

Correlations of the Boson Peak with Positron Annihilation in Series of Polycarbonate Copolymers

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ABSTRACT: The low-frequency vibrations of the Boson peak are observed with inelastic neutron and Raman scattering in a homologous series of polycarbonate copolymers. In accordance with the notion that the Boson peak is predominantly an acoustic phenomenon, the Boson peak energy is found to correlate with the velocity of sound. However, a striking inverse correlation is observed between the Boson peak energy and the average size of the unoccupied volume elements (approximately 5–6 Å in diameter) evidenced by positron annihilation lifetime spectroscopy (PALS). The apparent correlation between the Boson peak energy and PALS data is discussed in terms of a relationship between the elastic modulus and the electron density heterogeneities.

Introduction

A low-frequency excitation at energy transfers of approximately 1–10 meV is observed in the inelastic neutron and low-frequency Raman scattering spectra of most glassy materials. These collective vibrational modes, commonly referred to as the Boson peak, are lower in frequency than the high-energy optic modes characteristic of local bond stretching or bending yet higher in frequency than long-range acoustic modes. Boson peaks are observed in a wide range of glass-forming systems with significant variations in the peak positions and intensities. Despite their widespread occurrence, a molecular level interpretation of the glassy state phenomenon remains elusive. Undoubtedly, this lack of understanding is partially rooted in the fact that the Boson peak is such a ubiquitous feature. It is difficult to develop a molecular level interpretation of shifts in the peak frequency and/or intensity when comparing systems as different as vitreous silica, CKN, glycerol, polybutadiene, and lysozyme. There are numerous differences between network glasses, ionic glasses, supercooled small molecule liquids, polymers, proteins, etc., and it is difficult to isolate the factors that are germane to the Boson peak.

Here we try to establish structural insight into the Boson peak by studying a homologous series of polycarbonate copolymers. The advantage of this approach is that the structural modifications are *subtle* as opposed to comparing vastly different classes of materials. Hopefully, the gradual and systematic changes create a unique opportunity to identify what structural parameters are germane to the low-frequency collective vibrations of the Boson peak.

Experimental Section

The chemical structures, glass transition temperatures, and nomenclature of the polycarbonate copolymers are denoted in

Figure 1. The copolymers are derivatives of bisphenol A–polycarbonate (PC) and nominally divided into two classifications. The first group is made by inserting either a flexible cyclohexylene or rigid terephthalate linkage between every third bisphenol A PC monomer and thus referred to as B₃c and B₃t, respectively. The second group is based on the tetramethyl-substituted version of the bisphenol A monomer (T), where the dynamics of the phenyl rings are hindered through the addition of the bulky methyl groups. The previous linkages units are incorporated in an analogous manner, with T₃c and T₃t referring to the tetramethyl copolymers containing the cyclohexylene and terephthalate linkages, respectively. These copolymers have been studied extensively in terms of their deformation behavior^{1–5} and molecular mobility,^{4–8} with the synthetic details reported elsewhere.^{2,4,5}

Incoherent inelastic neutron scattering measurements are performed at the NIST Center for Neutron Research using the Fermi-Chopper time-of-flight spectrometer located on the NG6 beam line. The neutron wavelength is 4.8 Å, corresponding to a spectrometer resolution of approximately 140 μeV fwhm. The copolymers are compression molded under vacuum into films 0.03–0.10 mm thick. This thickness is sufficient to attain 90% transmission of the neutron beam or better,⁹ thus drastically reducing the possibility multiple-scattering events. Prior to collecting the spectra, the samples are heated under vacuum to $T_g + 20$ K for 12 h and quenched to room temperature to establish a well-defined thermal history. The films are wrapped inside a 50 mm annular aluminum cell of diameter 12.7 mm and bolted to a thermal stage equipped with a helium closed cycle refrigerator. The thermal stage is mounted in the sample chamber of the spectrometer and evacuated, and the inelastic spectra are collected between 100 and 500 K, in 100 K increments. Sufficient counting statistics are obtained after 6–15 h of data collection, with the greater times required at lower temperatures. The data are corrected for background scattering and detector efficiency with a blank aluminum sample cell and vanadium standard, respectively. Since the scattering is predominantly incoherent, each spectrum is summed over all available detectors, and the Q dependence is not extracted from the data. All spectra are then scaled with temperature according to the Bose population factor ($\exp(h\nu/kT) - 1$)⁻¹.

