*Macromolecules* **2003,** *36,* 520−521

# Notes

## Comparison of Boson Peaks in Polypropylenes

**B. K. Annis* and Man-Ho Kim**[†]

*Chemical Sciences Division,*
*Oak Ridge National Laboratory,*
*P.O. Box 2008, Oak Ridge, Tennessee 37831-6197*

**Craig Brown**

*Department of Material and Nuclear Engineering,*
*University of Maryland, College Park, Maryland 207421,*
*and NIST Center for Neutron Research,*
*National Institute of Standards and Technology,*
*Gaithersburg, Maryland 20899-8562*

*Received August 6, 2002*

### Introduction

A recent experimental study has found that the viscosity of molten syndiotactic polypropylene (sPP) is substantially higher than those of atactic (aPP) and isotactic (iPP) propylene at the same molecular weight.[1,2] NMR techniques[3] have found a similar difference in the segment dynamics of the melts as predicted by molecular dynamics computer simulations.[4] The faster elements of the chain dynamics responsible for Raman lines have also been found to be altered in both the solid and molten states by tacticity.[5] The effect of tacticity on melt structure is mixed. For example, structure functions from wide-angle X-ray scattering show little if any effect from tacticity,[6,7] and PRISM calculations found only subtle differences in various pair correlations of sPP and iPP.[6] However, a recent SANS study of molten sPP[8] found a larger segment length and consequently a larger characteristic ratio ($C_\infty$) of 9.3 as compared to values of 6.0 and 6.2 for aPP and iPP, respectively. This indicates a considerably stiffer chain for sPP.

The glass transitions for the three tacticities are all similar, and aPP, in the terminology of Angell et al.,[9] is a fragile glass former. Consistent with the ideas of Sokolov et al.,[10] it has been found to have a boson peak below $T_g$ that is rather indistinct and at relatively low energy.[11,12] The amorphous phase in iPP has recently been observed to have a very similar peak[13] while in contrast, amorphous, atactic head-to-head polypropylene has a considerably more distinct peak at higher energy.[12] With the recent finding that sPP can be quenched to an amorphous phase,[14] it is of interest to compare the dynamic behavior of the polypropylenes as exemplified by the boson peak and reexamine an earlier suggestion[15] that more flexible chains would be associated with lower energy boson peaks. Previous efforts have been made to relate the boson peaks in polydienes[16] and polyolefins[17] with changes in microstructure. Some differences in peak energy were observed, but no clear correlation with structure was apparent.

### Experimental Section

The neutron scattering data were obtained using the Fermi Chopper time-of-flight spectrometer (FCS) at the National Institute of Standards and Technology. A wavelength ($\lambda$) of 6 Å with an elastic energy resolution of approximately 65 $\mu$eV was used. Signals from detectors with 1.1 $\text{Å}^{-1} \le Q_{\text{el}}$ ($=(4\pi/\lambda)\sin(\theta/2)$) $\le 2.0$ $\text{Å}^{-1}$ were summed after correction for efficiencies determined from a vanadium standard. The sample shape was cylindrical.

Because of the high hydrogen atom content, the scattering is primarily incoherent, and in the approximation of a one-phonon scattering process involving harmonic vibrations, the scattered intensity is proportional to the sum of an incoherent elastic term $S_0 \exp(-2W)$ and a term for a neutron energy change of $\hbar\omega$:

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

where $M$ is the average atomic mass involved in the vibrational mode and $Q$ is the magnitude of the wave vector. The Bose−Einstein occupation number is $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$, the vibrational density of states is $g(\omega)$, and the Debye−Waller factor is given by $\exp(-2W) = \exp(-Q^2\langle u^2\rangle/3)$, where $\langle u^2\rangle$ is the mean-square displacement.

Syndiotactic polypropylene with $M_w$ of 180 000 and $M_w/M_n = 2.2$ was supplied by Fina, who also provided a value of the racemic pentad content of 93%. A subsequent measurement[8] at ORNL found a value of 86.3%. The sample was a film of average thicknesses of 0.11 mm backed by an aluminum foil of thickness ~0.003 mm. It was heated to 190 °C until liquid and then quenched in liquid nitrogen and subsequently maintained in dry ice (−78.5 °C) before installation on FCS. Wide-angle X-ray scattering from quenched sPP showed a broad amorphous peak similar to that in ref 14, and small-angle X-ray scattering showed no indication of a lamellar peak.

The atactic polypropylene was provided by Rexene Corp. and was from the same batch as was used in a previous study.[12] $M_w$ was 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.

### Results

The $S_{\text{inc}}(Q,\omega)$ for aPP and sPP are shown in Figure 1. For sPP at 100 K a weak boson peak is distinguishable at about 1.1 meV. At 150 K there is very little difference in the spectra for the two tacticities, and the results for aPP are in good agreement with previous investigations on different spectrometers.[11,12] Superposed on the plot is a vertical line indicating the position of a boson peak of similar appearance that was found in an analysis of the amorphous region in isotactic polypropylene.[13] Within the combined uncertainties of the data, the peaks are the same. Comparison of the

---

* To whom correspondence should be addressed.

[†] Current address: NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562.

