The local Free Volume in Polymers studied by Positron Annihilation Lifetime Spectroscopy (PALS)

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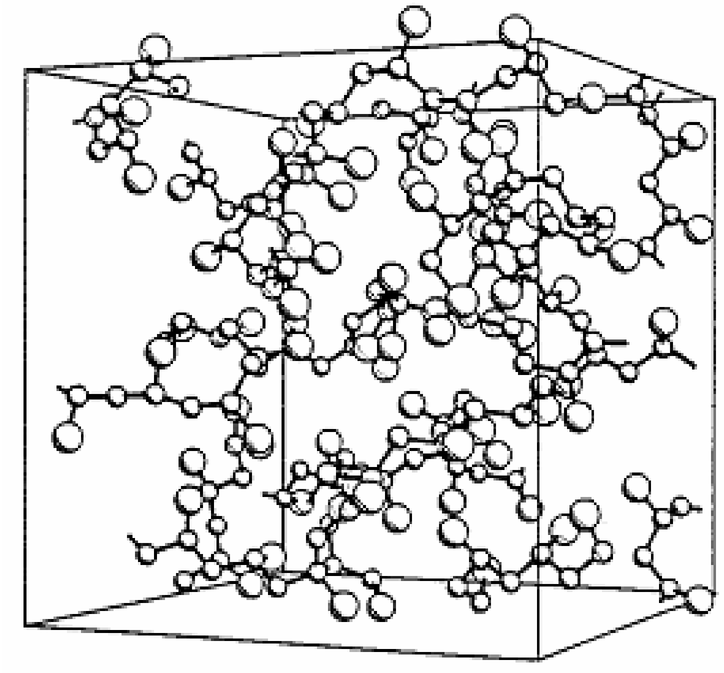
Structure of the free volume

- free volume due to structural, static or dynamic, disorder
- important for several macroscopic properties of these materials,
- viscosity, molecular transport, structural relaxation, and physical aging



Schematic representaion of a single Poly (Propylene) microstructure (X=76)

(Simulation, Theodoru et al. 1985)

Experimental Ways to determine Free Volume in Polymers

- **Positron Annihilation Lifetime Spectroscopy (PALS)**
  - Detection of subnanometric local free volumes (holes):
    Size distribution (mean hole volume $\langle \mathbf{v_h} \rangle$ and mean dispersion σ_h)

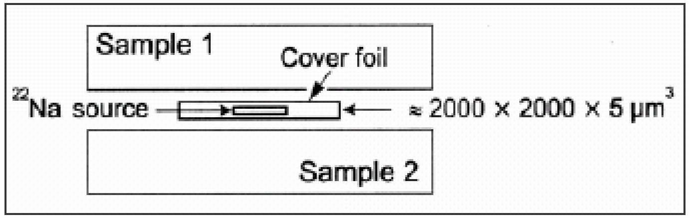
- **Pressure-Volume-Temperature-Experiments (PVT)**
  Analysis by Simha-Somcynsky lattice-hole model EOS
  - Fraction of vacancies **h**, specific hole free. $\mathbf{V_f = hV}$, and occupied volumes, $\mathbf{V_{occ} = (1-h)V}$

