Matter Meets Anti-Matter

Probing Polymers with Positrons

The University of Michigan
Positron Group

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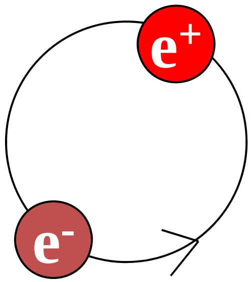
Why Positrons?

- Positron Annihilation Lifetime Spectroscopy (PALS) uses Positrons (e^+) as probes to investigate materials

- When injected, e^+ forms Positronium (Ps), finds vacancies in the material, and annihilates with a lifetime corresponding to the size of the vacancies.

- PALS is very sensitive to the “free volume” in a material

Positronium, Ps (Z=1, A=0)



Ps is its own anti-atom !

Hydrogen-like bound state

½ Rydberg (6.8 eV) binding energy

Spin singlet, S=0 (para-positronium): 1/8 ns lifetime, 2 γ rays

Spin triplet, S=1 (ortho-positronium): 142 ns lifetime, 3 γ rays

Positronium forms naturally in materials and ortho-Ps will be our probe

Radioactive ^{22}Na Decay

^{22}Na decays in (essentially) two ways

- Beta decay (90% of decays):

$$^{22}\text{Na} \rightarrow {}^{22}\text{Ne}^* + e^+ + \nu$$

$$^{22}\text{Ne}^* \rightarrow {}^{22}\text{Ne} + \gamma_{(1.275\ \text{MeV})}$$

- Electron capture (10% of decays):

$$^{22}\text{Na} + e\text{-} \rightarrow {}^{22}\text{Ne}^* + \nu$$

$$^{22}\text{Ne}^* \rightarrow {}^{22}\text{Ne} + \gamma_{(1.275\ \text{MeV})}$$

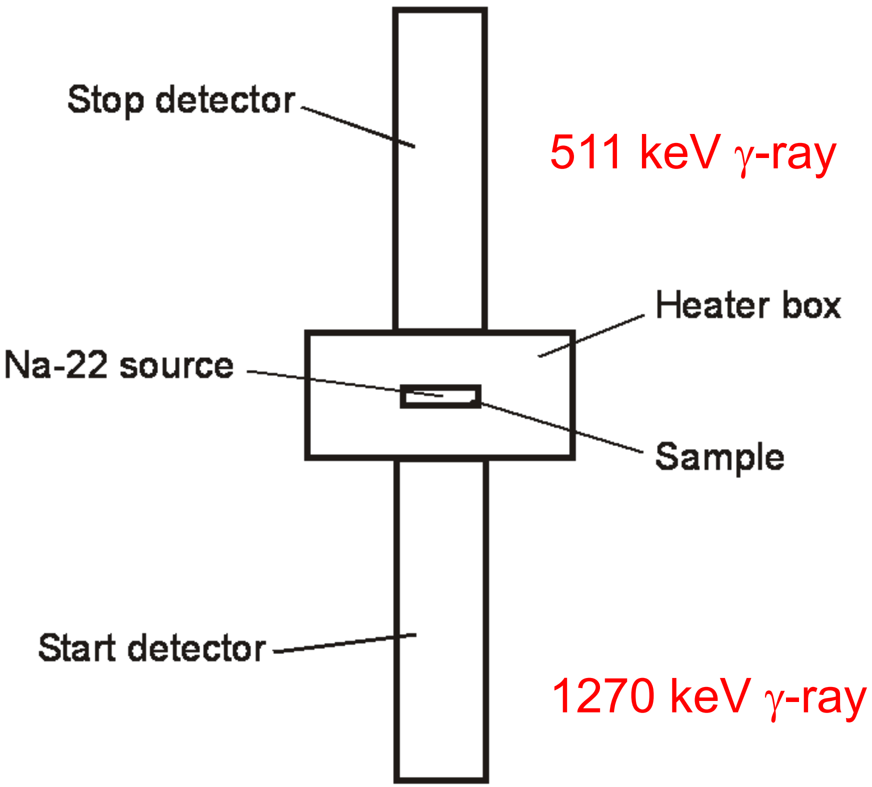
Beta Decay in ^{22}Na

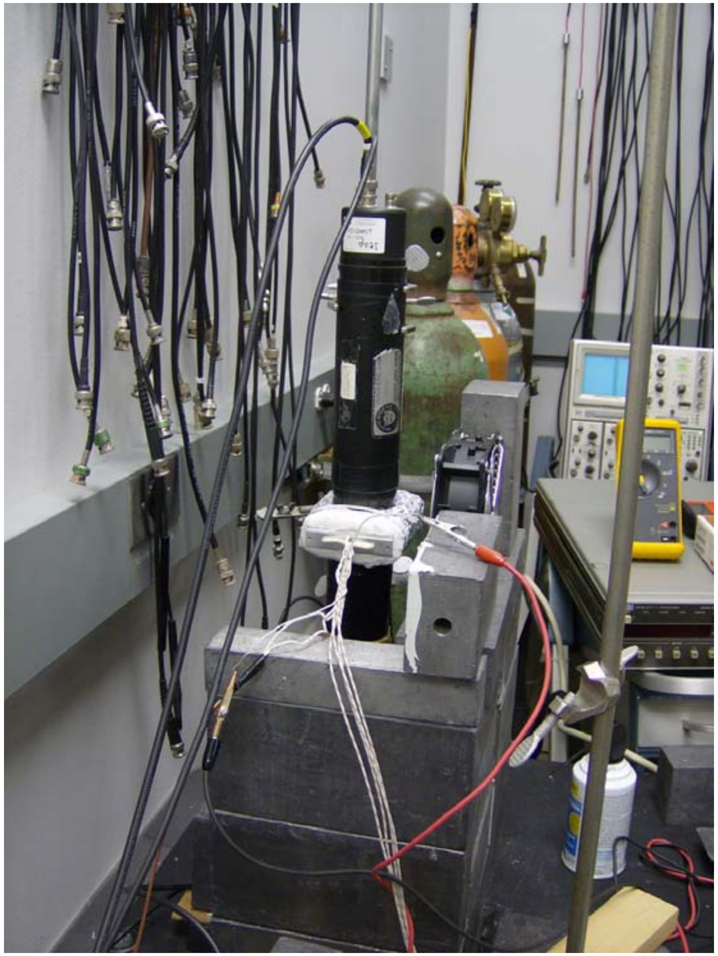
- β+ decay involves the following process:

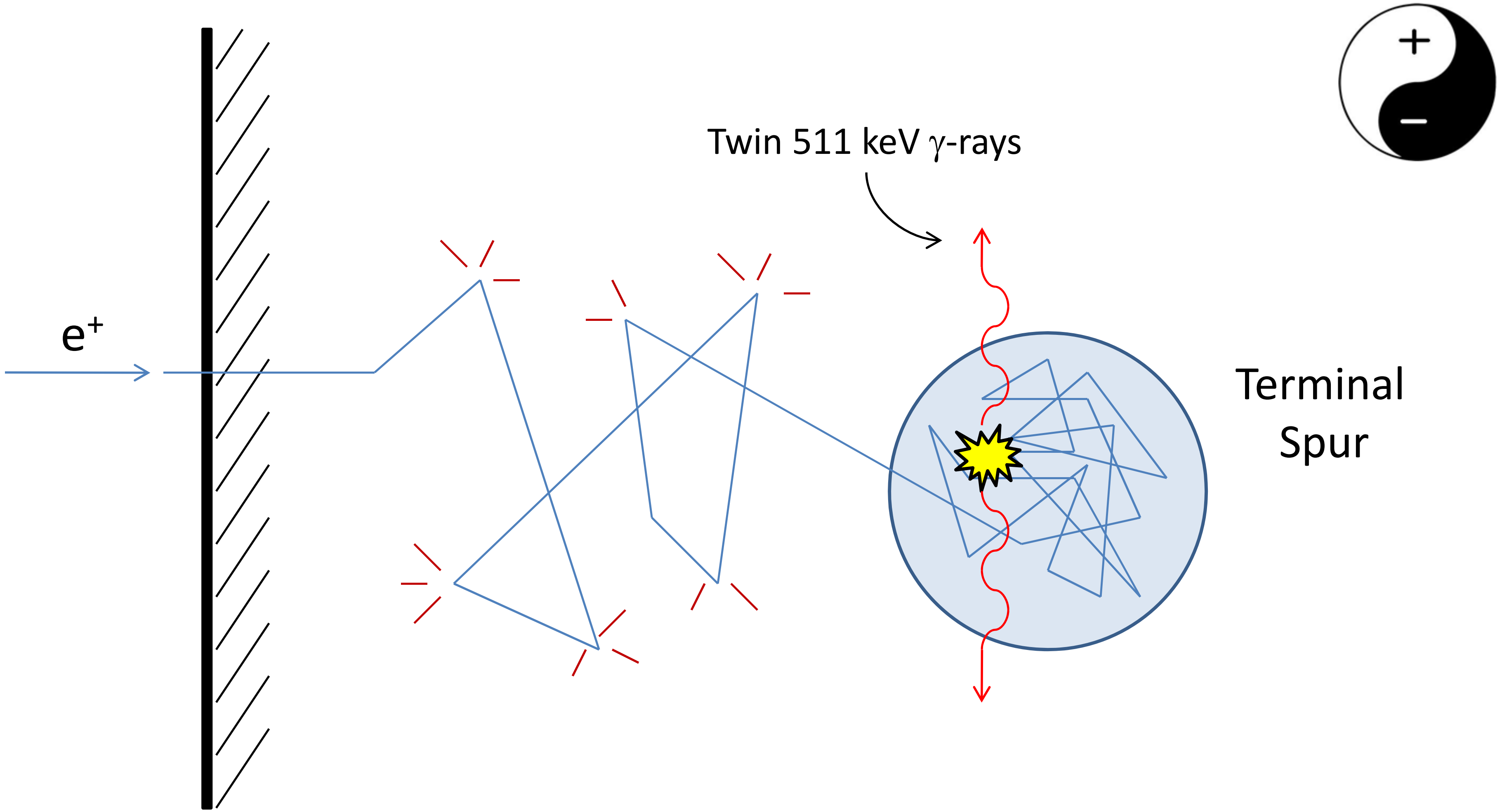
$$p^+ \rightarrow n^0 + e^+ + \nu$$

- The emitted e^+ have an energy distribution ranging from 0 - 0.54 MeV, with a peak in the distribution at 0.19 MeV
- Penetration of ~1mm in polymers.

Bulk PALS (Positronium Annihilation Lifetime Spectroscopy)



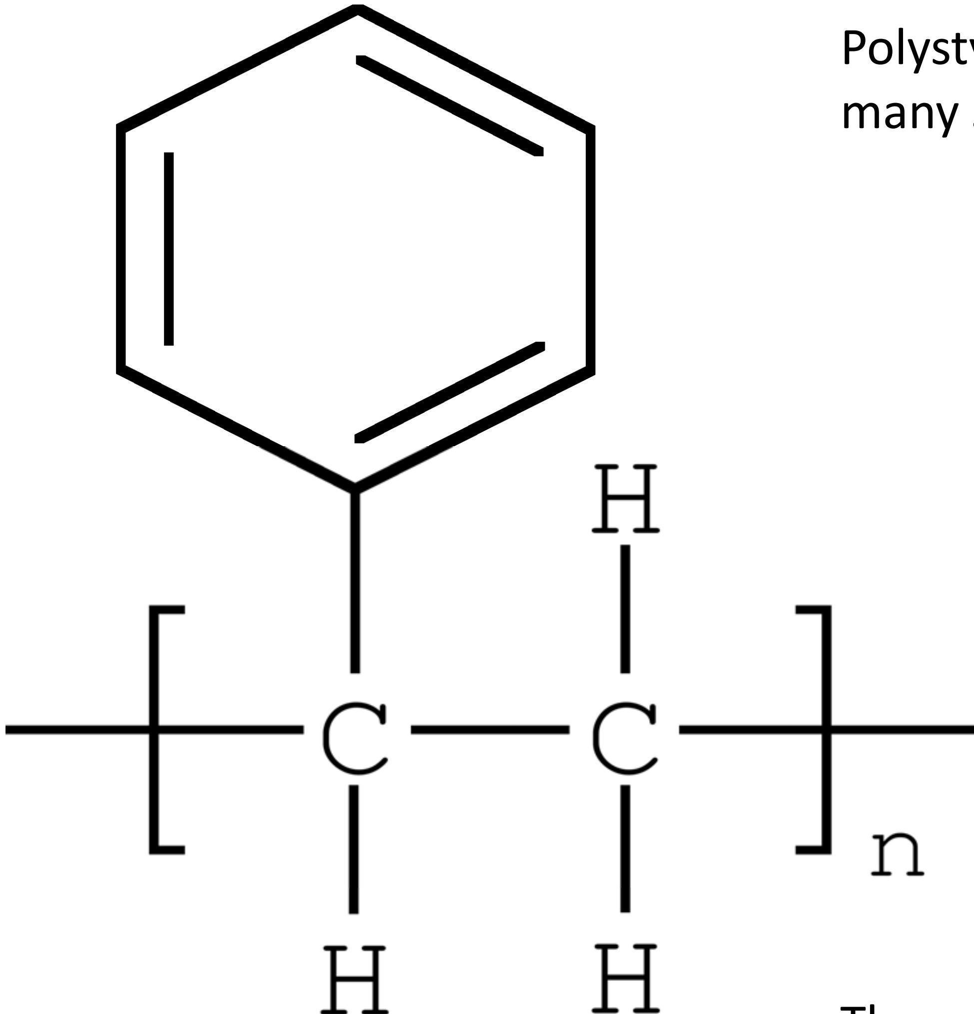




Positron behavior in a solid

The ‘hot’ (~200keV) positrons bounce around, ionizing atoms in the material. With each collision, they lose energy. After ~10^4 collisions, they have thermalized (KE ~1eV) and can form Ps.