Samples for the Raman and Brillouin light scattering experiments are made under conditions similar to the neutron scattering samples. Small disks approximately 13 mm in diameter and 3–4 mm thick are compression molded under

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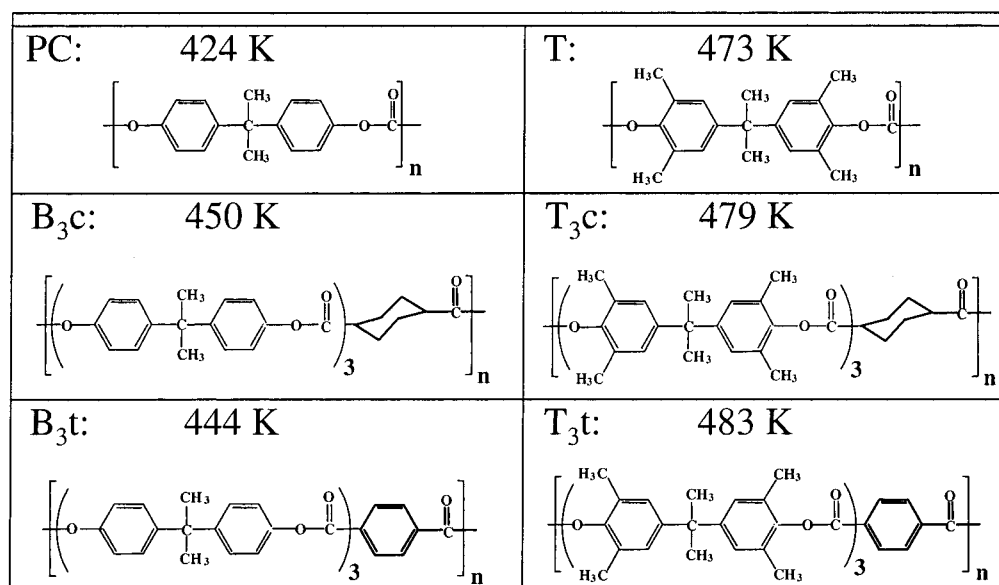


Figure 1. Chemical structures, glass transition temperatures, and sample nomenclature for the polycarbonate copolymers employed in this work. Copolymer T is shown for completeness although it was not explicitly studied with inelastic neutron or Raman scattering.

vacuum. Using an Ar²⁺ laser ($\lambda = 514.5$ nm) with 25 mW of power incident on the sample in the backscattering geometry, a triple monochromator (Jobin Yvon T64000¹⁰) equipped with CCD camera and six-pass tandem Fabry–Perot Interferometer (Sandercock) is used to obtain both the Raman and Brillouin spectra. The frequency ν of the intense longitudinal acoustic mode peaks (LA) in the polarized Brillouin scattering spectrum is directly related to the velocity of sound V through the relationship

$$\nu = \frac{2nV}{\lambda} \sin\left(\frac{\Theta}{2}\right) \quad (1)$$

where n is the refractive index and Θ is the scattering angle.

Results and Discussion

Figure 2 displays the Bose-corrected inelastic neutron scattering spectra as a function of temperature. The convention of a negative energy in these spectra denotes energy loss by the sample. Below 300 K, a distinct Boson peak is evident in the range of -1.5 to -1.0 meV in parts a, b, and c of Figure 2, corresponding to PC, B₃c, and B₃t, respectively. These Boson peak positions are generally consistent with previous reports on pure polycarbonate.^{13–15} At 400 K, just below the glass transition temperature for all of the materials, the Boson peak is no longer distinct, obscured by a strong quasi-elastic scattering. At 500 K in PC, well above the glass transition temperature, the quasi-elastic scattering from relaxational processes dominates the spectrum, and the Boson peak is no longer visible.

Very different spectra are obtained from the tetramethyl-based copolymers, as shown in parts d and e of Figure 2 for T₃c and T₃t, respectively. At 100 K, a very weak Boson peak appears near -1 meV in T₃c. However, at 200 K, still 275 K below the glass transition temperature, a strong quasi-elastic scattering obscures the Boson peak. In T₃t the quasi-elastic scattering is extremely strong, and a distinct Boson peak is not evident even at 100 K. This intense quasi-elastic scattering deep in the glassy state is attributed to facile rotations of the tetramethyl groups. Unfortunately, this strong quasi-elastic scattering precludes us from ac-

curately characterizing the Boson peaks (with neutron scattering) in most of the tetramethyl-based copolymers.