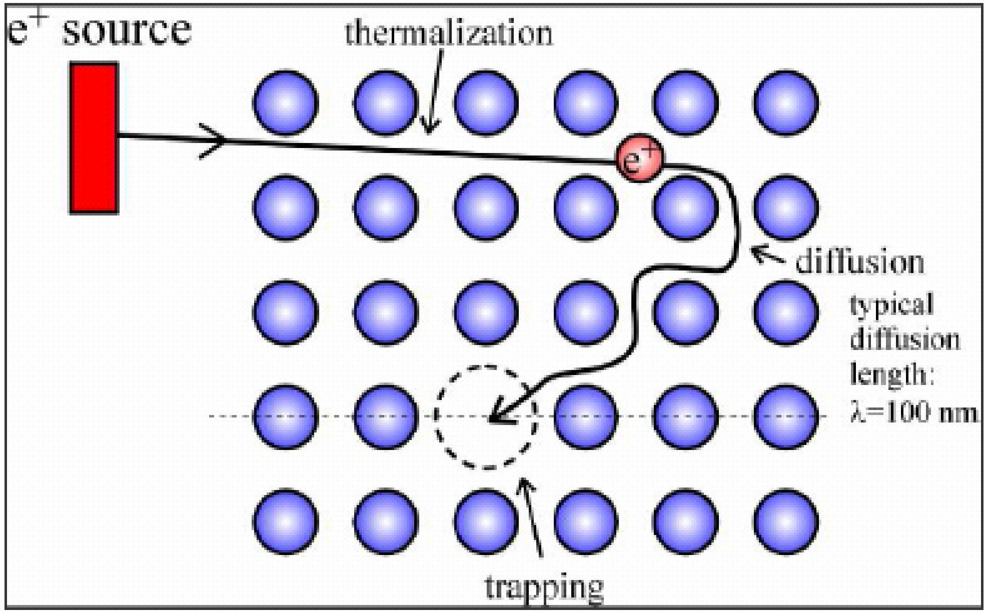
- **Correlation of PALS and PVT**
  - allows estimation of PALS hole density $\mathbf{V_f = N_h' \langle v_h \rangle}$

  →**All parameters of the structure of hole free volume can be obtained from PALS and PVT**

Basics of PALS

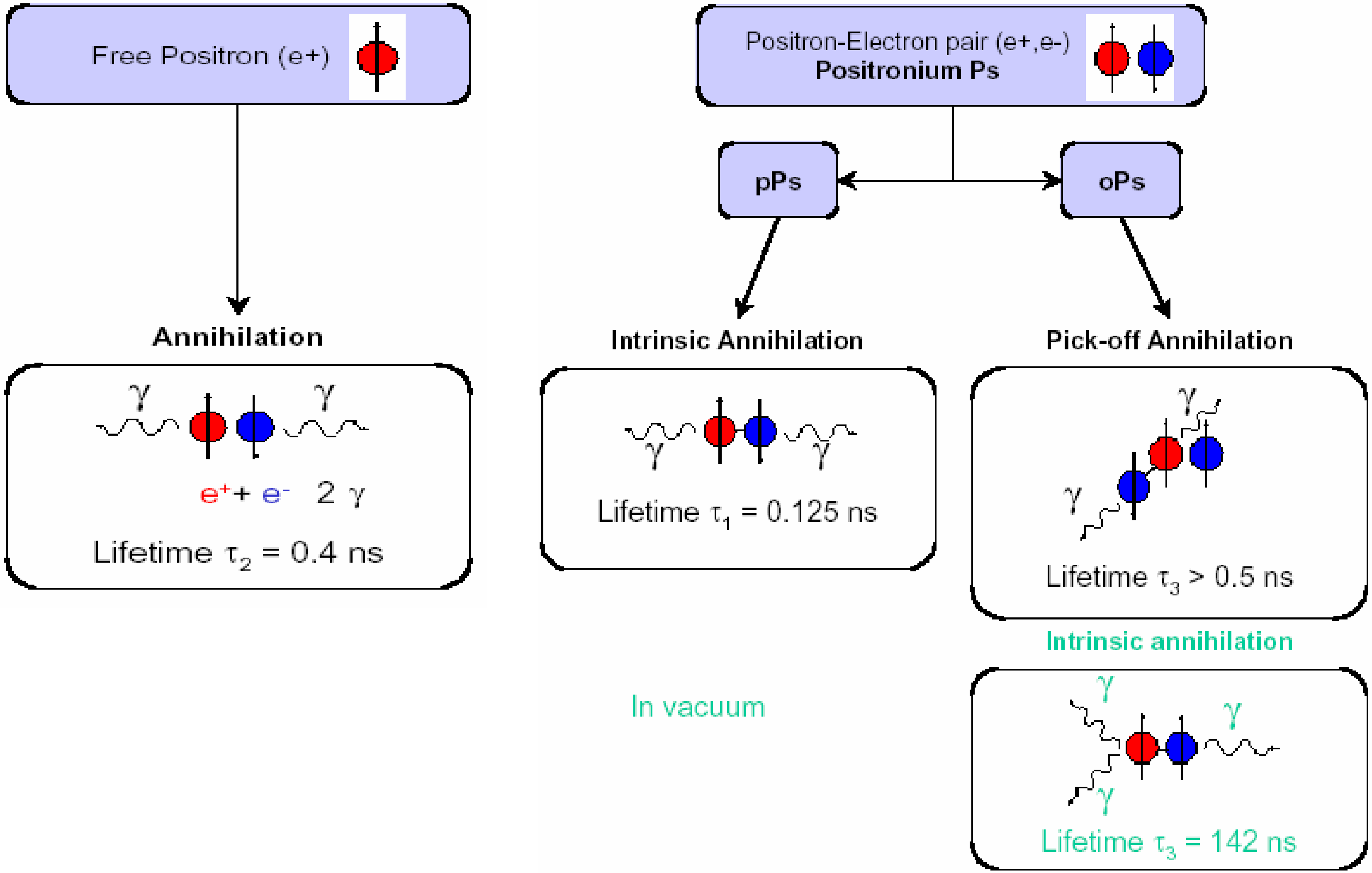
- β^+ decay: $^{22}Na \rightarrow {}^{22}Ne + \beta^+ + \nu_e + \gamma_{(1.27MeV)}$
  (half life: 2.6 years, up to 10^6 e^+/s)



