JOURNAL OF MATERIALS SCIENCE **38** (2003) 581 – 587

Free volume changes associated with solid state crystallization of syndiotactic polystyrene

P. J. SIMPSON*, D. M. SHINOZAKI‡,§, U. MYLER*,¶, K. L. M. EVANS*
Department of Physics and Astronomy, ‡Department of Mechanical and Materials Engineering, The University of Western Ontario, London, Ontario, Canada N6A 3K7
E-mail: shinozaki@uwo.ca

The temperature dependent crystallization of quenched syndiotactic polystyrene is characterized by in-situ positron annihilation spectroscopy. The experimental observations obtained using differential scanning calorimetry and dynamic mechanical thermal analysis are consistent with the positron results. It is shown that the changes in thermal and mechanical properties which occur during solid state crystallization are related to the changes in positron annihilation parameters which are in turn related to free volume in the specimen. © *2003 Kluwer Academic Publishers*

1. Introduction

Syndiotactic polystyrene (sPS) is a partially crystalline polymer which has low permeability, good chemical resistance and retains reasonable mechanical properties at relatively high temperatures. All of these properties are strongly affected by the amount and distribution of the crystalline phase, which can differ depending whether the sample is produced by crystallization from the melt or from a non-equilibrium amorphous state [1].

sPS can crystallize in a variety of structures [2–11] depending on its thermomechanical history. Of particular interest is the crystallization below the melting temperature from a quenched material. St. Lawrence and Shinozaki have shown that the lamellar morphology is quite different from that of a slow cooled, melt crystallized sample [1, 11], and the measured differences in storage modulus are directly attributable to this. An important useful property for sPS is the retention of reasonable mechanical properties to relatively high temperatures. This depends on the stability of the crystalline phase with a high equilibrium melting temperature. The speed of thermomechanical processing is often maximized, and nonequilibrium structures can result. Subsequent annealing or service can result in significant detrimental changes in mechanical properties or specimen dimensions. The standard methods to examine the molecular processes in annealing include microscopy, thermal analysis, dynamic mechanical thermal analysis, and a variety of chemical spectroscopies. The present work investigates the use of positrons in the study of crystallization from the quenched amorphous state, and correlates the measurements to mechanical and thermal properties.

Positron annihilation is used generally as a probe of structure in a variety of solids. Because the positron is repelled by ion cores and preferentially localized in open volumes, it is a sensitive probe of [1] vacancy-type defects in crystalline materials, and [2] the fraction, size, and distribution of open volume in amorphous materials. In polymers, annihilation characteristics have been studied in relation to phenomena such as structure, chemistry, crystallinity, additives, and radiation effects [12, 13].

Previous positron studies of polymers have most often used measurements of the positron lifetime, from which it is possible to determine the fraction of positrons annihilating as positronium (a hydrogen-atom-like positron-electron bound pair), as opposed to annihilating from the free state. This fraction is very sensitive to the structure of the material, and in particular to the size and number of open volumes in the sample, since positronium can only form where there is a sufficiently large open volume to accommodate the Ps 'atom'.

In the experiments reported here we have used a different technique, Doppler Broadening of Annihilation Radiation (DBAR), which has in the past been more commonly applied to crystalline materials. Compared to positron lifetime studies, DBAR provides the advantage that it is more readily used in conjunction with a slow positron beam, providing some depth resolution. Information from DBAR tends to be less specific than that obtained from positron lifetimes, however in this study we show that DBAR can successfully be applied to polymers.

2. Experimental methods

The starting material was a sample of syndiotactic polystyrene (XU 72104) (melting point 276°C) provided by The Dow Chemical Company (Midland). For the positron experiments, relatively thin samples

---

[§] Author to whom all correspondence should be addressed.

[¶] *Present Address:* Medical Physics Department, Hamilton Regional Cancer Centre, Hamilton, Ontario, Canada L8V 5C2.

0022–2461

(approximately 0.9 mm) were carefully compression molded and either slow cooled from the melt or quenched directly in cold water. Samples which were too thick did not cool rapidly enough to produce mainly amorphous samples. For a more detailed examination of the quenched material, thinner specimens, approximately 0.1 to 0.2 mm thickness were prepared. Samples were compression molded between sheets of aluminum foil, and the foil/sPS sandwich was quenched from the melt directly in cold water. The thinner samples allowed for more rapid cooling to ensure they were homogeneously amorphous. sPS has a crystallization rate which is fairly slow by the standards of many commercial polymers like polyethylene, but not so slow that it requires unreasonably long times to crystallize, either from the melt or from the solid amorphous state.