The Bose-scaled Raman spectra are shown in Figure 3. The Raman spectra for PC, B₃c, and B₃t in parts a, b, and c of Figure 3, respectively are similar to their corresponding inelastic neutron spectra presented in Figure 2. Here the convention of a positive energy denotes energy gained by the sample. The Boson peak is well-resolved at low temperatures but obscured by a growing quasi-elastic scattering as temperature increases. Parts d and e of Figure 3 display the Raman spectra for T₃c and T₃t, respectively. In the tetramethyl-based copolymers the Raman spectra are very different from their corresponding neutron spectra. The Boson peaks are easily resolved in the Raman spectra, and the strong quasi-elastic scattering observed in the neutron spectra is absent. This is because the torsional motions of the tetramethyl groups are not strongly Raman-active and therefore do not give rise to strong quasi-elastic scattering.

The inelastic spectra are fit to compare the Boson peak positions between different copolymers. The Boson peak line shape has been characterized within a number of models, all based on different physical assumptions. In the present we elect to parametrize the line shape with an arbitrary flat background and a model-independent log-normal distribution function:

$$P_{\text{LN}}(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \frac{1}{|x|} \exp\left[\frac{-(\ln|x| - \mu)^2}{2\sigma^2}\right] \quad (2)$$

where μ and σ are the center and width of the asymmetric distribution. This empirical model does not invoke any physics other than an asymmetric distribution. The peak maximum or mode is obtained through the relationship $x_{\text{peak}} = \exp(\mu - \sigma^2)$. In the Raman and neutron spectra at low temperatures where the quasi-elastic scattering is negligible, a distinct minimum is observed on the low-energy side of the peak, and the data can be fit with little ambiguity in the peak position. However, as temperature increases, the Boson peak