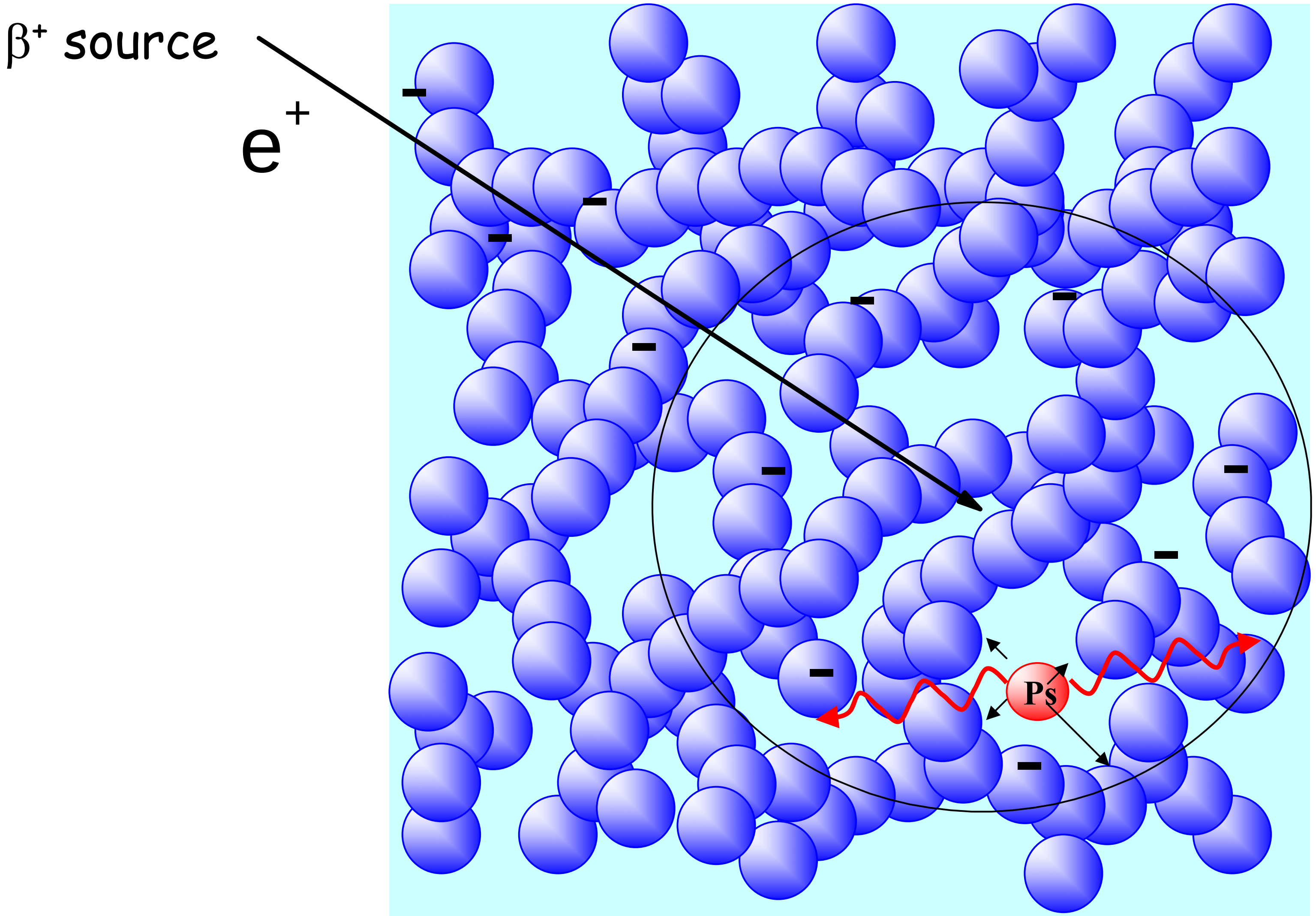


- Thermalization
- Diffusion
- Annihilation