Differential scanning calorimetry (DSC) was used to confirm the interpretation of the temperature dependent transitions observed in the DBAR experiments. A Perkin Elmer DSC7 was used at heating rates from 0.2°C/min to 20°C/min. The slowest rates were comparable to the heating rates obtained in the DBAR furnace. Thermal analysis specimens were approximately 3–12 mg. Samples were prepared in a manner similar to the DBAR specimens, although the DSC samples were thinner. Being thinner, quenching to amorphous would be easier. As with most DSC experiments, the samples were held in a clean, dry nitrogen atmosphere.

The mechanical response of the material was measured using a Polymer Laboratories dynamic mechanical thermal analyser over the temperature range (heating) from 50°C to 200°C. The material was prepared by quenching specimens of approximately 1mm thickness in ice water from 320°C.

Samples thin enough to show the spherulitic structure were prepared by quenching from the melt and slow cooling from the melt. Such specimens were examined directly with transmitted light optical microscopy using crossed polars.

Quenched samples were found to be visually transparent, indicating a largely noncrystalline state. Earlier studies using transmission electron microscopy of this material showed that quenching produces a largely amorphous material from which lamellae crystallize upon annealing at temperatures in the range greater than 20°C above the glass transition [1].

2.1. Positron annihilation spectroscopy

The University of Western Ontario slow positron beam provides a flux of $\sim 10^5$ s^{-1} positrons onto a target in vacuum. Beam energy is selectable in a range from 500 eV to 60 keV, which provides control over the sampling depth: for a target with density 1 g/cm^3, this corresponds to a range of probing depths from $\sim$10 nm to $\sim$30 microns. The width of the implanted positron distribution is comparable with the mean depth, and so the depth resolution of the technique degrades with increasing depth. Positrons injected into the sample lose their kinetic energy in $\sim$10ps, and diffuse randomly at thermal energy before annihilating with an electron. In crystalline materials the diffusion length can be significant (200 nm), but in amorphous samples it is typically $<$10 nm. In most cases, the annihilation results in two gamma rays with energies near 511 keV. Since the gamma rays must carry off the momentum of the annihilating electron, they will be Doppler shifted from 511 keV, with the result that the 511 keV spectral line has a FWHM of a few keV. It is this Doppler-broadening that provides information about the sample: in principle it contains in it the electron momentum distribution, but the detector resolution ($\sim$1.3 keV FWHM at 511 keV) smears out any detailed structure in the line. In insulating materials, the positron can form a bound pair with an electron provided by the sample, resulting in the hydrogen-atom-like positronium. Since this can only occur in the case that there is sufficient open volume to accommodate the positronium 'atom', the rate of positronium formation provides a sensitive probe of the open volume character of the material. Although it is not straightforward to interpret this quantitatively, it is extremely sensitive to changes in the open volume in the material.

3. Results and discussion

Air cooling of sPS from the melt results in a microstructure with a relatively large spherulite size (Fig. 1). Indexing of the wide angle diffraction pattern shows the crystal structure is a mixture of the α'' and β' forms [14, 15]. Presence of strong peaks at $2\theta = 13.95°$ and 15.50° together with a weaker peak at 10.3° is consistent with the α'' modification, which is more ordered and typically found in very slowly cooled melt crystallized material. Evidence for β' is observed in peaks at $2\theta = 6.03°$, 12.3°, and 18.6°.

The thin sample cools fairly rapidly through the solidification temperature, even when allowed to air cool. This can be seen in the thermal properties. The DSC scan was run at a heating rate of 10°C/minute, and the air cooled sample shows the characteristic glass transition at approximately 94.8°C, and a crystallization exotherm just below 150°C (Fig. 2a) which indicates the presence of a small amount of amorphous material frozen into the structure during the solidification process. As the scan proceeds to higher temperatures, another crystallization exotherm is observed at about 250°C, just below the melting endotherm. Microstructural examination of this material using transmission electron microscopy showed that the lamellar morphology which develops on crystallization in the solid state is very different from that which evolves on crystallization from the melt [11]. At crystallization temperatures similar to those observed in the DSC curves ($T < 150°C$), the lamellae are less well organized than those which develop on crystallizing directly from the melt. The melt crystallized material is organized in spherulites (Fig. 1). The small amount of amorphous material crystallizes on heating into isolated lamellae or small packets of parallel lamellae. This is best seen in Fig. 3, for quenched and annealed material. The local birefringent volumes are of the order of 1–2 μm in size. In the case of more slowly cooled material, most of the material is spherulitic, and the secondary crystallization occurs on heating during the DSC scan.