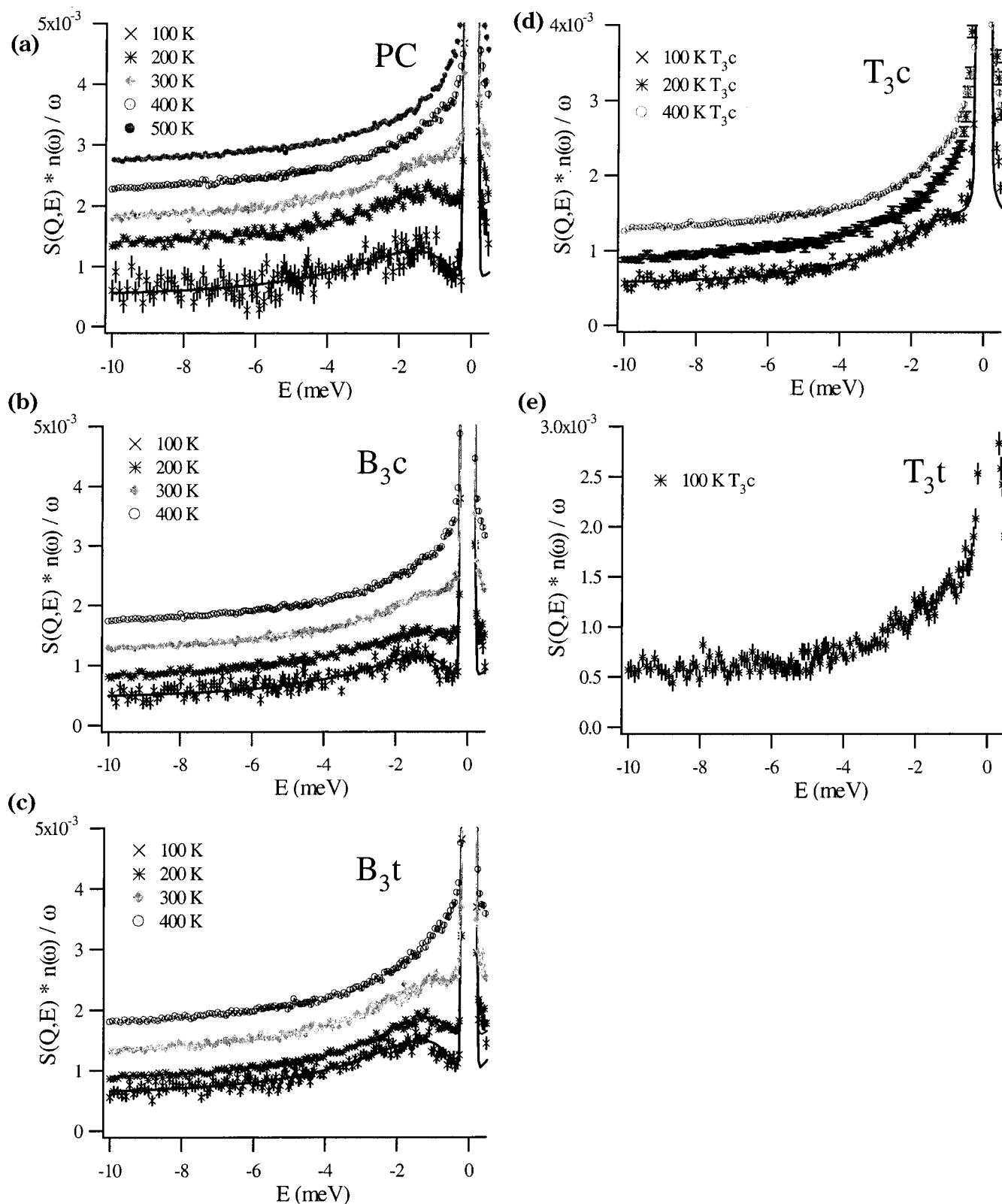


Figure 2. Bose-scaled neutron scattering spectra as a function of temperature for the polycarbonate copolymers are offset vertically for clarity. Fits to the experimental data are indicated with the solid lines (where applicable) in parts a, b, c, d, and e corresponding to the copolymers PC, B₃c, B₃t, T₃c, and T₃t, respectively. The error bars indicate the standard uncertainty from the counting statistics.

softens to lower energies, and it is difficult to separate the inelastic scattering from the growing quasi-elastic component. For instance, where a local minimum is not clearly evident on the low-energy side of the Boson peak, no attempts are made to extract peak positions.

The Boson peak is often reminiscent of a quasi-localized acoustic vibration. Consistent with this notion, Figure 4 demonstrates a general correlation between the velocity of sound, measured with Brillouin scattering, and the Boson peak position. Figure 4a compares

