspiration. Recent molecular dynamics simulations by Shi and Deng on similar metallic glasses further support this notion by showing that fracture in a brittle glass is characterized by a small ν and highly localized deformation. However, as ν increases, the mechanical response transitions from brittle to ductile while the deformation becomes delocalized across a greater number of atoms.[31]

Poisson's ratio is readily calculated from V_{LA} and V_{TA} that we presented earlier according to the following relationships

$$\nu = \frac{3B - 2G}{2(3B + G)} = \frac{3(B/G) - 2}{6(B/G) + 2} \tag{2}$$

$$\nu = \frac{V_{LA}^2 - 2V_{TA}^2}{2(V_{LA}^2 - V_{TA}^2)} \tag{3}$$

In Figure 3b, we overlay the temperature dependence of Poisson's ratio with $\langle u^2 \rangle$ to reveal another interesting correlation. The measured onset of ductility in the B_3t PC coincides with both an onset of $\langle u^2 \rangle_{excess}$ and a discontinuous increase in Poisson's ratio that is consistent with connections to toughness described above. The increase in ν with temperature implies that the material prefers to deform under shear relative to triaxial expansion. This is consistent with our previously reported mapping of the deformation behavior in the B_3t PC.[6] Below the BDT, the material fails via chain scission crazing and void formation, which is a triaxial deformation mechanism; above the transition, ductile and nondilatative shear flow are enabled by the relative softening under shear. The emergence of these dissipative 3 ps structural relaxations appears to be critical for staving off nanoscale void formation and enabling shear deformation and toughness.

Thus far, the discussion has focused on the role of the collective 3 ps relaxations in determining toughness. We have not focused on the role that the BP and the collective vibrations play in this process. We bring this up in the context of Poisson's ratio because much of our understanding of this parameter is couched in discussions about density and connectivity. Materials with large Poisson's ratios tend to exhibit dense packing, nondirectional connectivity (like a liquid), and volume-conserving isotropic deformation; materials with small Poisson's ratios often display frustrated packing, have highly directional connectivity, and exhibit a more anisotropic mechanical response.[30] It is recognized that packing and dynamics are correlated. Sokolov and co-workers correlate strong or large amplitude BPs with heterogeneous packing and a small Poisson's ratio.[32] Regions of the sample where the interatomic packing is relaxed provide more room and softer potentials for these collective interatomic vibrations to take place. This is consistent with our previous report of an inverse correlation between the energy of the BP and the size of the density heterogeneities in the glass as evidenced by positron annihilation lifetime spectroscopy (PALS).[33] Poor packing leads to soft BPs. There are also strong correlations between the amplitudes of $\langle u^2 \rangle$ and the size of the PALS density heterogeneities, indicating that poor packing also leads to dynamic fluctuations.[34] The ability of the density fluctuations measured by PALS to quickly relax under mechanical loading has been surmised as the origin of mechanical toughness in PCs modified with cyclohexyl linkages.[3] We suggest that the softening of the BP vibrations is a precursor to the collective relaxations that lead to toughness in PC glasses. It is a reasonable question to ask if a polymer glass with a softer, more delocalized BP deep in the glassy state leads to a tougher response about the brittle-to-ductile transition temperature.

The notion of a characteristic length scale for the dynamic heterogeneities that underpin the BP has been explored by Sokolov and co-workers.[35,36] They use the ratio of the transverse acoustic mode velocity (V_{TA}) to the energy of the BP (E_{BP}) to formally define a dynamic correlation length, ξ, according to the relationships

$$\xi = \left(\frac{1}{\pi\, c}\right)\left(\frac{V_{TA}}{E_{BP}}\right) \tag{4}$$

$$V_{BP} = \frac{4}{3}\pi\, \xi^3 \tag{5}$$

where c is the speed of light and V_{BP} is the average volume pervaded by the dynamic heterogeneity assuming a spherical model. Equations 4 and 5 imply that a "softer" (lower-energy) BP leads to a larger dynamic volume V_{BP}. Based on the data presented in Figure 2b, we estimate V_{BP} as a function of temperature in Figure 4. For the temperature range considered in the present paper, the dynamic correlation volumes range from approximately 7 to 18 nm^3 (left axis in Figure 4). The previous study of Sokolov indicates that this length tends to grow upon heating, which is consistent with the simulation