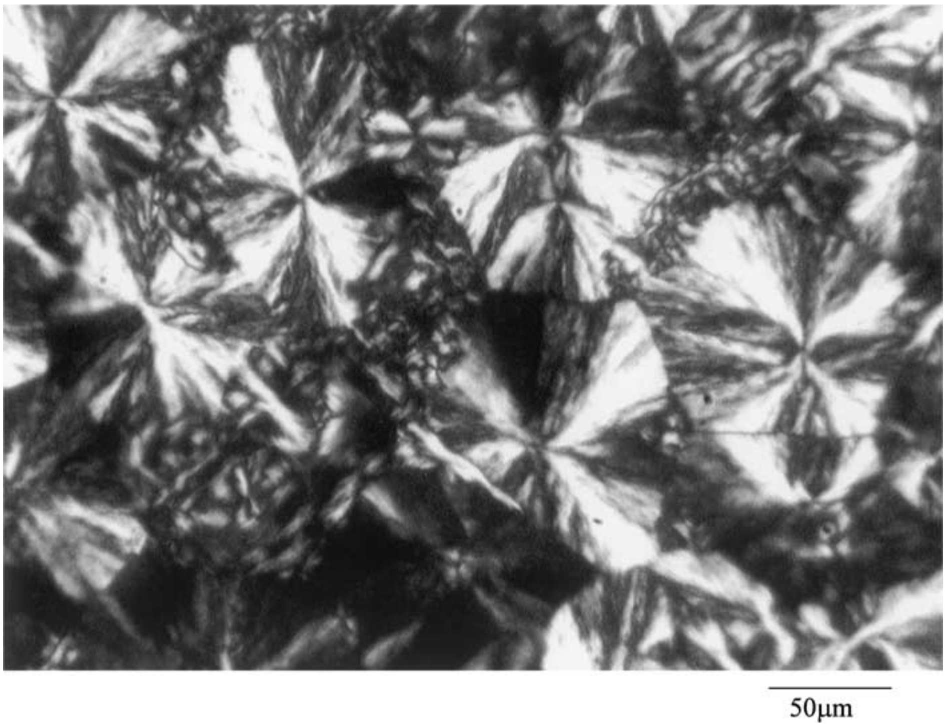

Figure 1 Optical micrograph of melt crystallized syndiotactic polystyrene. Transmitted light with crossed polars.

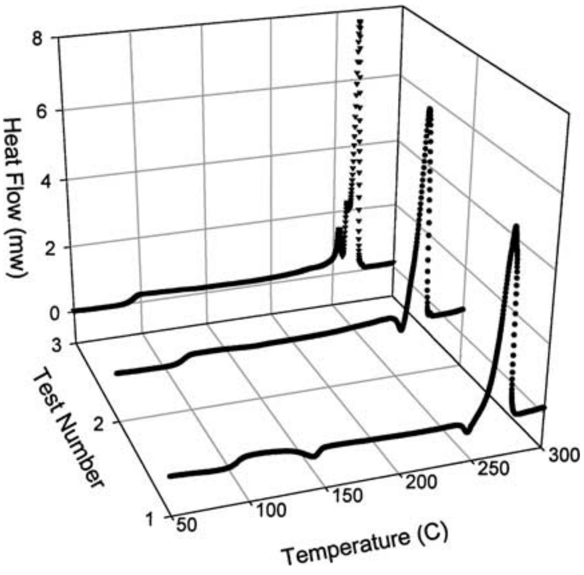

Figure 2 Differential scanning calorimetry of air cooled sPS. Successive scans on the same specimen (in sequence front to back).

Comparing the X-ray diffraction observations of the quenched material with those of the air cooled material, the secondary crystallization in the air cooled sample is likely of the less ordered α' form, which is evident in the air cooled sample as a slight decrease in the relative peak size at $2\theta = 10.5^\circ$, 14° and 15.5°.

At the end of the first DSC scan (curve 1), the sample was held in the molten state (300°C) for a few minutes, then cooled at 50°C/minute to room temperature. A heating DSC scan was run immediately on the same specimen, resulting in the second curve (curve 2), in which the crystallization exotherm at 146.4°C has disappeared but a residual crystallization just below the melting peak appears. Repeating the experiment and holding at 300°C for a longer time results in the DSC scan labelled (c) for a completely crystallized sample. Pasztor *et al*. report that to examine the detailed crystallization behaviour of sPS, it was necessary to heat the melt to 320°C to remove all traces of crystallinity [16]. Guerra *et al* similarly suggest that a melt temperature of 340°C is necessary to remove the microstructural memory [14]. The residual memory has been shown to affect the crystallization kinetics from the melt, and the subsequent re-melting behaviour. In particular, the positions and sizes of the multiple melting peaks are sensitive to the melt temperature [17]. In the present experiments, this subsequent melting behaviour is not the principle subject of concern. Of particular note here is the absence of a measurable crystallization endotherm upon heating during this heating run in the DSC. This shows that the material is fully crystallized on cooling from the melt at 300°C, and no further crystallization in the solid state is detectable upon heating during the DSC run shown.