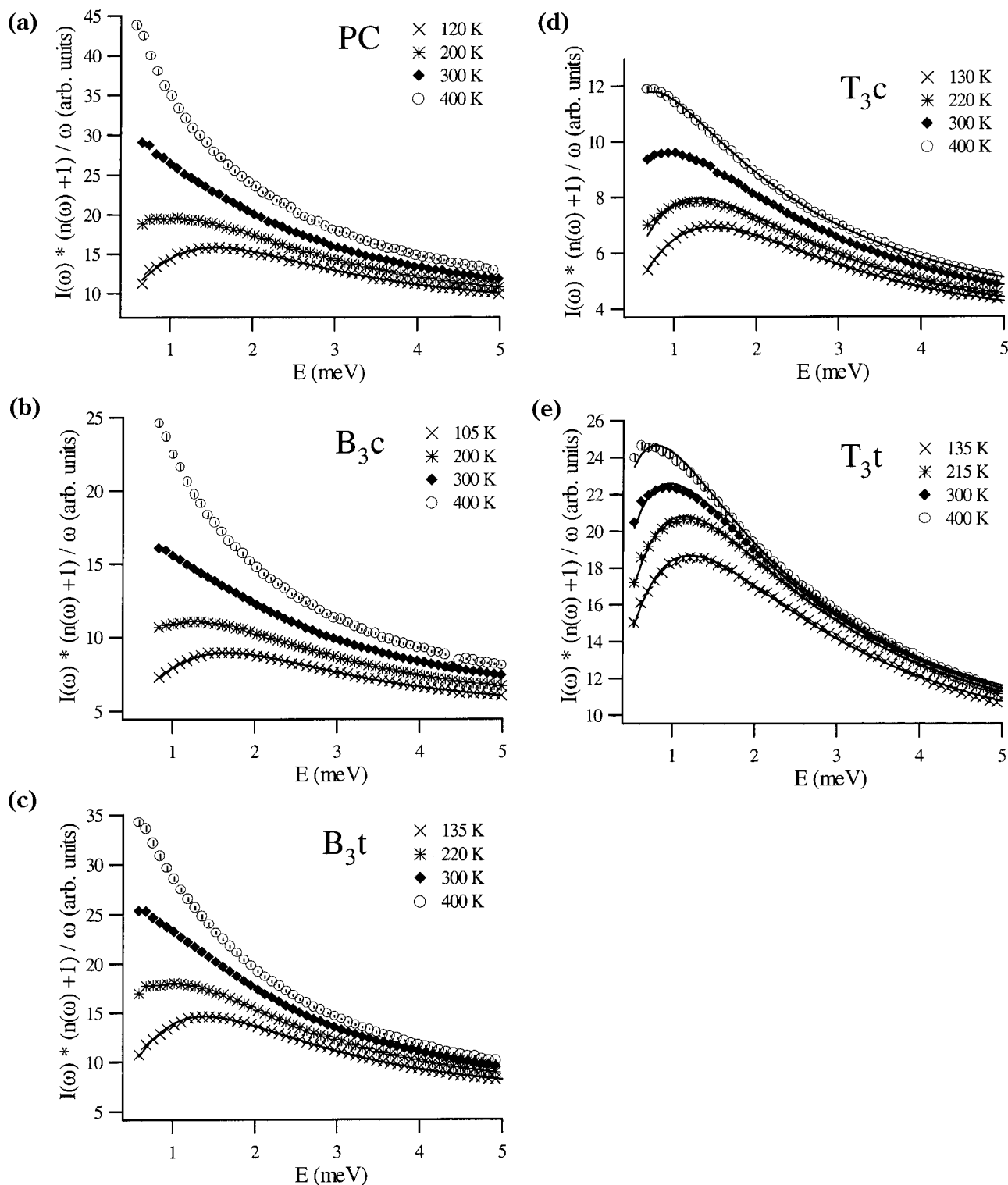


Figure 3. Bose-scaled Raman scattering spectra as a function of temperature for the polycarbonate copolymers of the PC, B₃C, B₃t, T₃C, and T₃t copolymers in parts a, b, c, d, and e, respectively. Where a Boson peak is clearly evident, the fit as described in the text, is indicated with a solid line. The standard uncertainty in the counting statistics is always less than the size of the data points.

the thermal softening of the neutron Boson peaks of PC, B₃C, and B₃t to the frequency of the longitudinal acoustic modes while Figure 4b shows a similar comparison for the Raman Boson peaks in T₃C and T₃t. There is good agreement between the softening of the Boson peak and the damping of the longitudinal acoustic mode. This general correlation between the Boson peak position and velocity of sound is consistent with observations in several different glass-forming systems.¹⁴

The origin of localization for the Boson peak modes is often argued to be structural heterogeneities.^{15–18} In this respect it is useful to characterize the structure of these glassy copolymers with positron annihilation lifetime spectroscopy (PALS). For a detailed discussion on the PALS technique, refer to a recent review on the subject.¹⁹ In short, PALS is a structural technique that quantifies electron density deficiencies or unoccupied volume elements that are typically 5–6 Å in diameter