Polystyrene is made by linking many styrene subunits together.



One Styrene Subunit

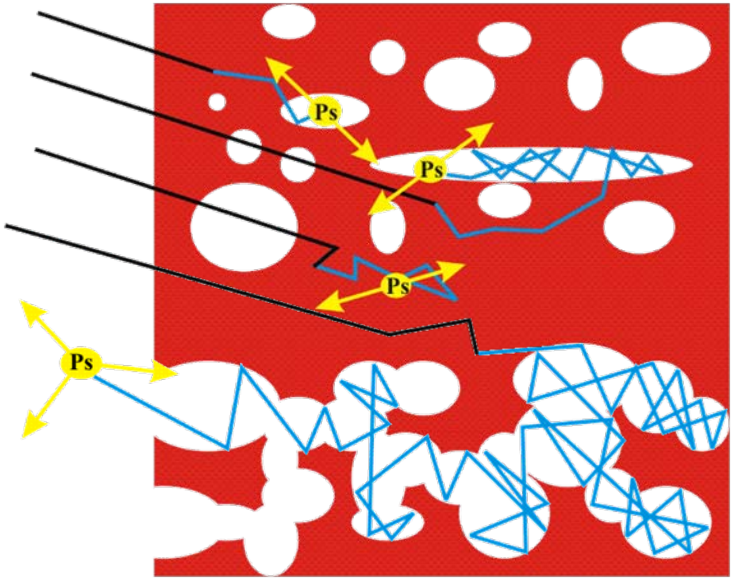
One styrene subunit has a molecular weight (M_w) of 104.

152k M_w PS, for example, is a chain of styrene groups approximately 1,460 units long!

These long chains fold around each other like a bowl of spaghetti noodles. The spaces left between noodles are the voids we probe using PALS!

Image from http://www.ciencias.ies-bezmiliana.org

Ps Formation in Nanoporous Materials

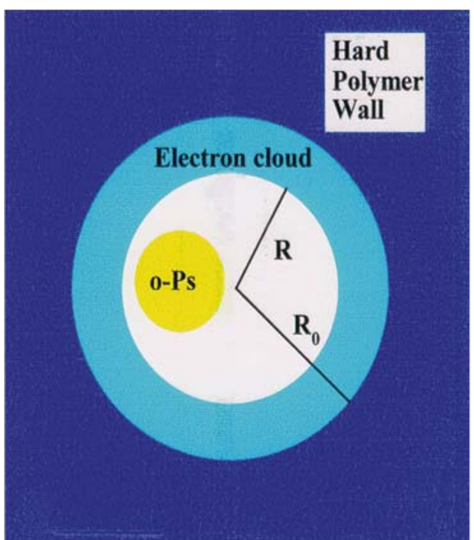


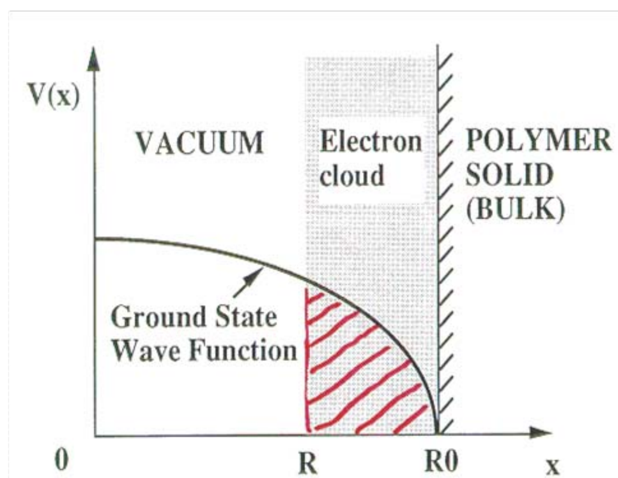
Thermalized e^+ in a nanoporous material either:

1. annihilates directly with e-
2. forms para-Ps (lifetime ~125 ps)
3. forms ortho-Ps (lifetime ~142 ns)

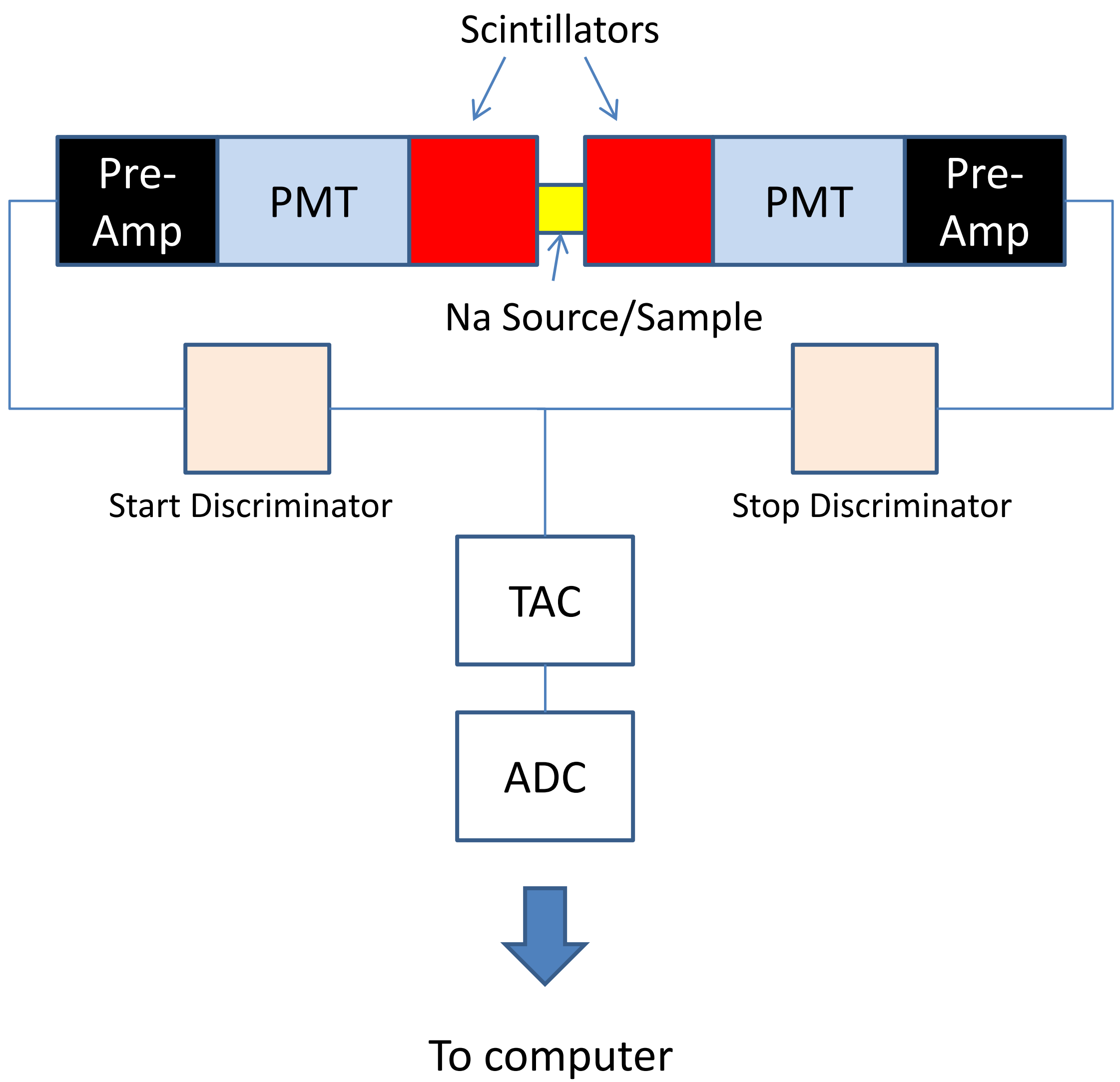
Ortho-Ps tends to find nanopores in the material (due to dielectric response of the medium)