The triple melting peak seen in Fig. 2 is a result of the different crystal structures which evolve on slow crystallization from the melt [14, 18, 19]. Recent work by St. Lawrence [1] has shown that the multiplicity of melting peaks is due to recrystallization processes which occur on firstly cooling from the melt and secondly on heating from room temperature (in the solid state). Appropriate annealing cycles can alter the relative sizes and numbers of melting peaks. There are distinct lamellar morphologies which result from the different thermal histories.

Quenching a thin specimen in ice water results in an amorphous material with no microstructure visible optically in thin films. The wide angle X-ray diffraction pattern is similar to that seen in an amorphous polystyrene, with two broad peaks at $2\theta = 10.5^\circ$ and 20°. Heating this material from room temperature results in changes in free volume detectable using positron spectroscopy.

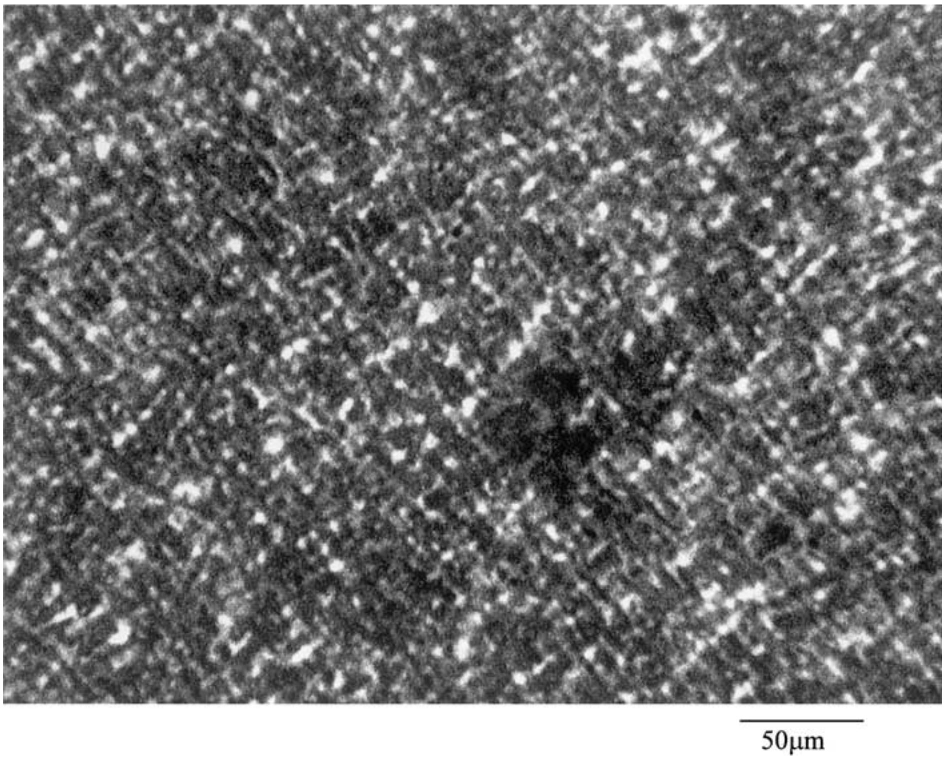

Figure 3 Optical micrograph of quenched and annealed sPS. Transmitted light with crossed polars. Quenching from the melt produces a featureless structure with no birefringence. Annealing reveals small birefringent crystalline regions.

3.1. Doppler broadened positron spectroscopy

A positron injected into a solid target annihilates with an electron, yielding gamma rays which carry information about the target material. That information can be accessed either by measuring the lifetime of the positrons in the target, or (as in the present case) by measuring the energy spectrum of the gamma rays. This method, called Doppler broadening of annihilation radiation (DBAR), was used in conjunction with a monoenergetic, low-energy positron beam. The DBAR technique uses an intrinsic germanium detector to obtain the energy spectrum of 511 keV gamma rays. In most cases, this spectrum is reduced to a single parameter, S, which is a measure of its 'sharpness'. In particular, the S-parameter is the ratio of counts in a central region of the 511 keV peak, to the total counts in the peak (510.3 to 511.7 keV), with the width of the central region (510.3 keV to 511.7 KeV) chosen so that $S \sim 0.5$. Sensitivity to positronium (and hence to open volumes in the sample) arises because the momentum of the electron in the positronium 'atom' is small (compared with an electron bound to an atom of the host material), and so there is very little Doppler broadening of the 511 keV peak, and the S (or Sharpness) parameter is increased.

In this study, samples were mounted in a specially-constructed copper can, 45 mm in diameter by 30 mm long, with a 15 mm diameter opening in the front to admit the positron beam. The beam spot is about 5 mm in size, and so sample information obtained is an average over a region of that size. This geometry, enclosing the sample as much as possible, was chosen in order to achieve the best possible temperature uniformity. The temperature was measured by a type-K thermocouple clamped directly to the sample, and the can was heated using ribbon heaters (Omega) attached to the outside.