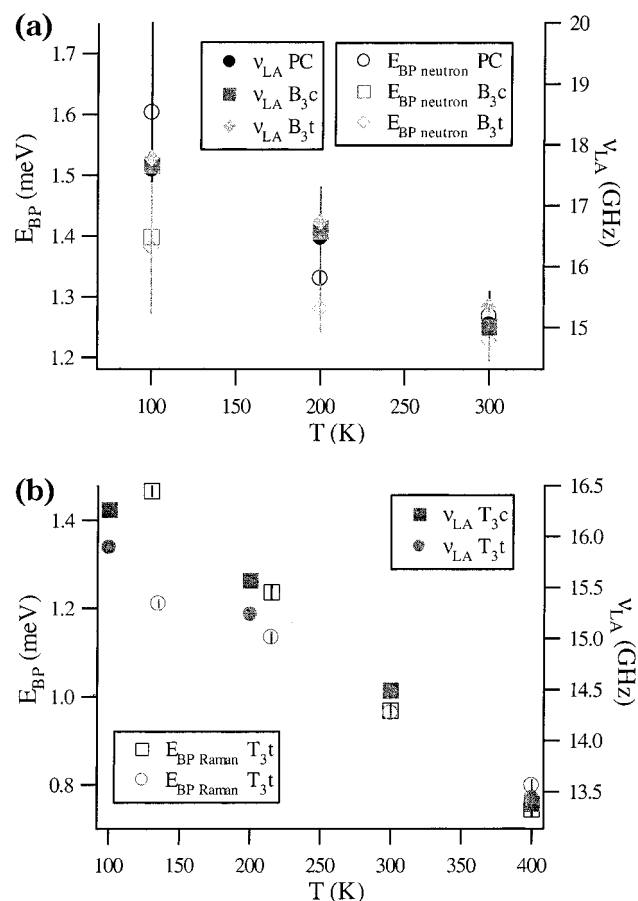


Figure 4. Thermal softening of the Boson peaks show the same general trends as the Brillouin scattering longitudinal acoustic modes. In part a the softening of the neutron scattering Boson peaks in PC, B_{3c} , and B_{3t} is compared to the Brillouin data while in part b the comparison is made with the Raman Boson peaks of T_{3c} and T_{3t} . The error bars indicate the least-squares standard uncertainty in the fit of the peak position (both Boson and Brillouin data) to the models described in the text.

for an amorphous polymer. Low-temperature PALS measurements on PC, B_{3c} , T_{3c} , and T_{3t} (reported elsewhere^{4,20}) indicate that the tetramethyl-based copolymers are more heterogeneous in terms of packing defects, exhibiting larger unoccupied volume cavities present in greater volume fractions. Here the discussion is limited to the average size of the density heterogeneities, which is directly obtained from the average orthopositronium lifetime and the admittedly gross oversimplification of spherical nanopores.^{21,22}

The parametric plot in Figure 5 compares the average PALS nanopore cavity volume with the Boson peak position for a range of amorphous systems, including both the copolymers studied here and other polymers found in the open literature. An inverse correlation is observed between the size of the PALS nanopores and the Boson peak energy for both the neutron and Raman scattering data. Those materials with larger electron density heterogeneities exhibit lower energy Boson peaks. The effect of the light-to-vibration coupling constant²³ is also evident in Figure 5 with the Raman peaks systematically shifted to higher energy in comparison with the neutron scattering data.

The apparent correlation between a small nanopore radius and a high-energy Boson peak is striking and provocative. However, it must be emphasized that the

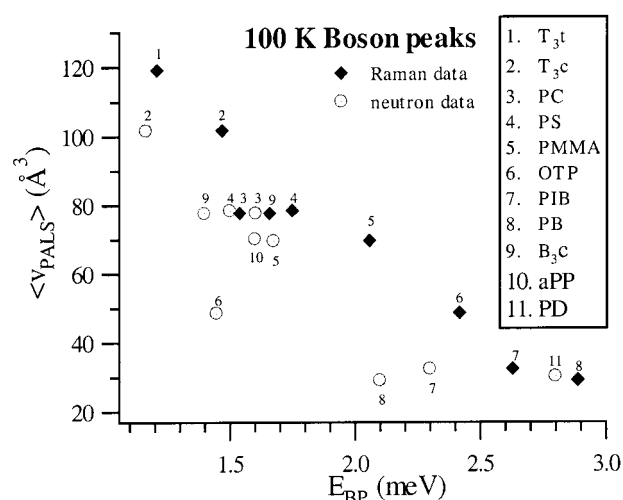


Figure 5. Apparent correlation between the average size of the PALS nanopores and the Boson peak energies obtained from both neutron and Raman scattering data near 100 K. With the exception of the copolymers described here, the data are taken from the literature so the standard uncertainties are omitted. The neutron (reference (a) if available) and Raman (reference (b) if available) Boson peak energies for polystyrene (PS),³⁴ atactic polypropylene (aPP),³⁵ *o*-terphenyl (OTP),³⁶ poly(methyl methacrylate) (PMMA),³⁷ polybutadiene (PBD),³⁸ polyisobutylene (PIB),³⁹ and propanediol (PD)⁴⁰ are taken from the aforementioned references, with the PALS data for PS,^{30,41} aPP,⁴² OTP,⁴³ PD,⁴³ PMMA,^{29,44} PBD,^{42,45,46} and PIB^{42,45} reported elsewhere.