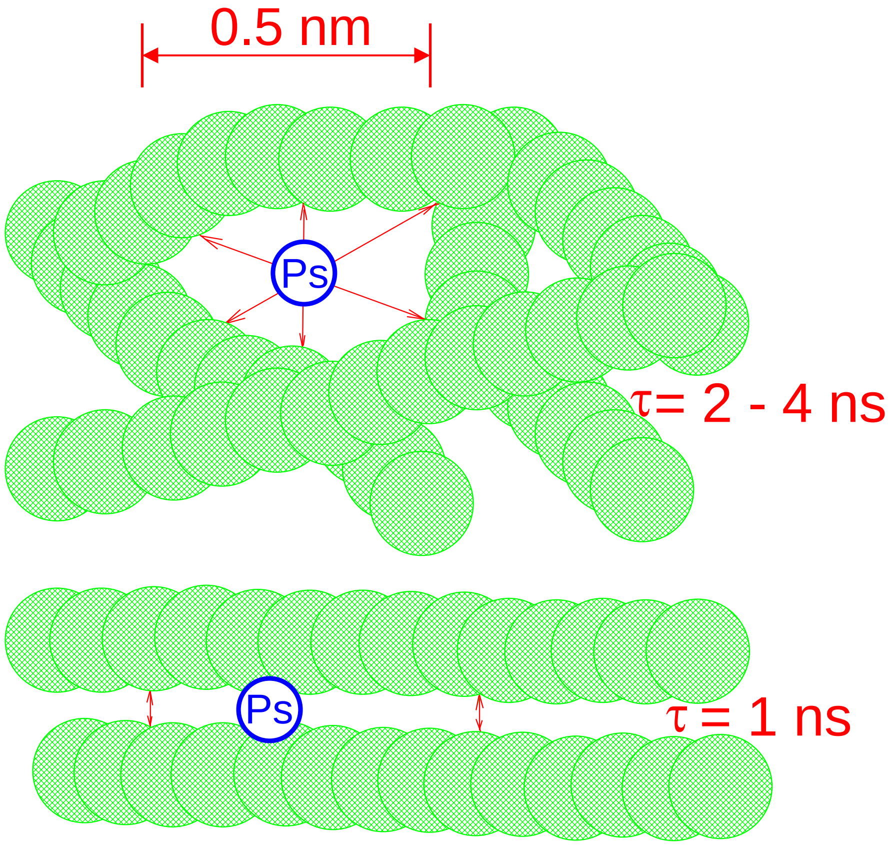
Basic Principles and Theories of Positron formation in Polymers