For the present experiments, a quenched sample of sPS was slowly heated in the copper can. The sample temperature was then increased at a rate of ~0.4 degrees C/minute, and a positron annihilation spectrum (5×10^5 events) obtained every ~5 minutes. At least ten such spectra were obtained and averaged at each temperature. When the highest temperature was reached (approximately 140°C), the temperature was lowered, and DBAR data acquired on the same sample as it cooled.

The S-parameter was plotted as a function of temperature in Fig. 4. The heating cycle shows a linearly

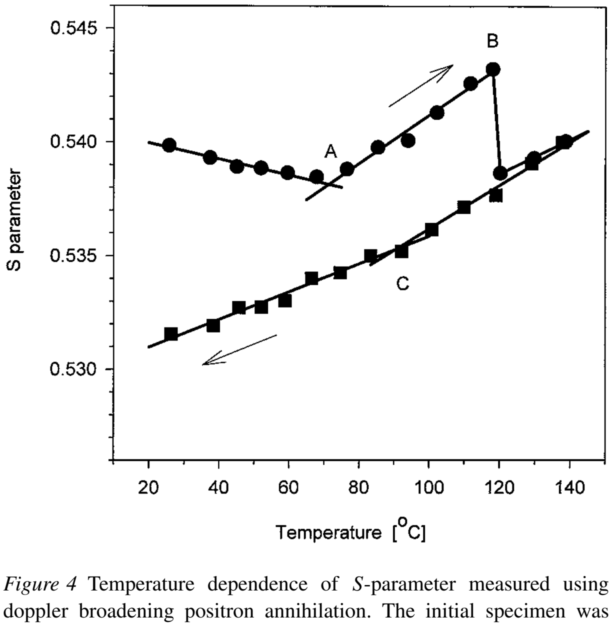

Figure 4 Temperature dependence of S-parameter measured using doppler broadening positron annihilation. The initial specimen was quenched sPS, heated from room temperature (AB) then cooled (C).

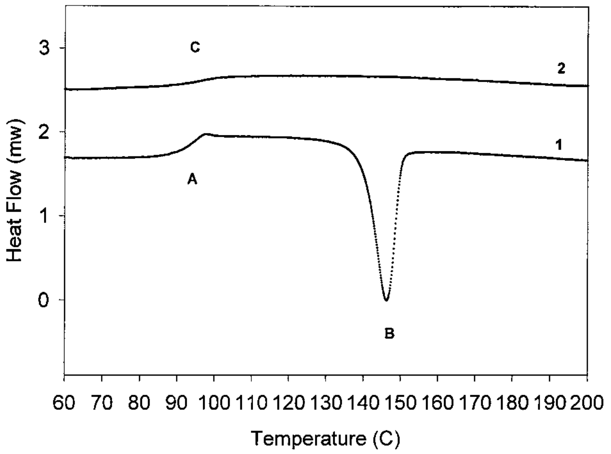

Figure 5 Differential scanning calorimetry of quenched sPS. The first heating scan (curve 1) shows the crystallization exotherm at B. After heating to 200°C the sample is cooled and immediately scanned again (curve 2).

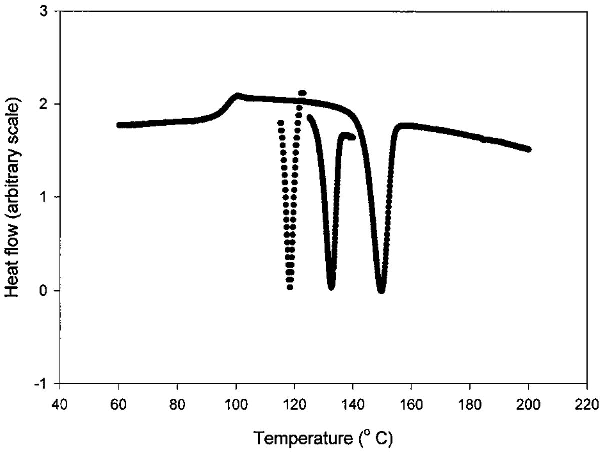

Figure 6 DSC heating rate dependence of crystallization exotherm temperature. The heating rates are 0.2, 1 and 10°C/minute for the peaks shown (left to right). The vertical scale is in arbitrary units as the peak height changes with scanning rate.