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Macromolecules 2021, 54, 2518−2528

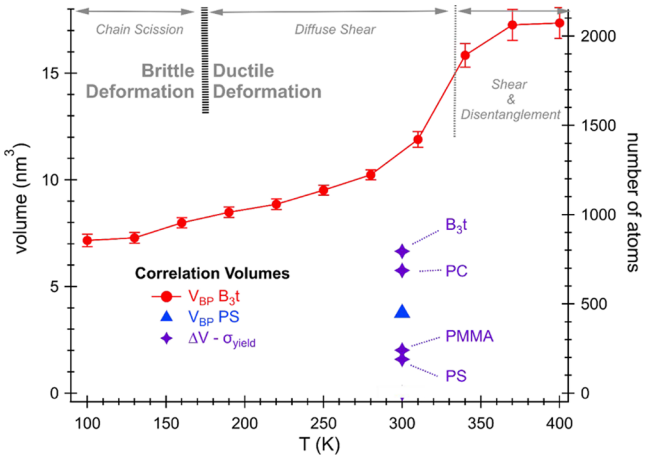

Figure 4. Ratio of the frequencies of the TA mode and BP is used to define a dynamic correlation volume (left axis) for the collection of atoms participating in the BP vibrations and gives estimates of the number of atoms (right axis) participating in these motions. Also shown are estimates of the activation volume for yield for BPA PC, PMMA, and PS, as reported in the literature,[3,43] making a comparison between dynamics and yield.

observations of collective motion taking the geometrical form of rearranging particles ("stringlets") on a picoseconds time scale;[37−41] dynamical structures also resolved in neutron scattering measurements.[42] The average length and distribution of these dynamic structures have only been quantified in recent works[40,41] where the stringlets are observed to be polydisperse polymeric structures whose shapes are roughly consistent with self-avoiding walks.

Given the room-temperature density of 1.2 g/cm^3 for B_3t PC[22] (and ignoring any T-dependence of density), this dynamic correlation volume corresponds to approximately 800−2000 atoms collectively participating in the quasi-localized vibrations. Sokolov and co-workers extend these concepts to an activated model of glass formation by exploring the pressure and temperature dependence of the α-relaxation (glass transition) in a series of glass-forming small molecules and polymers.[44] Through this approach, they quantify an activation volume of the glass transition and report strong correlations between ξ and the measured activation volume at T_g. This approach is analogous to the Eyring model of yield as an activated process, where one can similarly define an activation volume of yield ΔV-σ_{yield} by performing rate- and temperature-dependent deformation studies.[45,46] Using this approach, several authors have reported correlations between toughness and the activation volume for yield across several glassy polymers.[3,43] These studies have shown that tough polymer glasses are also characterized by a larger ΔV-σ_{yield}.

Inspired by these similarities, we summarize in Figure 4 some previously reported ΔV-σ_{yield} values in PC as a tough polymer, PS as a brittle polymer, and PMMA as an intermediate.[43] Using previously reported strain rate-dependent yield stress data,[6] we estimate the activation volume of yield for the B_3t to be 6.7 nm^3, which is slightly higher than the value of 5.4 nm^3 for published BPA PC.[3] These values at room-temperature are indicated by purple stars in Figure 4. It is striking that the magnitudes of ΔV-σ_{yield}, determined from macroscopic mechanical tests, are on par with the dynamic correlation volumes extracted from the QENS and BLS measurements. While it may seem far-fetched to link continuum mechanics models to the quiescent nanoscale molecular measurements reported here, this observation is consistent with our assertion that the time and length scales of the dynamics reported here are relevant for deformation and yield. We believe that there are some foundation and generality to this statement. In this manuscript, we have only performed QENS and BLS measurements on B_3t PC. However, estimates of the BP frequency[47] (15−18 cm^{-1}) and V_{TA} mode[48] (1500 m/s) for PS can be readily found in the literature. The corresponding room-temperature estimate of V_{BP} for PS is approximately 3.7 nm^3, indicated by the blue triangle in Figure 4. PS has both a smaller V_{BP} and a smaller ΔV-σ_{yield} than B_3t, consistent with the observation that PS is much more brittle than PC. This further supports our notion that the overall time and length scales of the fast dynamics, elucidated by the QENS measurements, are directly relevant for understanding the mechanical toughness in polymer glasses. In our view, this further supports the notion of damage mechanisms being characterized by characteristic microscopic volume, as embodied in the Erying model of yield.