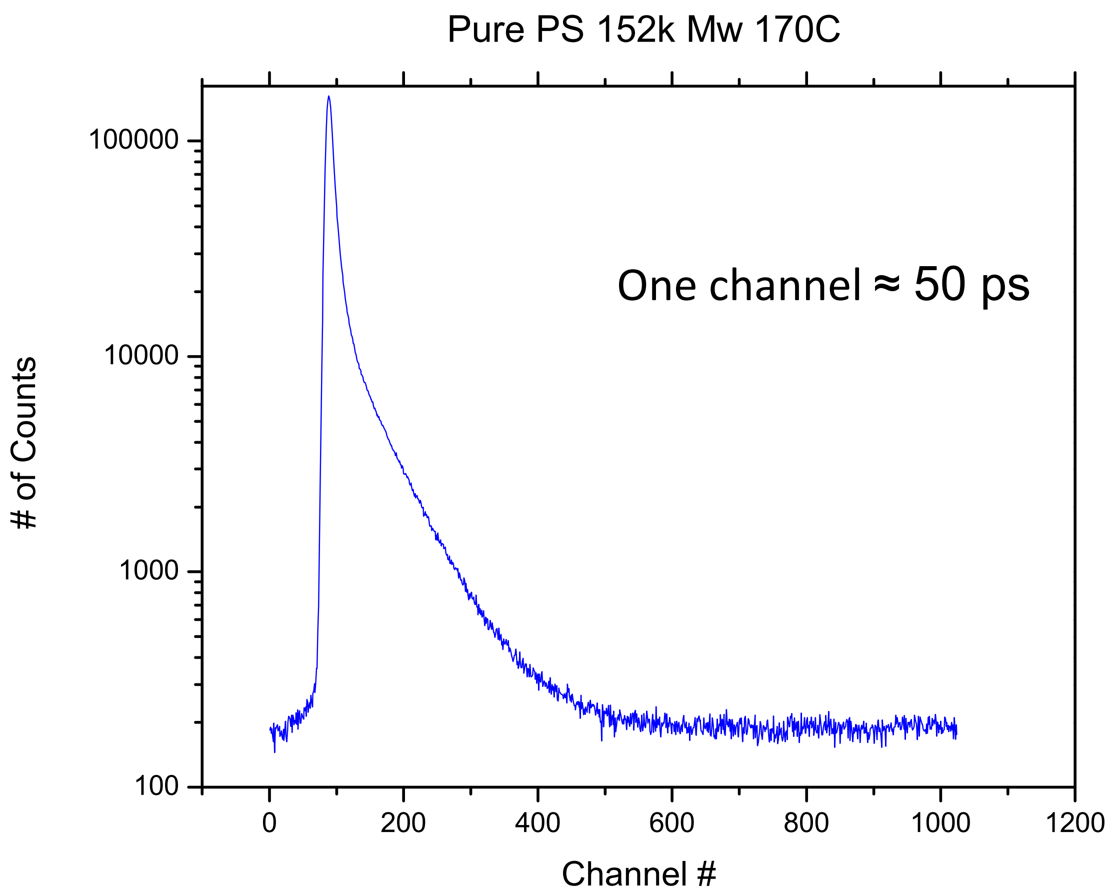
The lifetime of o-Ps is reduced by interaction with the electrons 'spilling' into the void from its Walls (from 142ns in vacuum to ~1ns in voids)