10.1021/ma0212689 CCC: $25.00

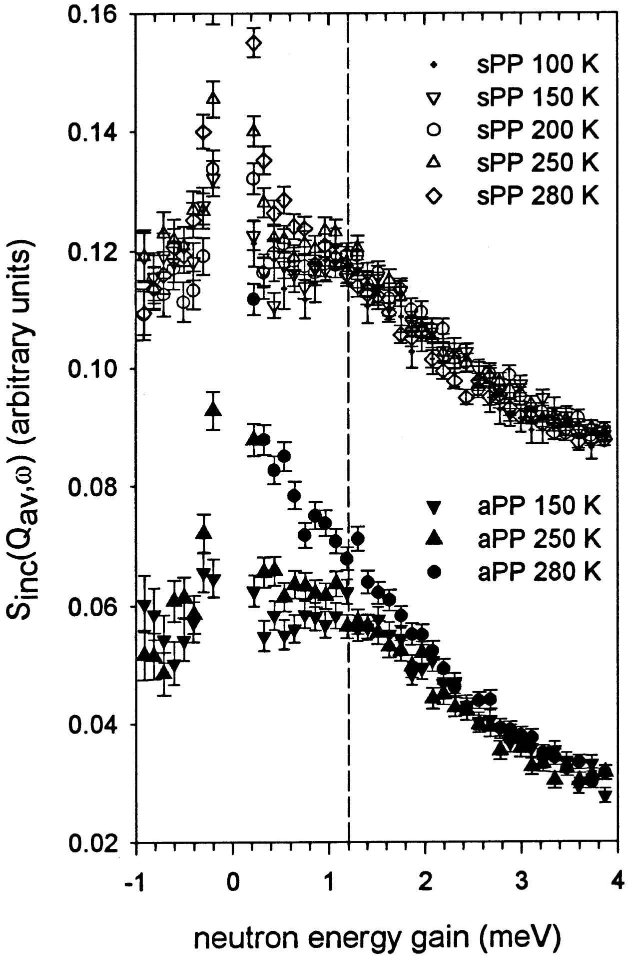

**Figure 1.** Comparison of aPP and sPP. Scaling by the Debye–Waller factor and the temperature dependence of the Bose–Einstein occupation number has been applied.

data at 280 K suggests a lower temperature onset of a fast relaxation process in aPP.

## Discussion

The results presented here show little if any indication that the dynamics responsible for the boson peak in the polypropylenes reflect the differences due to tacticity in the melt behavior at least as characterized by the viscosities, segment dynamics, and chain flexibility. Of the six polymers consisting of single bonds in the backbone with variations in the methyl groups for which boson peaks have been determined, aPP, sPP, and iPP have the lowest energy boson peaks. Both alternating atactic poly(ethylene–propylene) (PEP)[17] with one less methyl group and poly(isobutylene) with two more methyl groups per four backbone carbons have higher energy peaks. Similarly, the methyl group rearrangement to give head-to-head polypropylene results in a higher energy boson peak.[13]

## Conclusions

Despite affecting various aspects of the melt behavior, tacticity in the polypropylenes has little if any effect on the dynamics associated with the boson peak. Comparison with other related polymers suggests that the number of methyl groups and connectivity (end to end vs head to head) are more important factors, but the relation of these structural differences to the boson peak mechanism remains illusive.

**Acknowledgment.** This research was supported in part by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-00OR22725, Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. The authors acknowledge the assistance of Dr. A. Payzant in facilitating the use of an X-ray diffractometer which is sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle also under the preceding contract.

## References and Notes

(1) Eckstein, A.; Freidrich, C.; Lobbrecht, A.; Spitz, R.; Mülhaupt, R. *Acta Polym.* **1997**, *48*, 41.
(2) Pearson, D. S.; Fetters, L. J.; Younghouse, L. B.; Mays, J. W. *Macromolecules* **1988**, *21*, 478.
(3) Lippow, S. M.; Qiu, X.; Ediger, M. D. *J. Chem. Phys.* **2001**, *115*, 4961.
(4) Antoniadis, S. J.; Samara, C. T.; Theodorou, D. N. *Macromolecules* **1999**, *32*, 8635.
(5) Hsu, S. L.; Hahn, T.; Suen, W.; Kang, S.; Stidham, H. D.; Siedle, A. R. *Macromolecules* **2001**, *34*, 3376.
(6) Curro, J. G.; Weinhold, J. D.; Rajasekaran, J. J.; Habenschuss, A.; Londono, J. D.; Honeycutt, J. D. *Macromolecules* **1997**, *30*, 6264.
(7) Habenschuss, A. Private communication.
(8) Jones, T. D.; Chaffin, K. A.; Bates, F. S.; Annis, B. K.; Hagaman, E. W.; Kim, Man-Ho; Wignall. G. D. *Macromolecules* **2002**, *35*, 5061.
(9) Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
(10) Sokolov, A. P.; Rössler, E.; Kisliuk, A.; Quitmann, D. *Phys. Rev. Lett.* **1993**, *71*, 2062.
(11) Kanaya, T.; Kaji. K.; Bartos, J.; Klimova, M. *Macromolecules* **1997**, *30*, 1107.
(12) Annis, B. K.; Lohse, D. J.; Trouw, F. *J. Chem. Phys.* **1999**, *111*, 1699.
(13) Annis, B. K.; Kim, M.-H.; Alamo, R.; Pyda, M. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 2852.
(14) Loos, J.; Petermann, J.; Waldöfner, A. *Colloid Polym. Sci.* **1997**, *275*, 1088.
(15) Frick, B.; Richter, D. *Science* **1995**, *276*, 1939.
(16) Zorn, R.; Kanaya, T.; Kawaguchi, T.; Richter, D.; Keisuke, K. *J. Chem. Phys.* **1996**, *105*, 1189.
(17) Frick, B.; Richter, D.; Zorn, R.; Fetters, L. J. *J. Non-Cryst. Solids* **1994**, *172–174*, 272.

MA0212689