In Figure 4, we notably do not see a transition in V_{BP} with T in the region of the BDT. While at first this might seem troublesome, we reiterate that V_{BP} is influenced by collective vibrations and the overall stiffness of the material, rather than the collective relaxation processes and associated dissipation. In this respect, it is not surprising then that the collective vibrations do not exhibit a discontinuity at the BDT. Recall in Figure 3a that the amplitude of the BP component is constant as a function of T across this regime and the BP peak softens smoothly. However, the strong upturn in the average dynamic correlation volume V_{BP} in Figure 4 near 335 K nearly coincides with the previously identified transition from diffuse shear bands to mixed mode of shear bands plus widespread disentanglement crazing within the ductile regime. Dynamic mechanical analysis of B_3t also shows a shoulder that emerges from the low T side of the α-relaxation peak, sometimes referred to as the β peak in PCs, in the same temperature range.[6,22] The process produces a concomitant reduction in the storage modulus, which also manifests in V_{TA}. We believe that this change in the modulus of the "matrix" surrounding the BP vibration is the reason for the upturn in the dynamic correlation volume near 335 K. It is intriguing, however, that this temperature also corresponds to the transition from the pure diffuse shear to the mixed mode of shear plus disentanglement ductile deformation.

DISCUSSION

The data presented in this manuscript illustrate strong correlations between the fast fluctuations on the subnanosecond time scale and mechanical deformation and toughness of a polymer glass. Our findings suggest that a salient feature of mechanical toughness is the ability of a polymer glass to translate collective vibrations on the picoseconds time scale that are ubiquitous to polymers deep in the glassy state into collective relaxations that may underpin the origins of toughness and ductility. The findings presented suggest that the relevant time scales are 0.5−0.8 ps vibrations evolving into 3 ps relaxations and shed deeper insight into the types of motions that are responsible for our previously reported correlations between the amplitude of the anharmonicity in the subnanosecond atomic fluctuations and the magnitude of toughness. Estimates of the length scale of these collective motions are on par with the activation volumes of yield obtain

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Macromolecules 2021, 54, 2518−2528

from continuum mechanics models. These results are analogous to decades-old correlations between relaxation strengths and mechanical toughness in polymer glasses using macroscopic characterization techniques.[7−10] The seminal advance here is that the inelastic and quasi-elastic neutron scattering have the appropriate sensitivity to extend these correlations to the underlying molecular mechanisms that underpin toughness. Our hope is that this manuscript will stimulate future studies in this direction, an area we are currently exploring in greater detail.

It is worth emphasizing that subnanosecond time scales and the pervaded volumes of just a few cubic nanometers of the collective vibrations and relaxations quantified in this manuscript fit well within the window of atomistic molecular dynamics (MD) simulation. Both the time and length scales of the two methods are well matched. Because of this overlap, there are an increasing number of examples of where either QENS is used to validate MD simulations[49,50] or the nature of the motions observed in MD simulations is used to interpret experimental QENS data.[51−56] In this vein, we are encouraged that results presented here support recent assertions from Sirk and co-workers[57,58] where the ballistic impact resistance in a series of poly(dicyclopentadiene) polymers is facilitated by enhanced nanovoid fluctuations on the picoseconds to nanoseconds time scales. These fast fluctuations dissipate energy and stave off the formation of stabilized critical cracks that lead to failure. The correlation between our experimental QENS measurements, MD simulations (that are now routinely performed on volumes that are on the order of 10^3 nm^3 and can contain 10^5−10^6 atoms), and the bulk mechanical properties is enticing. This suggests that QENS has the potential to connect the world of continuum mechanics with molecular modeling, which has been a difficult chasm to bridge. It also provides critical insights into the fast relaxation mechanisms on the time scale of an nanosecond or faster. These fast relaxations are incredibly important for understanding impact resistance at ballistic rates where the strain rates can exceed 10^6 1/s; only fast relaxations can dissipate energy under these ballistic conditions.