Data Taking Apparatus

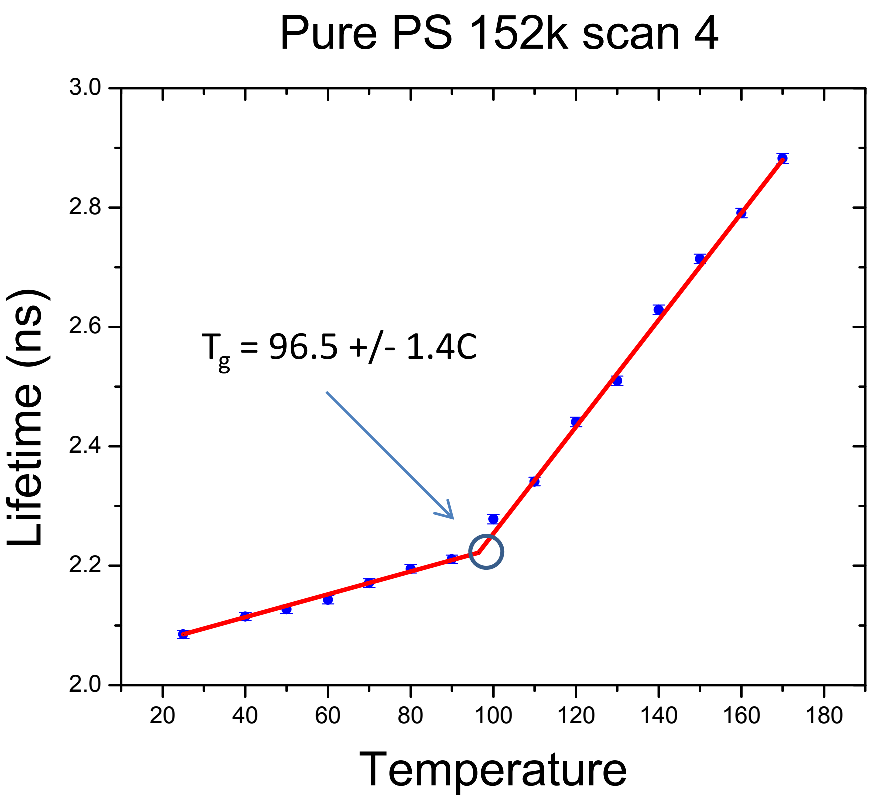


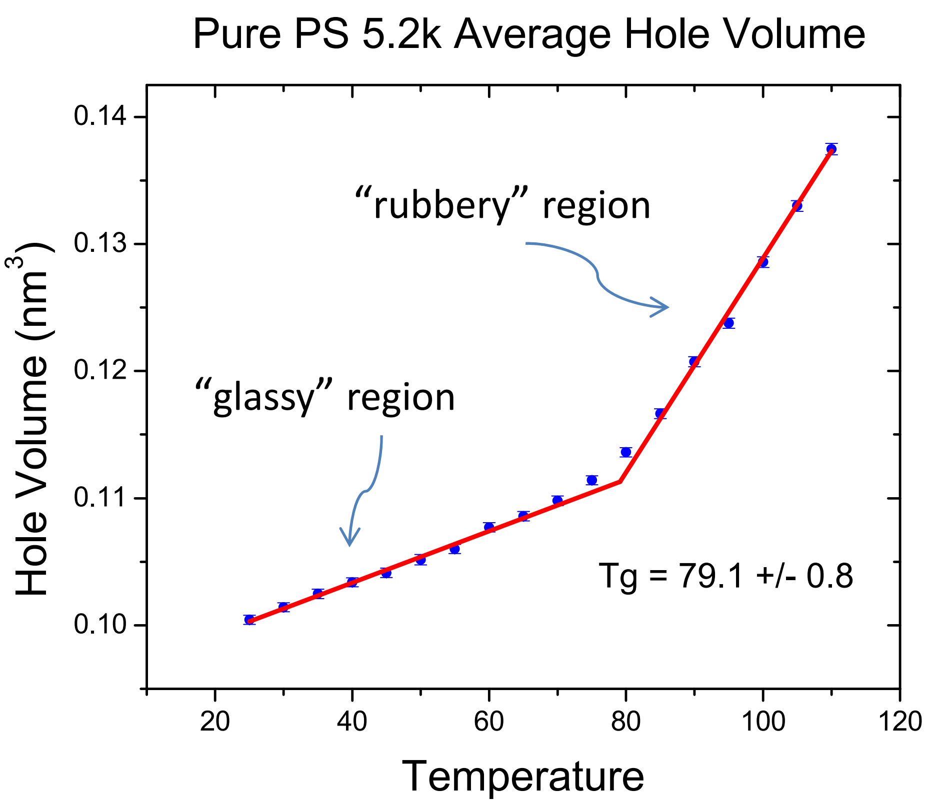


A typical spectrum

Time t = 0 corresponds to the 'prompt peak.' The offset is to allow the full spectrum to appear on the graph. The y-axis is a log-scale, so the straight portions of the spectrum indicate exponential decays. Each slope corresponds to a lifetime that we determine by fitting.

Glass Transition of a Polymer

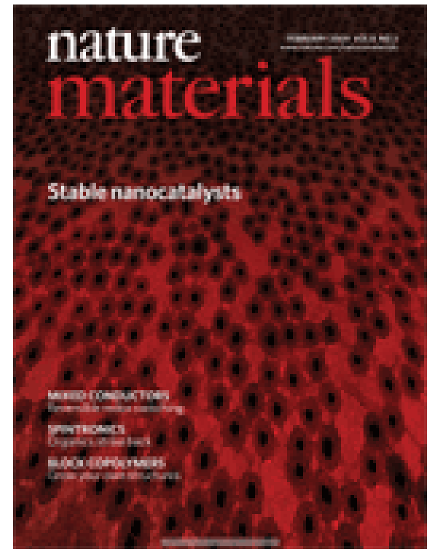




T_g is determined by finding the intersection of the fitted lines in each region

Materials Science Research

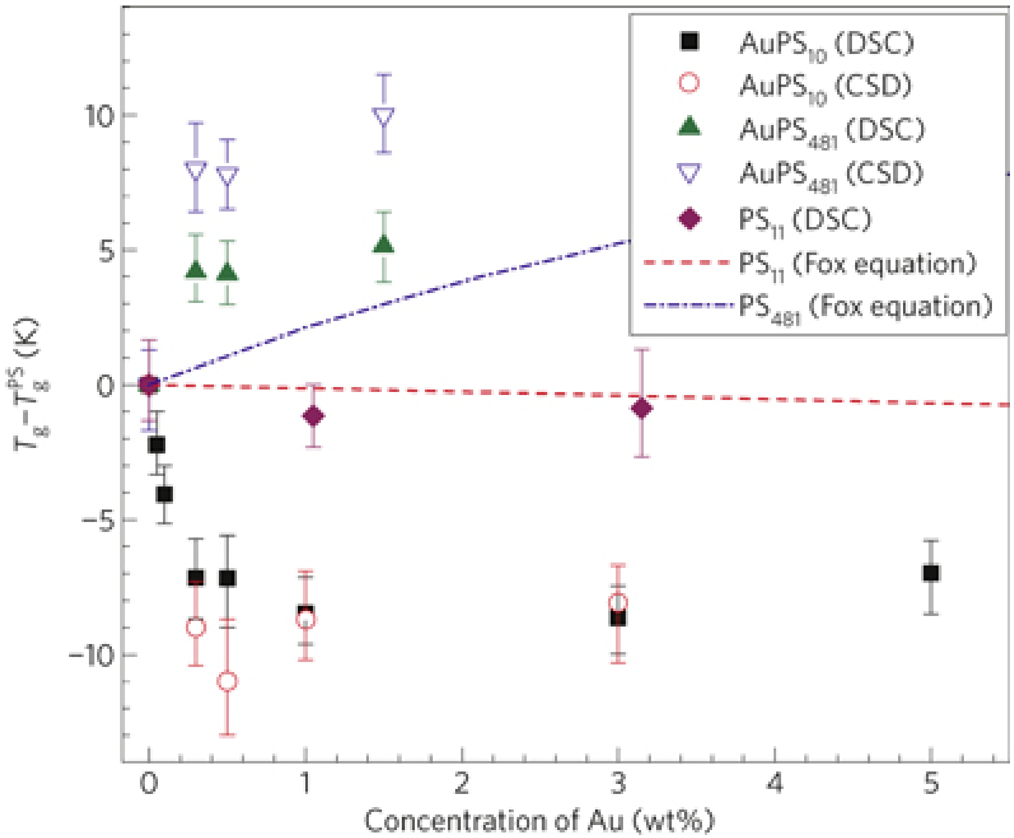
- Peter Green and Hyunjoon Oh reported in *Nature Materials* that the addition of gold nanoparticles (to which PS chains of varying lengths were grafted) to pure 5.2k M_w PS caused significant changes in glass transition.
- Grafted chains were 481 and 10 subunits long



