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Observation of boson peaks by inelastic neutron scattering in polyolefins

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Inelastic neutron scattering was used to probe the nature of the boson peak in atactic polypropylene (aPP), head-to-head polypropylene (hhPP), polyisobutylene (PIB) and a 1/1 mass ratio hhPP/PIB blend. Atactic polypropylene is among the most “fragile” of glass formers and was found to have a shoulder rather than the distinctive peak exhibited by the other three polymers. This difference is already apparent at 15 K where relaxations are not expected to occur. The results suggest that the fragility of hhPP is intermediate between aPP and PIB. Within this group of polymers which have similar chemical structures the position of the boson peak appears to correlate with the glass transition temperature and the cohesive energy density. The possibility of a correlation with chain stiffness as expressed by the characteristic ratio is also discussed. © 1999 American Institute of Physics. [S0021-9606(99)50128-1]

INTRODUCTION

Below the glass transition inelastic neutron and low frequency Raman scattering spectra from amorphous materials often exhibit a peak with an energy distribution proportional to a factor arising from Bose–Einstein statistics. Consequently, this feature is referred to as the boson peak. It typically occurs at energies of less than about 5 meV. For Raman scattering an additional frequency dependent term must be considered which can complicate interpretation of the spectra. The peak is thought to be the result of some form of vibrational motion. However, the nature of these vibrations is not well understood and has been attributed to localization of vibrational modes caused by disorder in the glass or to the predictions of the soft potential model.¹ Recent molecular dynamics simulations for polypropylene oxide led the authors to suggest that the peak is due to collective dynamics that are determined primarily by intermolecular interactions.² At temperatures well below T_g , the density of states associated with this peak is thought to be the origin of anomalous behavior of the heat capacity and in the case of polymers this is supported by the work of Inoue *et al.*³ for polyisobutylene (PIB) and of Kanaya *et al.*⁴ for polystyrene (PS).

As the temperature increases, a component of the scattering which appears to be quasielastic (an energy shift centered around zero) increases causing the boson peak to be less well defined and eventually overwhelming it. This is often called the “fast process” and has a time scale of a few picoseconds. The onset of the fast process can vary substantially from one polymer to another. For example, it can develop well below T_g for polycarbonate (PC),⁵ polymethyl-

methacrylate (PMMA),⁶ and PS,⁷ at about 50 K below T_g for polybutadiene (PB) and just above T_g for PIB.⁸ Like the boson peak the nature of the fast process remains an open question. It is not yet clear as to whether or not it is a true quasielastic (relaxation) process or whether it involves a shift of the peak in the inelastic density of states to lower energies. A discussion of this issue for PB and polyisoprene (PI) may be found in Ref. 9.

A useful characterization of glass forming materials is the fragility, m , which is defined by¹⁰

$$m = \left[\frac{d \log_{10} \langle \tau \rangle}{d(T_g/T)} \right]_{T=T_g}, \quad (1)$$

where $\langle \tau \rangle$ is a structural relaxation time which is typically on the order of 100 s at T_g . “Fragile” glass formers have high values of m and are more sensitive to temperature changes than are “strong” glass formers. For nonpolymeric materials, Sokolov *et al.*,¹¹ using an earlier definition of the fragility in which $\langle \tau \rangle$ is replaced by the viscosity, found a correlation between m and the ratio of the intensity at the minimum and maximum that define the boson peak. The stronger glass formers were associated with more distinct boson peaks and hence lower intensity ratios. A recent review¹² indicates that this may also be the case for polymers. For example, PVC with $m=191$ and PIB with $m=46$ are, respectively, the most and the least fragile of the polymers that have been classified¹⁰ and the neutron scattering measurements of Colmenero *et al.*¹³ for PVC show little if any indication of a peak even at 250 K below T_g while PIB (Ref. 8) has a very distinct peak at T_g and even higher tem-

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peratures. That there appears to be a connection between the dynamics at such different time scales is a paradox which remains to be resolved.