Ps Formation in Polymers



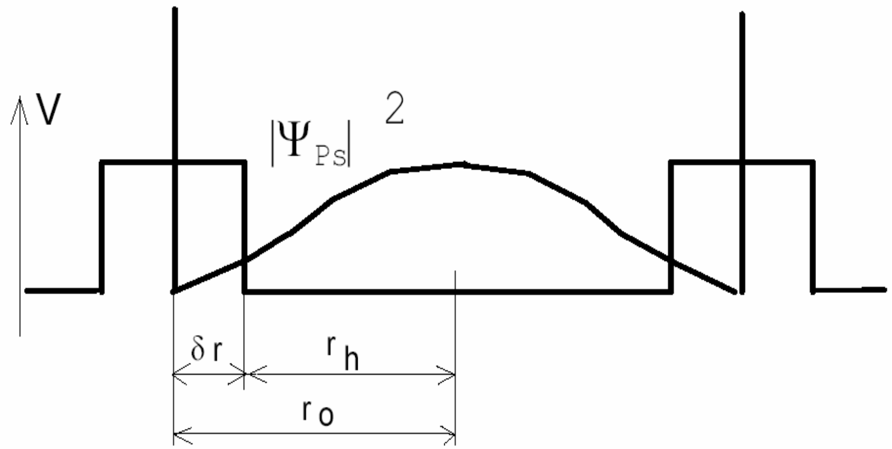
Pick-Off Annihilation



Ps localization in a hole of the (excess) free volume

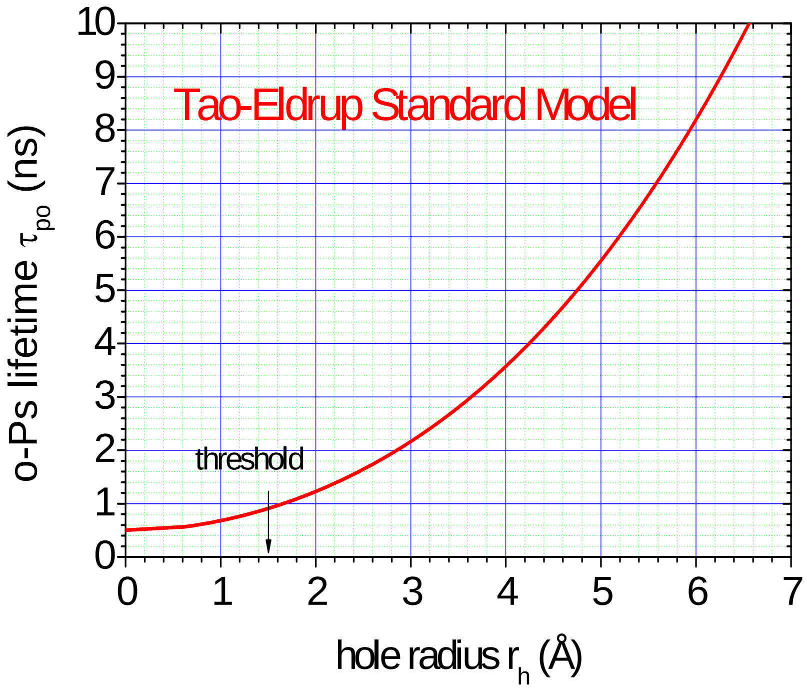
Ps localization in interstitial free volume gives the packing co-efficient ´C´ of the crystals

Theory of Tau-Eldrup (TE) Model



The height of the potential is infinity, and δr – empirical parameter δr = 0.166 nm