materials in Figure 5 are polymeric hydrocarbons (with the exception of *o*-terphenyl). The Boson peak is a general phenomenon in glass-forming materials, including inorganic glasses such as vitreous silica. The Boson peak of vitreous silica is evidenced between -4.5 and -7.5 meV at room temperature.^{24–26} Under similar conditions, the average nanopore volume is approximately $50\text{--}60 \text{ \AA}^3$,^{27,28} clearly contradicting a ubiquitous correlation between the PALS nanopore size and the Boson peak energy. The correlation in Figure 5 may be somewhat fortuitous in that nearly all of the glasses are linear polymers. In such a self-similar situation, changes in the average nanopore size probably track changes in the unoccupied volume fraction. For example, most polymers contain approximately 5 vol % of the PALS packing defects just below the glass transition temperature.^{29,30} However, the volume fraction of density defects in vitreous silica is probably much smaller in comparison to an amorphous polymer. Hence, the ramifications of Figure 5 remain to be established on a broader range of glass formers.

The Boson peak appears to correlate with both the velocity of sound and the PALS hole volume fraction. This in turn implies that large nanopores correspond to a reduced velocity of sound. It is not immediately evident why the PALS volume fraction of density heterogeneities should correlate with the acoustic modes of a material. The fraction of these heterogeneities is small, generally less than 5 vol %, and they are much smaller than the wavelength of the acoustic modes. The velocity of sound is often expressed as

$$v_{\text{sound}} \sim (B/\rho)^{1/2} \quad (3)$$

where the bulk modulus B and density ρ are assumed to be independent parameters. As the PALS hole volume fraction increases, intuitively one expects the density

to decrease. According to eq 3, this leads to an increase in the velocity of sound, not a decrease as implied by the trends observed here. Then the question is whether the bulk modulus should depend on density and, if so, how strong the dependence should be. If the dependence of B on ρ is strong enough, a decrease in the velocity of sound with an increase in the PALS hole volume fraction could be understood.

A strong dependence is anticipated given the simple observation that the moduli of solids and liquids differ by several orders of magnitude while the densities differ by factors much less than 10. The strong dependence is confirmed upon referring to an introductory text on condensed matter physics³¹ and plotting the room-temperature modulus of the elements on the periodic table as a function of density. On a log-log scale the elastic modulus empirically scales with density to approximate powers of 1.4, 2.0, and 2.2 for the row 4, 5, and 6 elements, respectively. This also is consistent with studies on fractal colloidal gels, often a model for glass-forming systems, where the elastic modulus scales as $G \sim \phi^n$ where ϕ is the volume fraction (a number density) of colloidal particles and n typically varies from 3.5 to 4.5.^{32,33} Of course, these examples are not completely analogous to amorphous polymers so the similarities are limited. However, the general trends support a strong dependence of B on ρ as is needed to rationalize the inverse correlation between the velocity of sound and the PALS hole volume.

In retrospect, the suggestion of an increased PALS hole volume fraction corresponding to a decreased velocity of sound appears reasonable. This is consistent with the growing notion that the Boson peak is predominantly a quasi-localized acoustic phenomenon. The level of structural heterogeneity in a glass appears to affect both the nature of this localization and thus the Boson peak frequency. However, the concepts and arguments introduced on these self-similar copolymers should be extended to a wide range of nonpolymeric glass formers to see if generality is maintained. It remains to be seen whether structural heterogeneities are the root cause of the Boson peak or a related coincidence.

In conclusion, we demonstrate in a series of polycarbonate copolymers that it is possible to shift the Boson peak position through careful structural modifications. The structural modifications here generally lead to a softening of the Boson peak in comparison to pure PC. However, the dependence of the Boson peak frequency on the detailed copolymer architecture is subtle. Consistent with an acoustic-like phenomenon, there appears to be a general correlation between the Boson peak position, measured by both inelastic neutron and Raman scattering and the velocity of sound as measured by Brillouin scattering. The thermal softening of the Boson peak is generally consistent with the shifts of the longitudinal acoustic modes to lower frequencies. A surprising correlation is observed between the Boson peak energy and the size of the unoccupied volume elements evidenced positron annihilation lifetime spectroscopy. An increase in the size of the approximately 5–6 Å diameter nanopores correlates with a decrease in energy Boson peak. An attempt to rationalize these different observations is made through a discussion of the heterogeneous nature of the glass, and it is argued that a more heterogeneous glass gives rise to a lower energy Boson peak.

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