We conclude our discussion with a word of caution on the generality of our observations. First, there can be variability in both the BDT and $\langle u^2\rangle_{excess}$ depending on the nature of the measurements. The BDT will vary slightly with the rate of mechanical testing, while both the onset and magnitude of $\langle u^2\rangle_{excess}$ depend upon the Q and energy resolution of the spectrometer. These can induce slight shifts in locations of the different transitions, but on the scale of the large-temperature range studied here, these shifts or differences will be negligible. We demonstrate this in the SI with respect to the calculating the magnitude of $<u^2>_{excess}$. The more important caveat is that both the present work and our previous study[1] were restricted to series of PC polymers and copolymers that nominally have similar chemical structures. Extending this framework to other polymer structures requires careful consideration of the type of molecular motion that contribute to the INS and QENS signals, what types of molecular motions contribute to toughness, and whether the two types of motions are related. To illustrate this issue, we consider methyl rotation. In PC, it is known that the rotation of the two methyl groups of the isopropylidene is strongly coupled to the adjacent phenyl rings.[59,60] These methyl groups cannot rotate unless the phenyl rings flip. The phenyl rings also exhibit a significant degree of intermolecular coupling through π−π interactions, which means that phenyl ring flips are accompanied by motions of the main chain, and cis−trans conformations of the carbonate unit. This coupling is a part of the intramolecular cooperativity, which gives rise to toughness in PC. QENS measurements by Arrese-Igor and co-workers highlight the complexity of the motions in glassy PCs. They reported that the phenyl rings undergo a multitude of motions that can be described as oscillations, rotations, and flips, which are then coupled to both the methyl group rotations and carbonate group motions.[61−63] These motions are all coupled and complicated. Conversely, freely rotating methyl groups, such as those on the phenyl rings of tetramethyl bisphenol-A polycarbonate, do not contribute to toughness. These four additional methyl groups can rotate freely deep in the glassy state with very little restriction[64] and contribute significantly to $\langle u^2\rangle$ and the QENS spectra at low T.[65] However, these aromatic methyl groups are also isolated and decoupled from the rest of the polymer and do little to dissipate energy. In fact, the additional tetramethyl groups hinder phenyl ring flips and can actually retard cooperative motions deep in the glassy state and lead to a brittle response.[60] In this case, the large contribution to the INS and QENS spectra at low T does not contribute to toughness. This is primarily because the motions have a fixed center of mass and do not lead to relaxations that dissipate energy. In these instances, one must also account for the full Q-dependence of the motion to understand the implications on mechanical properties. We are currently extending these measurements to a broader series of materials, including cross-linked epoxies and dicyclopentadienes, and are finding that the concepts described herein, when judiciously applied, reliably predict toughness. These studies will be reported in a forthcoming manuscript. The picture that is evolving is that the measurement tools developed in the present work have tremendous potential for understanding, and ultimately engineering, enhanced impact resistance in glassy polymer materials.

CONCLUSIONS

The nanoscopic motions in an undeformed polycarbonate glass have been characterized across a broad temperature range using inelastic and quasi-elastic neutron scattering. We find striking correlations between the fast relaxations in the quiescent glass and essential trends in the mechanical toughness, a nonlinear property of consequence for polymer engineering. The onset of macroscopic ductility (accompanied by a substantial increase in toughness), demarcated by the brittle-to-ductile transition (BDT), correlates with the onset of anharmonic motions in the mean-squared atomic displacement, $\langle u^2\rangle$, on time scales faster than 1 ns. This finding emphasizes the role of anharmonic motions in dissipating energy in the glassy state. Poisson's ratio, characterized by Brillouin light scattering, shows an upturn in the same temperature region. Further investigation into the full inelastic neutron scattering spectra reveals two nanoscopic processes: (1) collective vibrational modes (the so-called Boson peak) with a characteristic time scale $\tau \approx 0.5$−0.8 ps and (2) collective relaxations with $\tau \approx 3$ ps. We show that the macroscopic phenomenon of the BDT corresponds to a change in the dominant nanoscale process from vibration-dominated to relaxation-dominated dynamics. These motions are estimated to involve 100s to 1000s of atoms as determined from the ratio of transverse acoustic mode velocity and the Boson peak frequency. This first-order estimate of the size of

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Macromolecules 2021, 54, 2518−2528

dynamic heterogeneities is strikingly similar to the activation volume of yield derived from macroscopic mechanical measurements and the Eyring model of stress activation, further strengthening the connection across length and time scales.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c02574.