In this article we investigate this possible correlation for the case of atactic (head to tail) polypropylene (app), one of the more fragile glass formers ($m=137$),¹⁰ and, in addition, present inelastic neutron scattering data for the head to head form of polypropylene (hhPP), PIB ($m=46$),¹⁰ and a blend of hhPP with PIB. For hhPP and the blend the necessary relaxation data do not appear to be available for an evaluation of the fragility. The mixing behavior of PIB and the two polypropylenes has been found to be quite different.¹⁴ In its deuterated form aPP and PIB are immiscible while hhPP and PIB are miscible and the resulting blend is characterized by a large, negative Flory–Huggins parameter, χ . This indicates that the interaction between the unlike molecules is greater than the average of those between the like pairs. To our knowledge the effect on the boson peak due to blending with the associated changes in the intermolecular interactions has not been explored and these data provide an initial step in that direction.

EXPERIMENT

The scattering measurements were carried out on the QENS spectrometer¹⁵ at the Intense Pulsed Neutron Source located at Argonne National Laboratory. The spectrometer is an inverse geometry time-of-flight instrument with an elastic energy resolution of approximately 100 meV for quasielastic and low energy inelastic scattering. This increases to about 3%–4% of the energy transfer in the vibrational frequency range. There are three banks of detectors, each rotatable to three positions for a total of nine spectra with elastic scattering momentum transfers in the range $0.5 \leq Q [= (4\pi/\lambda)\sin(\theta/2), \lambda = 4.73 \text{ \AA}] \leq 2.5 \text{ \AA}^{-1}$. The energy window extends from 1.5 meV (neutron energy gain) to about 100 meV (neutron energy loss). The detector efficiencies were corrected by comparison with a vanadium standard.

The aPP was from Rexene Corp. and had a M_w of approximately 70 000 and $M_w/M_n = 3$ –4. The midpoint of the glass transition as determined by differential scanning calorimetry (DSC) was 270 K. The hhPP was made by first polymerizing 2,3-dimethyl-1,3-butadiene anionically, and then following with hydrogen saturation using Pd on CaCO_3 . The weight average molecular weight was approximately 75 000 with $M_w/M_n = 1.24$. The T_g was estimated to be about 247 K.¹⁶ The PIB was Exxon Vistanex L100 with weight average molecular weight of 1×10^6 , $M_w/M_n = 2.0$, and a T_g of 209 K. The 50/50 blend of hhPP and PIB was made by dissolving equal masses of each polymer into cyclohexane to give a 5 wt% solution. This was followed by precipitation into chilled (278 K) methanol. The precipitate was dried in a vacuum oven for three days until no solvent remained. The DSC results for the blend showed a broad transition between 213 and 243 K for a midpoint T_g of 228 K.

The samples were mounted in a closed-cycle helium refrigerator which allows measurements in the range of 12–300 K. The typical temperature stability is within 0.5 K with temperature gradients along the sample of less than 2 K. The samples were heat pressed into sheets 0.28 mm thick and

wrapped around an aluminum cylinder with an outer diameter (o.d.) of 9.5 mm and a 0.25 mm wall thickness. The beam height was 10 cm and counting times of 10–12 h per sample per temperature were used. Container scattering was generally negligible. Although the sample thicknesses were greater than those used by Frick and Richter⁸ in their study of PIB, the peak positions and shape of their curves are quite similar to the results reported here. Since the H atom number densities are close to that of PIB, the polypropylene results should likewise be unaffected.