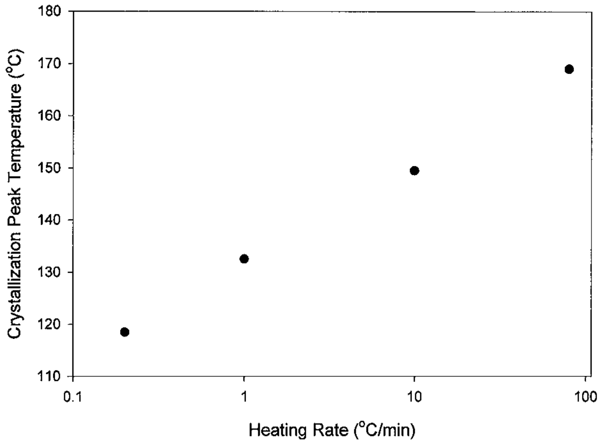

Figure 7 Crystallization peak temperature measured from DSC. The horizontal axis is logarithmic, indicating a saturation near 120°C as the scanning rate decreases.

decreasing S-parameter up to approximately 72°C (A), at which temperature it abruptly begins to rise, again linearly with temperature. At 120°C (B) there is a discrete, large drop in the S-parameter, with a further linear rise at higher temperatures. Upon cooling, the S-parameter falls along the heating line, with no evidence for the change at 120°C seen on heating. Around 90°C (C) a change in slope is observed, and the linear drop in S-parameter continues to room temperature. The interpretation of these data can be understood by considering the DSC and DMTA results which follow.

3.2. Differential scanning calorimetry

Quenched sPS is largely amorphous and crystallizes on heating above T_g. The crystallization process can be followed using differential scanning calorimetry (Fig. 5). On the initial heating scan (10°C/minute) from the quenched condition (curve 1), the amorphous material is randomly oriented polystyrene, and shows a glass transition ($T_g = 92.5$°C) at the point A. As the specimen is heated above T_g a crystallization endotherm (B) appears starting at 140°C with a peak at 146.4°C. The fraction of amorphous material is reduced, as observed on the second DSC scan for the same specimen (curve 2) which followed shortly after the first scan. The crystallization has been completed on the first heating cycle and the glass transition step is much smaller. The sample in this experiment was not melted, and the maximum DSC temperature was 200°C.

The temperature of crystallization from the quenched state is a sensitive function of heating rate, as seen in Fig. 6. The rate of the DSC heating scan is systematically reduced, and the crystallization peak shifts to lower temperatures (Fig. 7), consistent with the crystallization kinetics discussed earlier [20]. At lower heating rates accessible to reasonable experimental methods, the dependence on the logarithm of the heating rate suggests the crystallization peak position would remain at approximately 120°C.

The slowest DSC heating rate tested was 0.2°C/munite, which is similar to the heating rate used in the positron experiment. The crystallization peak of Fig. 6 is centered at the same temperature (the sudden drop in the S-parameter at approximately 120°C seen in Fig. 4). The drop in S-parameter at this temperature thus is likely due to the drop in free volume as the amorphous structure transforms to crystalline. This can be inferred from the measurement of specimen dimensions over this heating range. The length of the specimen decreases by approximately 1% after annealing above 120°C, consistent with a decrease in free volume.

Cooling the sample after heating to 140°C results in a change in slope of the S-parameter versus temperature curve (Fig. 4) at approximately 90°C. This is associated with the glass transition seen in Fig. 5 at the point C.

The T_g for the quenched amorphous state (92.5°C) on heating is about 3.8°C lower than the T_g for the same sample after crystallization above 130°C. This appears to be a smaller difference than that measured using positrons, where the difference is approximately 10°C, with the T_g after crystallization most similar in the two methods. The apparent T_g measured with the positron analysis (Fig. 4) differs from that obtained by DSC, and this can be understood by considering the region $T < T_g$ more carefully.

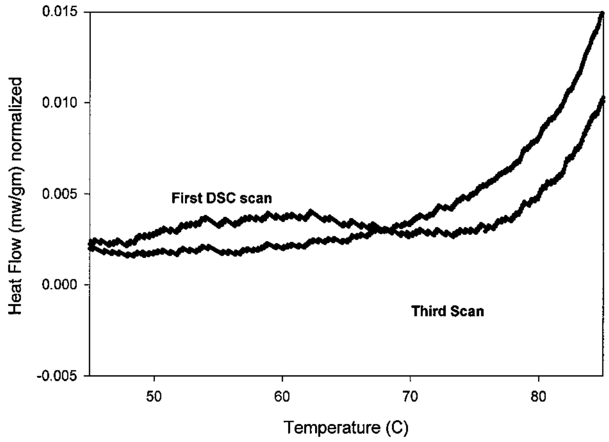

Figure 8 Successive DSC scans taken for an initially quenched sample. Maximum scan temperature is 85°C (well below the onset of crystallization at 120°C).