Details on the fitting of the elastic neutron scattering spectra to quantify $\langle u^2 \rangle$ and how the selection of different Q ranges of these fits can lead to different $\langle u^2 \rangle$ values (Figure S1); and details of the fitting of the full inelastic and quasi-elastic neutron scattering spectra, including the Bose scaling of the spectra, the different fit functions used, the methodology for fitting the spectra, and a breakdown of the individual fitting functions at each temperature reported in the manuscript (Figure S2) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. C.L.S. conceived the study, performed the neutron scattering experiments, and was the primary author in writing the manuscript. J.W. and A.F.Y. synthesized the B_xt polycarbonate and performed basic characterization of the thermophysical properties. A.B.B., K.I., E.P.C., and J.F.D. helped with the data analysis, interpretation, and writing. M.T. and R.M.D. assisted with the neutron scattering measurements and data analysis. Y.-T.S. and L.H. performed the Brillouin light scattering measurements.

Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTE

[1]Certain commercial products or company names are identified here to describe our study adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology nor is it intended to imply that the products or names identified are necessarily the best available for the purpose.

■ REFERENCES

(1) Ritchie, R. O. The conflicts between strength and toughness. *Nat. Mater.* **2011**, *10*, 817−822.

(2) Liu, J.; Yee, A. F. Enhancing Plastic Yielding in Polyestercarbonate Glasses by 1,4-Cyclohexylene Linkage Addition. *Macromolecules* **1998**, *31*, 7865−7870.

(3) Liu, J.; Yee, A. F. Effect of Local Conformational Transition on Craze Initiation in Polyestercarbonates Containing Cyclohexylene Linkages. *Macromolecules* **2000**, *33*, 1338−1344.

(4) Li, X.; Yee, A. F. Design of Mechanically Robust High-Tg Polymers: Mechanical Properties of Glassy Poly(ester carbonate)s with Cyclohexylene Rings in the Backbone. *Macromolecules* **2004**, *37*, 7231−7239.

(5) Kausch, H. H. *Intrinsic Molecular Mobility and Toughness of Polymers*; Springer: Berlin; London, 2005.

(6) Plummer, C. J. G.; Soles, C. L.; Xiao, C.; Wu, J.; Kausch, H. H.; Yee, A. F. Effect of Limiting Chain Mobility on the Yielding and Crazing Behavior of Bisphenol-A Polycarbonate Derivatives. *Macromolecules* **1995**, *28*, 7157−7164.

(7) Wada, Y.; Kasahara, T. Relation between Impact Strenght and Dynamic Mechanical Properties of Plastics. *J. Appl. Polym. Sci.* **1967**, *11*, 1661−1665.

(8) Locati, G.; Tobolsky, A. V. Studies of the toughness of polycarbonate of bisphenol a in light of its secondary transition. *Adv. Mol. Relax. Processes* **1970**, *1*, 375−408.