Green, P. Oh, H.
"Polymer chain dynamics
and glass transition in athermal
polymer/nanoparticle mixtures."
Nature Materials 8, 139 – 143 (2009)

Gold Polymer Nanocomposites

- $AuPS_{10}$ nanoparticles increase the free volume, lowering T_g by ~ 7 ^oC
- $AuPS_{481}$ nanoparticles reduce free volume, raising T_g by ~ 5 ^oC
- Green et al. used DSC and CSD to measure T_g. These methods are less sensitive to free volume than PALS
- They asked our group to measure T_g using PALS

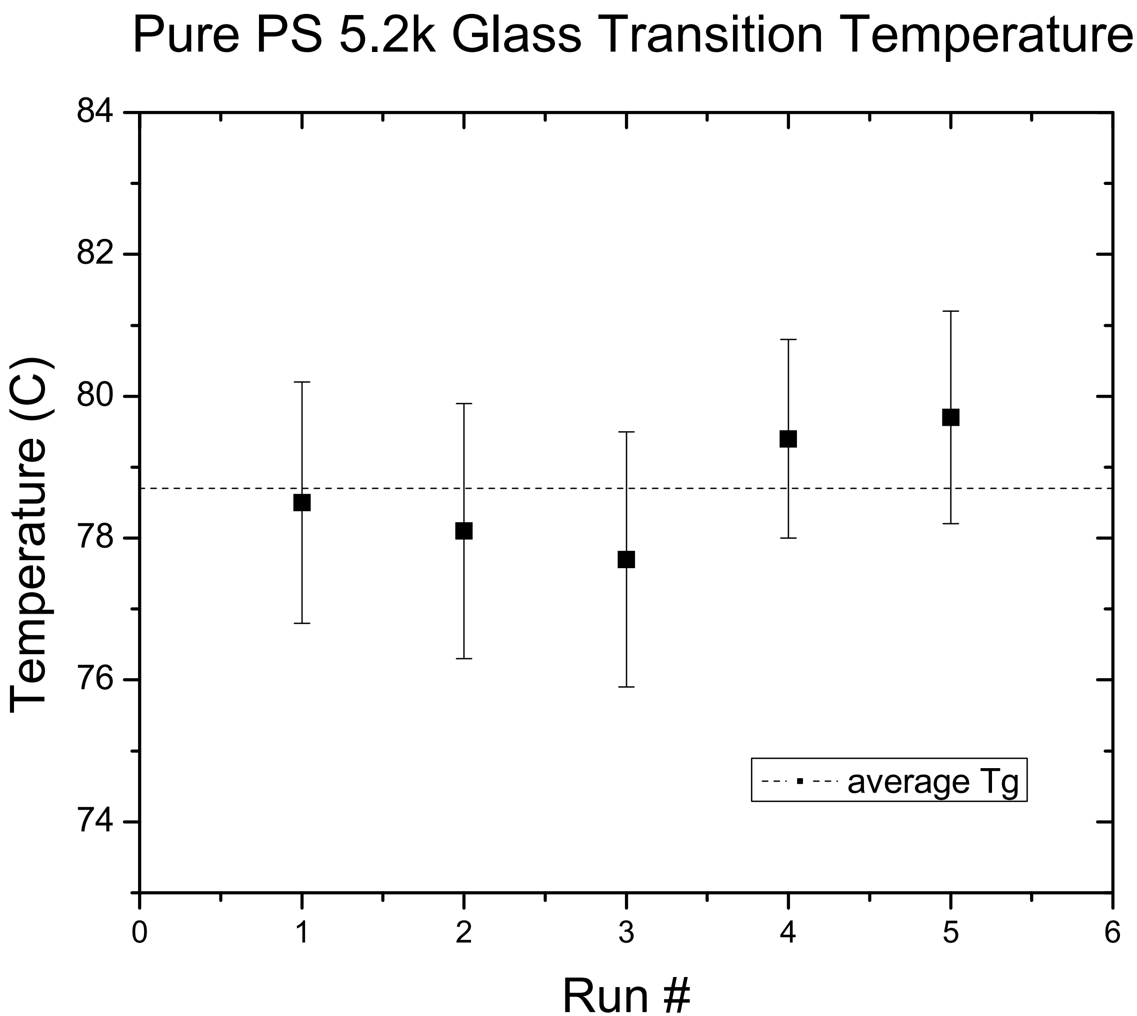


Green, P. Oh, H. "Polymer chain dynamics and glass transition in athermal polymer/nanoparticle mixtures." *Nature Materials* 8, 139 – 143 (2009)

Pure Polystyrene Matrix

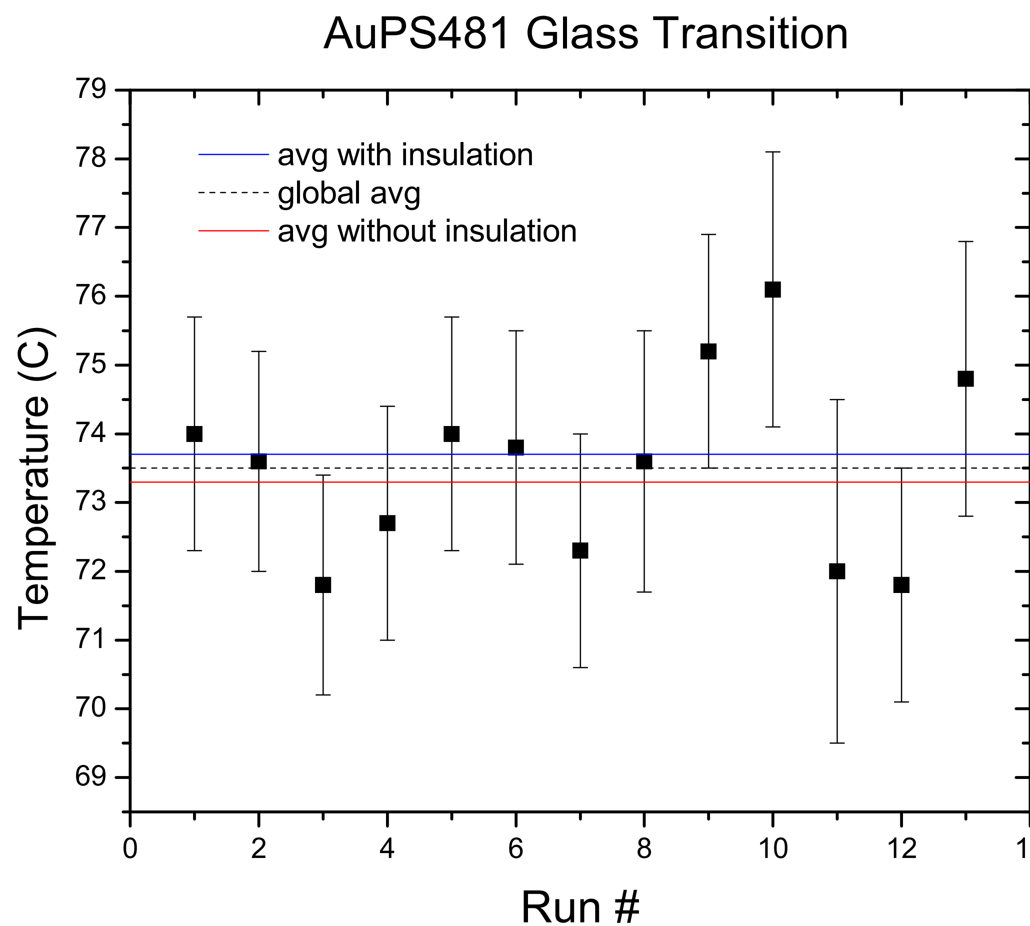
- The matrix into which the $AuPS_{10}$ and $AuPS_{481}$ nanoparticles were added is pure 5.2k PS (N = 50).
- We analyzed pure 5.2k PS using PALS and deduced a glass transition of 78.7