3.3. Glassy state free volume changes

An interesting feature of the positron results (Fig. 4) is the negative slope in the low temperature region on heating up to the point A. A simple interepretation of this observation is that the free volume in the quenched amorphous state is decreasing steadily as T increases. Careful DSC experiments reveal a thermal effect which correlates with some change in heat capacity over this temperature range. Fig. 8 shows the successive DSC scans taken of one specimen which was originally in the quenched condition. On the first heating cycle ($35°\mathrm{C} < T < 85°\mathrm{C}$), there is a slight hump in the DSC curve. This is most clearly seen by comparing it to a second DSC scan, taken on the same specimen, immediately following the first heating cycle. In this scan the "hump" in the curve has disappeared. Upon repeating the same heating cycle repetitively, the second curve is identically reproduced and the "hump" is not observed. The observation is repeatable from specimen to specimen, and is a small thermal effect visible only at high magnification of the scale of the vertical axis. The DSC scans here are much more rapid than are the positron annihilation tests, so if the DSC scan could be run at the slower rate, it is expected that the heat capacity would show a steady decrease over this temperature range, corresponding to the steady decrease in free volume indicated by Fig. 4. The relatively high rate of temperature change is necessary for the DSC experiment to increase the heat flow resolution.

The decrease in heat capacity with decreasing free volume is consistent with a local loss of molecular mobility.

The molecular rearrangement which reduces the free volume and changes the heat capacity during heating in the temperature range below the glass transition also results in a slight decrease in T_g from 93.6°C in the as quenched state to 92.5°C in the subsequent heating cycle. The results are systematically reproducible, and since the successive tests are run on the same specimen, and the maximum temperature is held below or near the glass transition, no molecular degradation is expected and the mass of the sample should remain constant.

The glassy state obtained from the quenched sPS appears to be distinct from that of atactic polystyrene (aPS). DSC scans were run under identical test conditions as those applied to the quenched sPS, and no differences in successive scans were detectable. However T_g was significantly higher than that observed for all variations of thermal history used for the sPS samples. The T_g for aPS was consistently found to be in a narrow range near 102°C; while the sPS (depending on thermal history) was in the range $89.7°\mathrm{C} < T_g < 95.6°\mathrm{C}$, with the higher T_g found for slowly cooled melt crystallized samples.

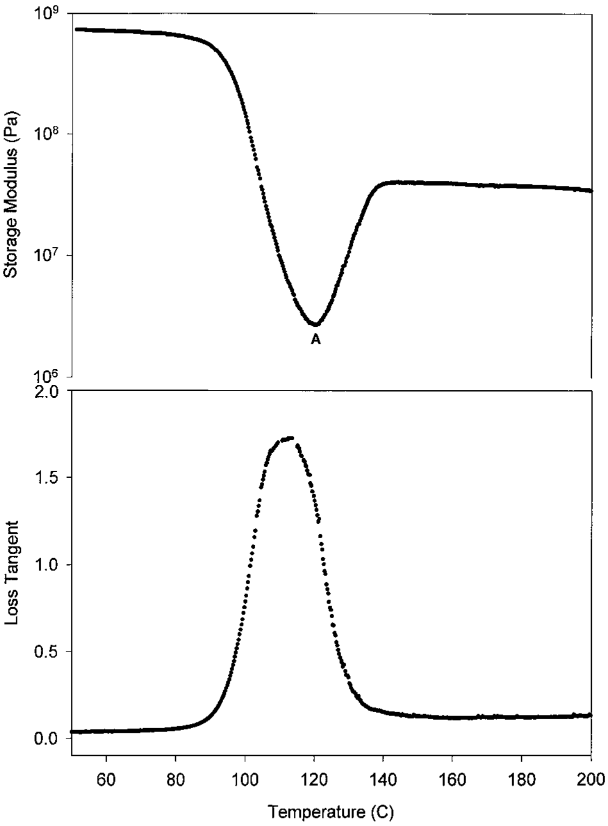

Figure 9 Temperature dependent dynamic mechanical properties for a quenched sample. The crystallization process starts near 120°C, and is completed near 140°C.

3.4. Mechanical properties

The state of molecular packing is expected to affect the mechanical properties. Dynamic mechanical thermal analysis confirms the major features of the positron results. Fig. 9 shows the storage modulus and associated loss tangent measured for a quenched sample. The rate of heating is 2°C/minute, which is faster than the positron scans. The specimens are thicker than are the DSC specimens, which results in a larger thermal lag and a shift of the apparent glass transition to higher temperatures. For atactic polystyrene, the modulus decreases continuously and rapidly as the temperature rises above T_g, whereas the crystallization of sPS shown here causes the rise in modulus, followed by a region of constant modulus even as the temperature rises. The free volume decrease manifested clearly in the positron results (Fig. 4) in the region $T < T_g$ does not affect the average modulus of the material, and is not evident in the loss tangent.