Because of the high H atom content the bulk of the scattering is incoherent and in the approximation of a one phonon scattering process involving harmonic vibrations we write the total incoherent scattering law $S_{\text{inc}}(Q, \omega)$ as the sum of an incoherent elastic term $S_0 \exp(-2W)$ and a term for a neutron energy loss of $\hbar\omega$:⁸

$$S_{\text{inc}}(Q, \omega) \propto \exp(-2W) \left(S_0 \delta(\omega) + \frac{Q^2}{8\pi M} [n(\omega) + 1] \frac{g(\omega)}{\omega} \right), \quad (2)$$

where M is the average atomic mass involved in the vibrational mode. The Bose–Einstein occupation number is $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ and $g(\omega)$ is the vibrational density of states. The Debye–Waller factor is given by

$$\exp(-2W) = \exp\left(-\frac{Q^2}{3} \langle u^2(T) \rangle\right), \quad (3)$$

where $\langle u^2 \rangle$ is the mean square displacement and in the harmonic approximation is given by

$$\langle u^2(T) \rangle = \langle u_0^2 \rangle + (\delta \langle u_1^2 \rangle / \delta T) T. \quad (4)$$

In order to obtain the mean square displacement it is necessary to consider the Q dependence of the amplitude of the elastic scattering. This amplitude was evaluated by using the spectra at the lowest temperature of 15 K to provide the instrumental resolution and then, at higher temperatures, fitting the central peak with a δ function convoluted with this resolution function.

RESULTS

The boson peak is apparent in the raw data for the various samples as can be seen in Fig. 1. For purposes of comparison the data are usually corrected by the Debye–Waller factor (DWF), an appropriate Bose factor, and summed over scattering angles. The first step in this process is obtaining an estimate of the mean square displacement from the elastic scattering. In principle the Q dependence of the elastic (incoherent) scattering is determined by the DWF so that $\ln[I_{\text{el}}(Q)]$ vs Q^2 should be linear and the mean square displacement follows from the slope. Generally this was not found to be the case so the normalization procedure used by Frick and Richter⁸ and by Kanaya *et al.*^{7c} was adopted. The elastic amplitudes $I_{\text{el}}(Q, T)$ are divided by those at the lowest temperature and then, with the exception of the hhPP/PIB blend, linearity with Q^2 resulted. Examples for 200 K are shown in Fig. 2. From the slopes of these curves the differences between the mean square displacement at a given temperature and at 15 K are evaluated and are plotted in Fig. 3.

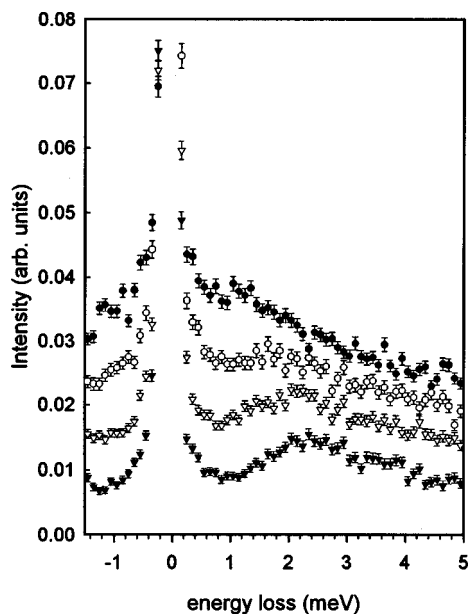


FIG. 1. Unscaled data for $2\theta=145^\circ$ and 200 K, shifted along the vertical axis for clarity. aPP (●); hhPP (○); hhPP/PIB (▼); PIB (▽).

In the case of the hhPP/PIB blend only the data for $Q^2 < 4.0 \text{ \AA}^{-2}$ were used. The upturn of the curves resembles that found for other polymer data^{7c,8,17} where it was attributed to the onset of a fast process. For the present purposes this contribution should not be included in the DWF correction, so linear fits were forced on the data below 240 K and the resulting values of $(d\langle u^2 \rangle / dT)$ were used to estimate the mean square displacement at the higher temperatures. The data shown in Figs. 4–7 are the results of summing the data for scattering angles of 90° – 145° after dividing by $\exp(-2W)Q^2 \times [n(\omega) + 1]$ for each temperature and then multiplying by $[n(\omega) + 1]$ for 200 K.