T_g = 78.7 ± 0.8 ^oC

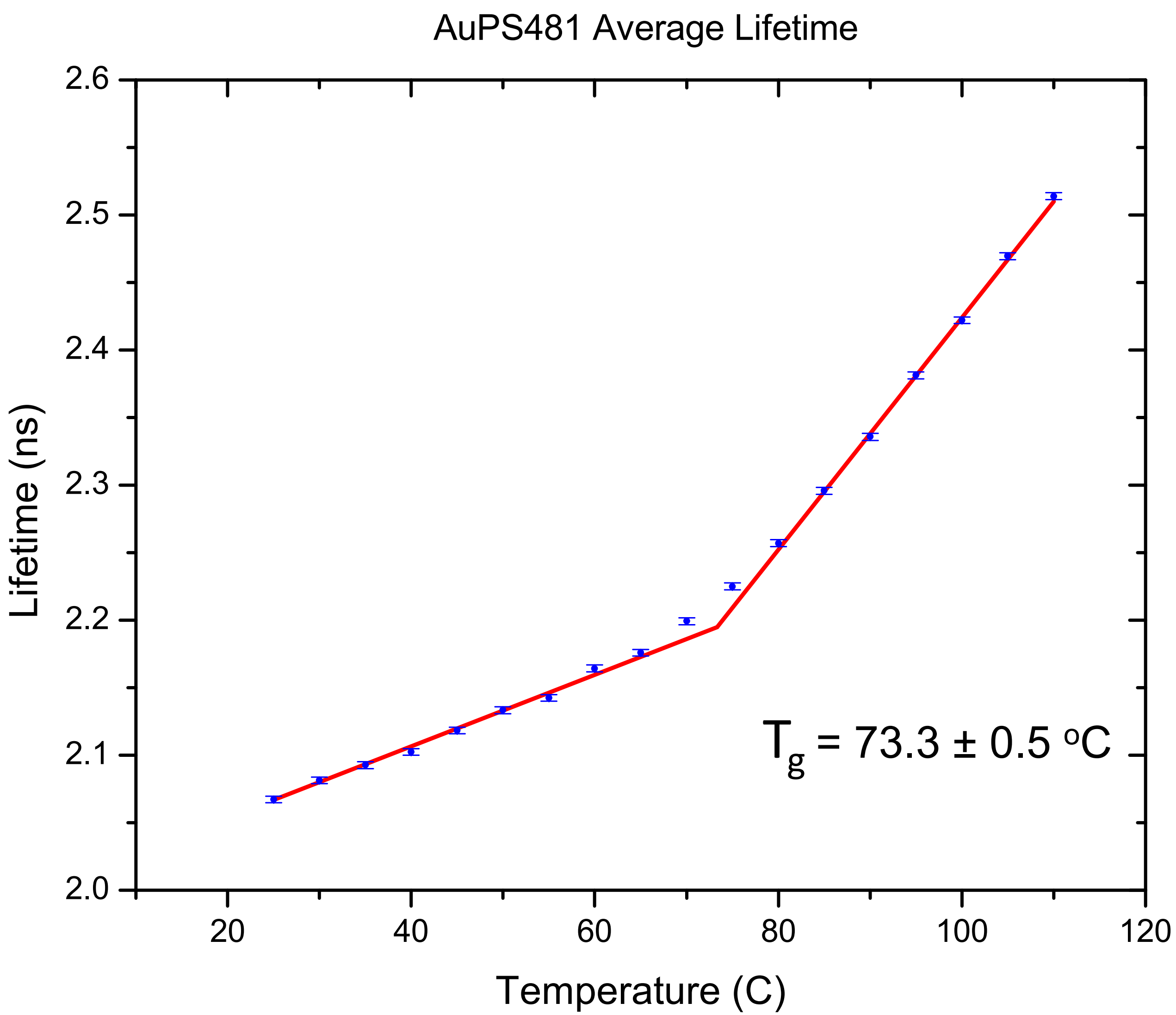


Our Results – $AuPS_{481}$ Glass Transition

- We deduced an T_g of 73.5 ± 0.5 °C. This represents a ΔT_g of ~ -5 °C.
- For $AuPS_{481}$ Peter Green et al. predicted a ΔT_g of ~ +5 °C!