(9) Allen, G.; Morley, D. C. W.; Willias, T. Impact Strength of Polycarbonate. *J. Mater. Sci.* **1973**, *8*, 1449−1452.
(10) Vincent, P. I. Impact strength and mechanical losses in thermoplastics. *Polymer* **1974**, *15*, 111−116.
(11) Soles, C. L.; Burns, A. B.; Ito, K.; Chan, E.; Liu, J. W.; Yee, A. F.; Tyagi, M. S. Importance of Sub-Nanosecond Fluctuations on the Toughness of Polycarbonate Glasses. *Macromolecules* **2020**, *53*, 6672−6681.
(12) Novikov, V. N. Phonon-density fluctuations and fast relaxation in glasses. *Phys. Rev. B* **1997**, *55*, R14685−R14688.
(13) Kanaya, T.; Kawaguchi, T.; Kaji, K. Local Dynamics of Some Bulk Polymers above Tg As Seen by Quasielastic Neutron Scattering. *Macromolecules* **1999**, *32*, 1672−1678.
(14) Roe, R. J. *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: New York, 2000; p xiv, 331.
(15) Higgins, J. S.; Benoît, H. C. *Polymers and Neutron Scattering*; Clarendon Press: Oxford, 1994; p xix, 436.
(16) Be′e, M. *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology, and Materials Science*; Adam Hilger: Bristol, England; Philadelphia, 1988; p xii, 437.
(17) Wu, J. H.; Xiao, C. D.; Yee, A. F.; Klug, C. A.; Schaefer, J. Controlling molecular mobility and ductile-brittle transitions of polycarbonate copolymers. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1730−1740.
(18) Soles, C. L.; Douglas, J. F.; Wu, W. L.; Dimeo, R. M. Incoherent neutron scattering as a probe of the dynamics in molecularly thin polymer films. *Macromolecules* **2003**, *36*, 373−379.
(19) Soles, C. L.; Douglas, J. F.; Wu, W. L.; Dimeo, R. M. Incoherent neutron scattering and the dynamics of confined polycarbonate films. *Phys. Rev. Lett.* **2002**, *88*, No. 1939.
(20) Azuah, R. T.; Kneller, L. R.; Qiu, Y. M.; Tregenna-Piggott, P. L. W.; Brown, C. M.; Copley, J. R. D.; Dimeo, R. M. DAVE: A Comprehensive Software Suite for the Reduction, Visualization, and Analysis of Low Energy Neutron Spectroscopic Data. *J. Res. Natl. Inst. Stand. Technol.* **2009**, *114*, 341−358.
(21) Guerette, M.; Huang, L. P. A simple and convenient set-up for high-temperature Brillouin light scattering. *J. Phys. D: Appl. Phys.* **2012**, *45*, No. 275302.
(22) Wu, J. *Correlated Motions and Relaxation Behavior in Polycarbonate Copolymers*; University of Michigan, 1997; Vol. *9732206*, p 237.
(23) Rufflé, B.; Parshin, D. A.; Courtens, E.; Vacher, R. Boson peak and its relation to acoustic attenuation in glasses. *Phys. Rev. Lett.* **2008**, *100*, No. 015501.
(24) Gurevich, V. L.; Parshin, D. A.; Schober, H. R. Anharmonicity, vibrational instability, and the Boson peak in glasses. *Phys. Rev. B* **2003**, *67*, No. 3765.
(25) Zorn, R. Viewpoint: The boson peak demystified? *Physics* **2011**, *4*, No. 439.
(26) Chumakov, A. I.; Monaco, G.; Monaco, A.; Crichton, W. A.; Bosak, A.; Rüffer, R.; Meyer, A.; Kargl, F.; Comez, L.; Fioretto, D.; Giefers, H.; Roitsch, S.; Wortmann, G.; Manghnani, M. H.; Hushur, A.; Williams, Q.; Balogh, J.; Parliński, K.; Jochym, P.; Piekarz, P. Equivalence of the Boson Peak in Glasses to the Transverse Acoustic van Hove Singularity in Crystals. *Phys. Rev. Lett.* **2011**, *106*, No. 225501.
(27) Nakagawa, H.; Joti, Y.; Kitao, A.; Kataoka, M. Hydration affects both harmonic and anharmonic nature of protein dynamics. *Biophys. J.* **2008**, *95*, 2916−2923.
(28) Kojima, S.; Sato, H.; Yosihara, A. Light scattering of supercooled propylene glycol. *J. Phys.: Condens. Matter* **1997**, *9*, 10079−10085.
(29) Lewandowski, J. J.; Wang, W. H.; Greer, A. L. Intrinsic plasticity or brittleness of metallic glasses. *Philos. Mag. Lett.* **2005**, *85*, 77−87.
(30) Greaves, G. N.; Greer, A. L.; Lakes, R. S.; Rouxel, T. Poisson's ratio and modern materials. *Nat. Mater.* **2011**, *10*, 823−837.
(31) Deng, B.; Shi, Y. On measuring the fracture energy of model metallic glasses. *J. Appl. Phys.* **2018**, *124*, No. 035101.
(32) Novikov, V. N.; Ding, Y.; Sokolov, A. P. Correlation of fragility of supercooled liquids with elastic properties of glasses. *Phys. Rev. E* **2005**, *71*, No. 293.