Boson peaks of 2.3, 1.8, and 2.2 meV were found for PIB, hhPP, and the blend, respectively. aPP was found to have a distinct change in slope in the range of 1–2 meV but no definite peak. The QENS instrument also provides information on inelastic processes at energies much greater than the boson peak and, although not of primary concern here, at 15 K, peaks at 28, 30, and 40 meV were observed for hhPP,

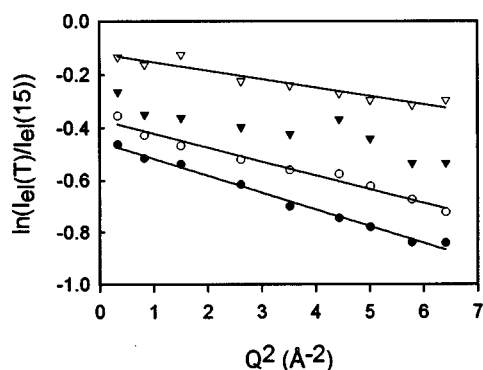


FIG. 2. Logarithm of normalized elastic intensity vs Q^2 . The data sets were shifted vertically for clarity. aPP (●); hhPP (○); hhPP/PIB blend (▼); PIB (▽).

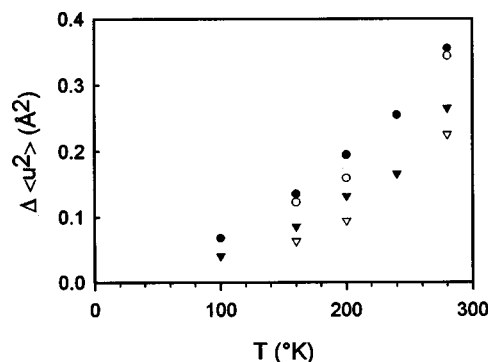


FIG. 3. Mean square displacements: aPP (●); hhPP (○); blend (▼); PIB (▽).

aPP, and PIB, respectively. In the case of aPP and PIB these are in agreement with previous observations^{18,19} where they were attributed to methyl group rotation.

DISCUSSION

According to Eq. (1), after application of the various factors discussed in the preceding, the data at different temperatures should lie on a universal curve if the scattering is due to harmonic vibrations. In an investigation of PIB which covered a more extensive temperature range, Frick and Richter⁸ found this to be the case for $T \leq T_g$ for all energy transfers, but only for $\Delta E \geq 3 \text{ meV}$ when $T > T_g$. They also observed a distinct peak at about 2.3 meV. Figure 4 shows our scaled PIB data and they are quite similar to the previous work. From Fig. 5 it is clear that the more fragile aPP has a much less distinct boson peak than does PIB and the correlation between fragility and the boson peak qualitatively holds for this case.

Figures 5 and 6 show a substantial difference in the two types of polypropylene. A direct comparison of the data at

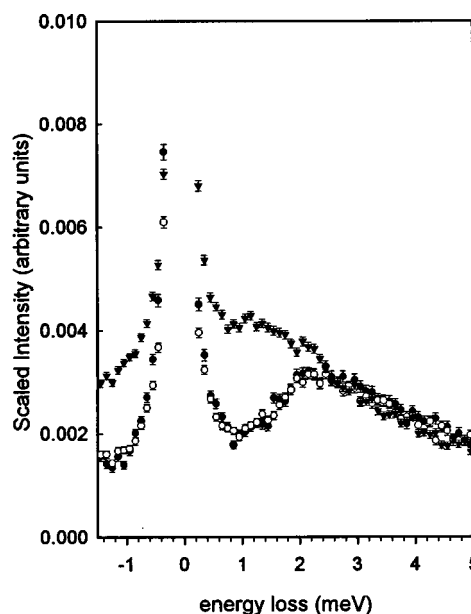


FIG. 4. PIB corrected and scaled data at 160 (●), 200 (○), and 280 K (▼).