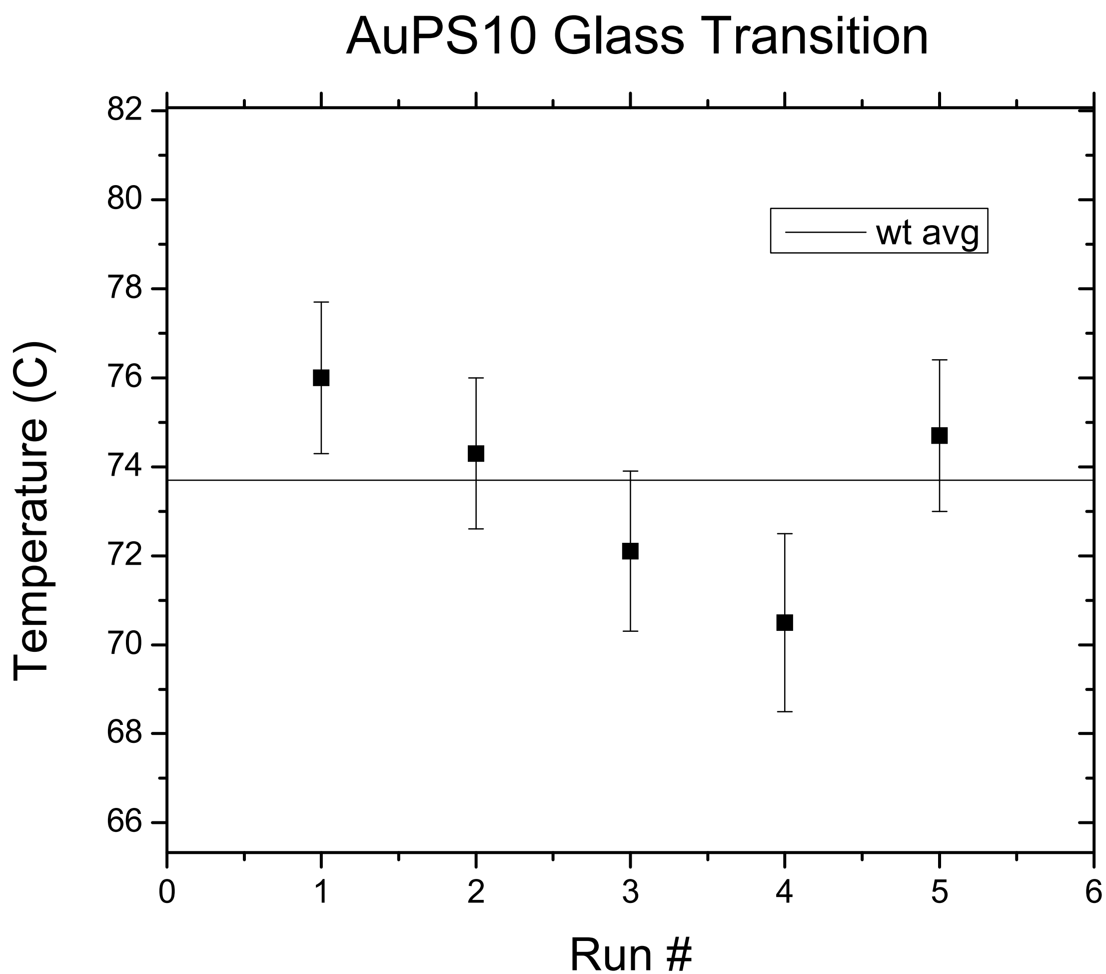
Fitted T_g Using Averaged Lifetime



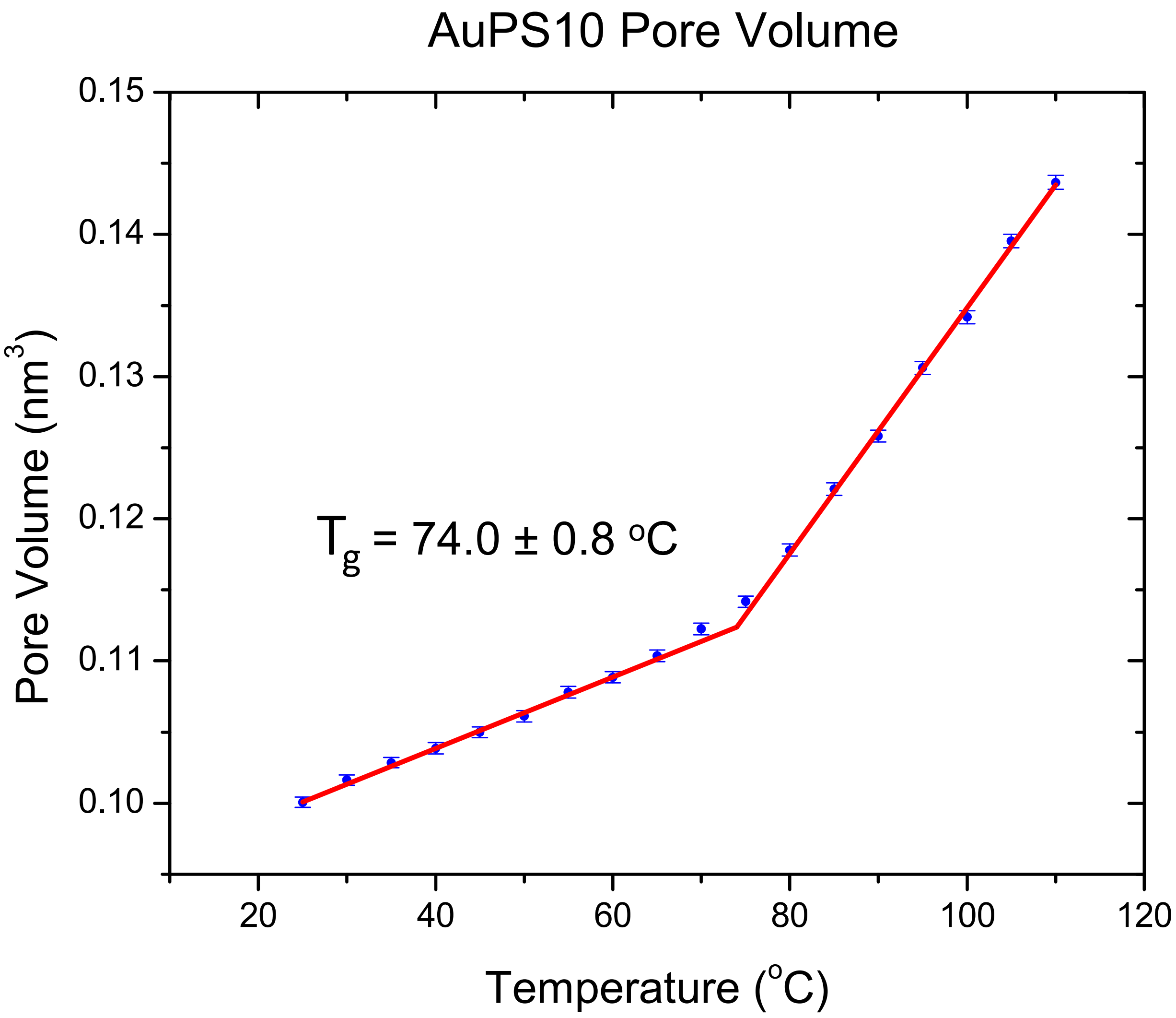
Our Results – $AuPS_{10}$ Glass Transition

- We analyzed pure 5.2k PS matrix (chains with 50 subunits) with gold nanoparticles whose attached PS chains were only 10 subunits long.
- We deduced a glass transition of 73.7 ± 0.8 ^{o}C.

T_g = 73.7 ± 0.8 ^{o}C



Fitted T_g Using Pore Volume



Conclusion: ΔT_g

$AuPS_{10}$

- For $AuPS_{10}$, we measured: $\Delta T_g \approx -5\ ^oC$.
- Our colleagues in Materials Science reported, using DCS and CSD: $\Delta T_g \approx -7\ ^oC$
- Our research confirms their result

$AuPS_{481}$

- For $AuPS_{481}$, we measured: $\Delta T_g \approx -5\ ^oC$.
- Our colleagues reported: $\Delta T_g \approx +5\ ^oC$ - a discrepancy of 10 ^oC!
- We are currently confirming this result with a new $AuPS_{481}$ sample.
- Results should be in by Friday!

Acknowledgements

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&

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Paul Dirac – for predicting the existence of the positron

Arthur Rich Memorial
University of Michigan
Sculpture/photo: Jens Zorn

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