(33) Soles, C. L.; Dimeo, R. M.; Neumann, D. A.; Kisliuk, A.; Sokolov, A. P.; Liu, J. W.; Yee, A. F.; Wu, W.-l. Correlations of the boson peak with positron annihilation in series of polycarbonate copolymers. *Macromolecules* **2001**, *34*, 4082−4088.
(34) Ngai, K. L.; Bao, L. R.; Yee, A. F.; Soles, C. L. Correlation of positron annihilation and other dynamic properties in small molecule glass-forming substances. *Phys. Rev. Lett.* **2001**, *87*, No. 5499.
(35) Malinovsky, V. K.; Sokolov, A. P. The nature of boson peak in Raman scattering in glasses. *Solid State Commun.* **1986**, *57*, 757−761.
(36) Malinovsky, V. K.; Novikov, V. N.; Sokolov, A. P.; Bagryansky, V. A. Light-Scattering by Fractions in Polymers. *Chem. Phys. Lett.* **1988**, *143*, 111−114.
(37) Oligschleger, C.; Schober, H. R. Collective jumps in a soft-sphere glass. *Phys. Rev. B* **1999**, *59*, 811−821.
(38) Oligschleger, C.; Schober, H. R. Localized Relaxations in Glasses. *Solid State Commun.* **1995**, *93*, 1031−1035.
(39) Schober, H. R.; Oligschleger, C.; Laird, B. B. Low-Frequency Vibrations and Relaxations in Glasses. *J. Non-Cryst. Solids* **1993**, *156−158*, 965−968.
(40) Zhang, H.; Douglas, J. F. Glassy interfacial dynamics of Ni nanoparticles: Part II Discrete breathers as an explanation of two-level energy fluctuations. *Soft Matter* **2013**, *9*, 1266−1280.
(41) Betancourt, B. A. P.; Starr, F. W.; Douglas, J. F. String-like collective motion in the alpha- and beta-relaxation of a coarse-grained polymer melt. *J. Chem. Phys.* **2018**, *148*, No. 104508.
(42) Russina, M.; Mezei, E.; Lechner, R.; Longeville, S.; Urban, B. Experimental evidence for fast heterogeneous collective structural relaxation in a supercooled liquid near the glass transition. *Phys. Rev. Lett.* **2000**, *84*, 3630−3633.
(43) Ho, J.; Govaert, L.; Utz, M. Plastic Deformation of Glassy Polymers: Correlation between Shear Activation Volume and Entanglement Density. *Macromolecules* **2003**, *36*, 7398−7404.
(44) Hong, L.; Novikov, V. N.; Sokolov, A. P. Dynamic heterogeneities, boson peak, and activation volume in glass-forming liquids. *Phys. Rev. E* **2011**, *83*, No. 605.
(45) Ree, T.; Eyring, H. Theory of Non-Newtonian Flow. I. Solid Plastic System. *J. Appl. Phys.* **1955**, *26*, 793−800.
(46) Ward, I. M.; Sweeney, J. *Mechanical Properties of Polymers*; John Wiley & Sons Ltd.: The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, U.K., 2013.
(47) Sokolov, A. P.; Buchenau, U.; Steffen, W.; Frick, B.; Wischnewski, A. Comparison of Raman- and neutron-scattering data for glass-forming systems. *Phys. Rev. B* **1995**, *52*, R9815−R9818.
(48) Lee, B. W.; Jeong, M.-S.; Choi, J. S.; Park, J.; Ko, Y. H.; Kim, K. J.; Ko, J.-H. Pressure and molecular-weight dependences of elastic properties of polystyrene polymers studied by Brillouin spectroscopy. *Curr. Appl. Phys.* **2017**, *17*, 1396−1400.
(49) Bedrov, D.; Borodin, O.; Smith, G. D.; Trouw, F.; Mayne, C. Simulation and QENS Studies of Molecular Dynamics in Aqueous Solutions of 1,2-Dimethoxyethane. *J. Phys. Chem. B* **2000**, *104*, 5151−5154.
(50) Saboungi, M.-L.; Price, D. L.; Mao, G.; Fernandez-Perea, R.; Borodin, O.; Smith, G. D.; Armand, M.; Howells, W. S. Coherent neutron scattering from PEO and a PEO-based polymer electrolyte. *Solid State Ionics* **2002**, *147*, 225−236.
(51) Hansen, F. Y.; Criswell, L.; Fuhrmann, D.; Herwig, K. W.; Diama, A.; Dimeo, R. M.; Neumann, D. A.; Volkmann, U. G.; Taub, H. Intramolecular Diffusive Motion in Alkane Monolayers Studied by High-Resolution Quasielastic Neutron Scattering and Molecular Dynamics Simulations. *Phys. Rev. Lett.* **2004**, *92*, No. 046103.
(52) Calvo-Almazán, I.; Fouquet, P. The application of quasi-elastic neutron scattering techniques (QENS) in surface diffusion studies. *Eur. Phys. J.: Spec. Top.* **2012**, *213*, 149−163.
(53) Sakai, V. G.; Arbe, A. Quasielastic neutron scattering in soft matter. *Curr. Opin. Colloid Interface Sci.* **2009**, *14*, 381−390.