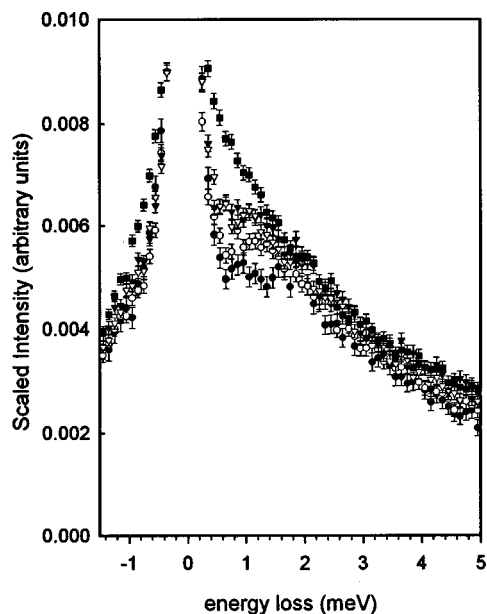


FIG. 5. aPP corrected and scaled data at 100 (●), 160 (○), 200 (▼), 240 (▽) and 280 K (■).

temperatures of 160 and 200 K is given in Fig. 8 and it is apparent a deviation from the “universal” curve is occurring between these two temperatures for aPP but not for hhPP. This indicates the onset of a “fast process” in aPP occurs at a lower temperature than in hhPP. A comparison of plots of $\ln[g(\omega)/\omega^2]$ in Fig. 9 demonstrates that aPP has an increased density of states in the range of about 0.8–2.5 meV even at 15 K where relaxations are not expected.

It has recently been suggested that there is a correlation between polymer flexibility above T_g and the energy of the boson peak.²⁰ It was argued that stiffer chains would lead to a boson peak at higher energies. A quantitative method of expressing flexibility is by means of Flory’s characteristic ratio C_∞ defined by²¹

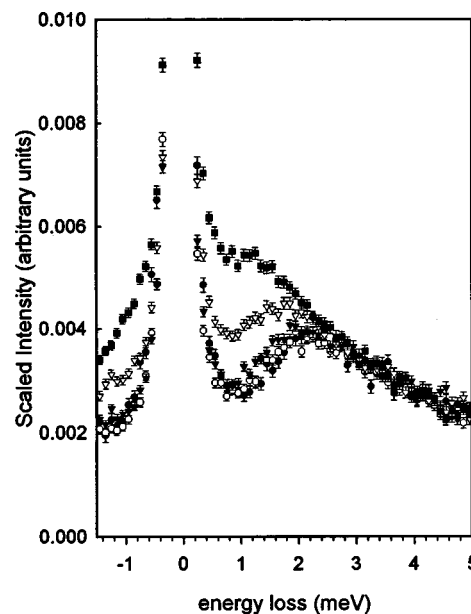


FIG. 7. hhPP/PIB blend corrected and scaled data at 100 (●), 160 (○), 200 (▼), 240 (▽), and 280 K (■).

$$C_\infty = \langle r^2 \rangle_0 / Nl^2, \quad (5)$$

where $\langle r^2 \rangle_0$ is the unperturbed mean square end-to-end distance and N is the number of main chain bonds of length l . For a freely jointed chain $C_\infty = 1$ and larger values indicate diminished flexibility. Fetters *et al.*²² have reported results from small angle neutron scattering (SANS) which can be used to calculate values of C_∞ of 6.0, 6.2, and 6.8 at 298 K for aPP, hhPP, and PIB, respectively. These are in the same ordering as the position of the boson feature in the vicinity of 200 K where it is still discernable. A caveat here is that $\langle r^2 \rangle_0$ can be inferred from dilute solution viscosities at the Θ condition. Consideration of that data leads to a value of 5.8 for