Recent work by St Lawrence *et al.* [1] shows that the crystallized sPS can be modelled micromechanically as a two phase solid, in which the amorphous fraction is microstructurally similar to the atactic form. At $T > T_g$ the amorphous fraction has an apparent modulus much higher than expected due to a mechanical constraint imposed by the lamellae which surround the amorphous phase. The change in free volume observed with positrons may be the microstructural manifestation of this mechanical constraint in the region $T > T_g$. The slope and magnitude of the S-parameter at temperatures above the crystallization temperature (Fig. 4) remains similar on both heating and cooling, suggesting the free volume changes occurring on heating are not reversible for irreversible phase transformations (crystallization of the metastable quenched state). This is consistent with the irreversible change in mechanical properties seen in Fig. 9: that is, the micromechanical constraint is dependent only on the continued mechanical properties of the constraining crystalline phase.

4. Conclusions

The crystallization of quenched syndiotactic polystyrene has been examined using doppler broadening positron annihilation spectroscopy, differential scanning calorimetry and dynamic mechanical thermal analysis. In the quenched state the material is in a metastable amorphous state. Heating above the glass transition temperature results in crystallization which appears as a discrete change in S-parameter in the positron experiments. The interpretation that the S-parameter as a measure of the free volume of the amorphous fraction is confirmed by correlating the positron data with the thermal and mechanical results. The decrease in S-parameter as the specimen is heated at $T < T_g$ is revealed in the DSC results as a small change in heat capacity. The relatively high modulus of the material at $T > T_g$ reported by St. Lawrence [1] is consistent with the positron results.

Acknowledgements

The financial support of NSERC, ESTAC and MMO is gratefully acknowledged. Syndiotactic polystyrene was provided by Michael Malanga of The Dow Chemical Company (Midland). The Polymer Laboratories DMTA was provided by Dow (Canada).

References

1. S. ST. LAWRENCE and D. M. SHINOZAKI, *J. of Mater. Sci.* **33** (1998) 4059.
2. N. ISHIHARA, T. SEIMIYA, M. KURAMOTO and M. UOI, *Macromolecules* **19** (1986) 2465.
3. L. C. LÒPEZ, R. C. CIESLINSKI, C. L. PUTZIG and R. D. WESSON, *Polymer* **36** (1995) 2331.
4. Y. ULCER, M. CAKMAK, J. MIAO and C. M. HSIUNG, *J. Appl. Polym. Sci.* **60** (1996) 669.
5. S. WU, R. A. BUBECK and C. J. CARRIERE, *ibid.* **62** (1996) 1483.
6. F. DE CANDIA, R. RUSSO and V. VITTORIA, *J. Polym. Sci., Part C: Poly. Letters* **28** (1990) 47.
7. F. DE CANDIA, G. ROMANO, R. RUSSO and V. VITTORIA, *Colloid & Polym. Sci.* **268** (1990) 720.
8. V. VITTORIA, A. RUVOLO FILHO and F. DE CANDIA, *J. Macro. Sci., Phys.* B **29** (1990) 411.
9. E. J. C. KELLAR, C. GALIOTIS and E. H. ANDREWS, *Macromolecules* **29** (1996) 3515.
10. A. M. EVANS, E. J. C. KELLAR, J. KNOWLES, G. GALIOTIS, C. J. CARRIERE and E. H. ANDREWS, *Polym. Eng. and Sci.* **37** (1997) 153.
11. S. ST. LAWRENCE and D. M. SHINOZAKI, *ibid.* **37** (1997) 1825.
12. See numerous papers in "Positron Annihilation," in proceedings of the 12th International Conference ICPA-12, edited by W. Trifshauser, G. Kogel and P. Sperr (Trans Tech Publications, 2001).
13. U. MYLER, X. L. XU, M. R. COLEMAN and P. J. SIMPSON, *J. Polymer Sci.* B **36** (1998) 2413.
14. G. GUERRA, V. VITAGLANAO, C. DE ROSA, V. PETRACCONE and P. CORRADINI, *Macromolecules* **23** (1990) 1539.
15. GREIS, Y. XU, T. ASANO and J. PETERMANN, *Acta Polymer* **45** (1994) 294.
16. A. J. PASZTOR, JR, B. G. LANDES and P. J. KARJALA, *Thermochimica Acta* **177** (1991) 187.
17. S. ST. LAWRENCE, PhD thesis, University of Western Ontario, London, Canada, 1997.
18. C. DEROSA, M. RAPACCIUOLO, G. GUERRA, V. PETRACCONE and P. CORRADINI, *Polymer* **33** (1992) 1423.
19. J. ARNAUTS and H. BERGHMANS, *Polymer Communications* **31** (1990) 343.
20. S. ST. LAWRENCE and D. M. SHINOZAKI, *Polym. Engin. Sci.* **37** (1997) 1825.

Received 13 September 2001
and accepted 2 October 2002