https://dx.doi.org/10.1021/acs.macromol.0c02574
Macromolecules 2021, 54, 2518−2528

(54) Sinha, K.; Maranas, J. K. Segmental Dynamics and Ion Association in PEO-Based Single Ion Conductors. *Macromolecules* **2011**, *44*, 5381−5391.
(55) Frischknecht, A. L.; Paren, B. A.; Middleton, L. R.; Koski, J. P.; Tarver, J. D.; Tyagi, M.; Soles, C. L.; Winey, K. I. Chain and Ion Dynamics in Precise Polyethylene Ionomers. *Macromolecules* **2019**, *52*, 7939−7950.
(56) Middleton, L. R.; Tarver, J. D.; Cordaro, J.; Tyagi, M.; Soles, C. L.; Frischknecht, A. L.; Winey, K. I. Heterogeneous Chain Dynamics and Aggregate Lifetimes in Precise Acid-Containing Polyethylenes: Experiments and Simulations. *Macromolecules* **2016**, *49*, 9176−9185.
(57) Elder, R. M.; Knorr, D. B.; Andzelm, J. W.; Lenhart, J. L.; Sirk, T. W. Nanovoid formation and mechanics: a comparison of poly(dicyclopentadiene) and epoxy networks from molecular dynamics simulations. *Soft Matter* **2016**, *12*, 4418−4434.
(58) Elder, R. M.; Long, T. R.; Bain, E. D.; Lenhart, J. L.; Sirk, T. W. Mechanics and nanovoid nucleation dynamics: effects of polar functionality in glassy polymer networks. *Soft Matter* **2018**, *14*, 8895−8911.
(59) Schaefer, J.; Stejskal, E. O.; Mckay, R. A.; Dixon, W. T. Molecular-Motion in Polycarbonates by Dipolar Rotational Spin-Echo C-13 Nmr. *Macromolecules* **1984**, *17*, 1479−1489.
(60) Ngai, K. L.; Rendell, R. W.; Yee, A. F. Local Molecular Motions in Glassy and Dissolved Polycarbonates. *Macromolecules* **1988**, *21*, 3396−3401.
(61) Arrese-Igor, S.; Arbe, A.; Alegría, A.; Colmenero, J.; Frick, B. Phenylene ring dynamics in phenoxy and the effect of intramolecular linkages on the dynamics of some engineering thermoplastics below the glass transition temperature. *Phys. Rev. E* **2007**, *75*, No. 051801.
(62) Arrese-Igor, S.; Arbe, A.; Alegría, A.; Colmenero, J.; Frick, B. Sub-Tg dynamics in polycarbonate by neutron scattering and its relation with secondary γ relaxation. *J. Chem. Phys.* **2005**, *123*, No. 014907.
(63) Arrese-Igor, S.; Mitxelena, O.; Arbe, A.; Alegría, A.; Colmenero, J.; Frick, B. Molecular motions in glassy polycarbonate below its glass transition temperature. *J. Non-Cryst. Solids* **2006**, *352*, 5072−5075.
(64) Roy, A. K.; Jones, A. A. Study of Spin-Lattice Relaxation and Local Motion in Dissolved Poly[2,2-Propanediylbis(3,5-Dimethyl-4,Hydroxyphenyl)Carbonate]. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1793−1802.
(65) Besancon, B. M.; Soles, C. L.; Green, P. F. Glass transition of miscible binary polymer-polymer thin films. *Phys. Rev. Lett.* **2006**, *97*, No. 057801.

https://dx.doi.org/10.1021/acs.macromol.0c02574
Macromolecules 2021, 54, 2518−2528