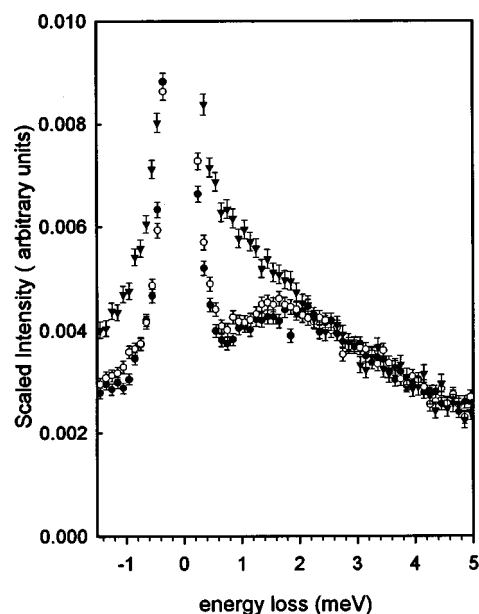


FIG. 6. hhPP corrected and scaled data at 160 (●), 200 (○), and 280 K (▼).

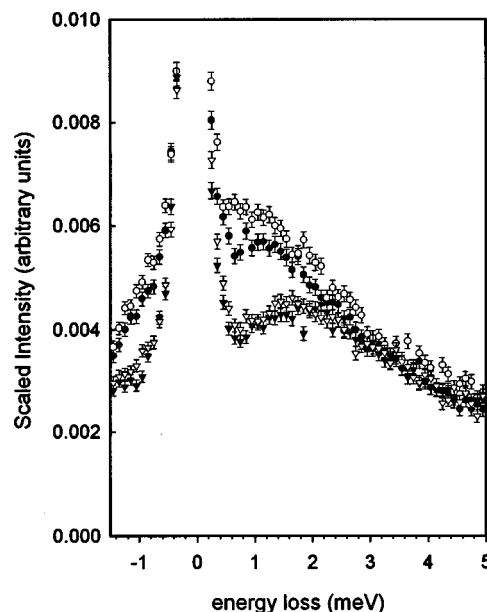


FIG. 8. Comparison of aPP and hhPP; aPP at 160 (●) and 200 K (○); hhPP at 160 (▼) and 200 K (▽).

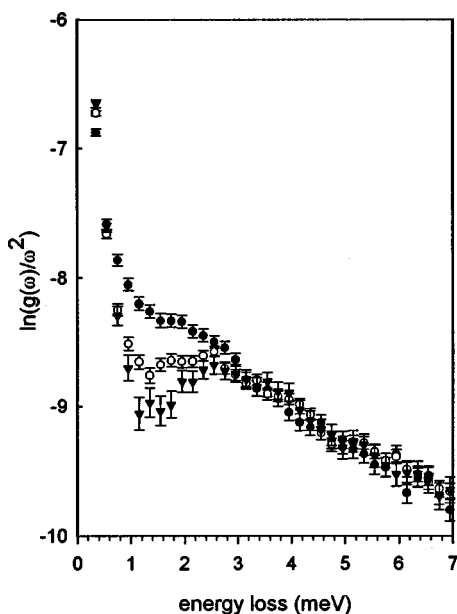


FIG. 9. Comparison of the density of states at 15 K in the form $\ln(g(\omega)/\omega^2)$. The data sets were translated in the vertical direction so that the curves superpose in the range of 3.3–7 meV. To improve the statistics the data were binned in 0.2 meV intervals. aPP (●); hhPP (○); PIB (▼).

hhPP; however the authors of Ref. 22 have the most confidence in the SANS determinations. PS and PMMA with C_∞ between 9 and 10 (also based on SANS data) are considerably stiffer than PIB but the former have lower lying peaks in the 1–1.7 range.^{6,7} Thus this measure of flexibility does not in general correlate with the peak position.

The relatively high density, low thermal expansion coefficient, and low isothermal compressibility suggest that PIB chains pack more compactly and interact more strongly than other saturated hydrocarbon polymers. This is expressed quantitatively by a comparison of the cohesive energy densities as estimated from the internal pressure, i.e.,

$$\rho_{\text{coh}} = \frac{T\alpha}{\beta}, \quad (6)$$

where α is the thermal expansion coefficient and β is the isothermal compressibility. The square root of the cohesive energy density is often used to calculate solubility parameters from pressure–volume–temperature (PVT) data and a tabulation¹⁴ of these parameters establishes that the order of the cohesive energy density at 300 K is PIB>hhPP>aPP which is the same as the ordering of the boson peaks. The respective values of 360, 340, and 320 MPa were determined relative to an average value of 313 MPa for poly (1-butene). However, a survey of the literature indicates that this correlation does not hold for molecules that are chemically dissimilar, for example, ρ_{coh} (PVC) is substantially greater than ρ_{coh} (PIB),²³ but the boson peak lies below that of PIB. Previously the fragility of liquids has been qualitatively related to the density of the minima and to the heights of the barriers in the potential energy hyperspace or “energy landscape.”²⁴ The cohesive energy density is an average over this hyperspace which, for those molecules investigated here, appears to adequately reflect the requisite topological detail.

The necessary data to estimate the cohesive energy of the blend are not available but the negative value of the Flory–Huggins χ parameter for the blend suggests that the attractive interaction of the two components exceeds the average of that for the pure components. Then, if the boson peak position is related to the interaction strength, it would be expected that the peak for the blend would occur at a value above that for hhPP which is in accord with the measurements. It is also worth noting that the ordering of the positions of the boson peaks of the four samples discussed here is the inverse of the ordering of the glass transition temperatures. In this case a survey of the literature suggests that the inverse correlation of peak position to T_g is common to those polymers that have been investigated.

Three other observations result from consideration of the blend data. (1) From a comparison of the quasielastic peaks ($-0.5 \text{ meV} < \text{energy loss} < 0.5 \text{ meV}$) for hhPP, PIB, and the blend to within the instrumental resolution, there is no indication that concentration fluctuations play a role in the onset of the fast process in the blend. (2) To a first approximation the spectra for the blend can be represented by a linear combination of those of the pure components with a weighting determined by the relative numbers of monomers, but the peaks are sufficiently close so that this observation does not provide a useful test to determine whether or not the motions responsible for the boson peaks of the two components are independent in the blend. (3) The elastic amplitudes of the blend have a local maximum in the vicinity of $Q^2 = 4.5 \text{ \AA}^{-2}$ in a plot of the $\log I_{\text{el}}$ vs Q^2 for temperatures below 240 K. An example can be seen in Fig. 2 for 200 K. (The data shown in Fig. 2 were scaled by the amplitudes at 15 K. The presence of the maxima is independent of the scaling.) This was not observed in the pure component data and may indicate an additional contribution from coherent scattering in the case of the blend.

CONCLUSIONS

The nature of the boson peak in aPP is consistent with the designation of this material as a fragile glass former¹⁰ and the conjecture of Sokolov *et al.*¹¹ regarding a connection between fragility and the boson peak. The boson peak behavior observed for hhPP suggests that it is a stronger glass former than aPP but more fragile than PIB. Differences in the density of states for the three molecules are apparent already at 15 K and the data at higher temperatures indicate that the onset of a fast process occurs at the lowest temperature for aPP. In terms of the characteristic ratio both polypropylenes are more flexible than PIB and the observation of lower energies of the boson feature is consistent in a qualitative sense with the suggestion of Frick and Richter.²⁰ Although the chemical structures of the three pure polymers are quite similar there are differences in the cohesive energy densities which correlate with the relative positions of the boson peaks. The hhPP/PIB blend appears to also be consistent in this regard. The ordering of the boson peak position for the four materials investigated was found to vary inversely with the glass transition temperature.

Note added in proof: Results similar to those shown in Fig. 5 for aPP have been reported by Kanaya *et al.*²⁵

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