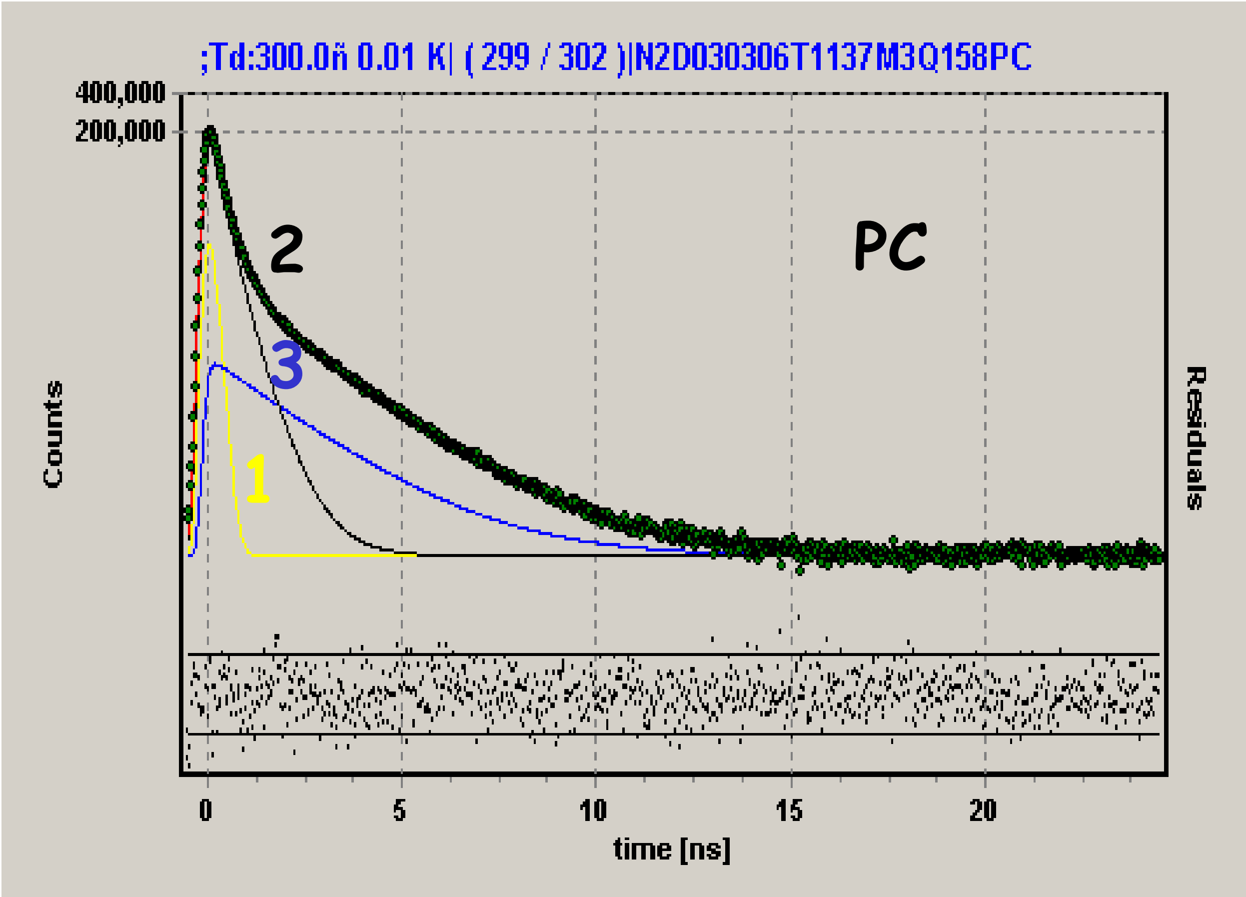
$$\tau_{o-Ps\ pickoff} = \frac{0.5ns}{\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi} Sin\left(\frac{2\pi r_h}{r_h + \delta r}\right)\right]}$$



mean hole volume

$$v_h(\tau_3) = (4/3)\pi r_h^3(\tau_3)$$

Typical PALS Spectrum



p-Ps

τ_1 = 0,125 ns

Free Annihilation

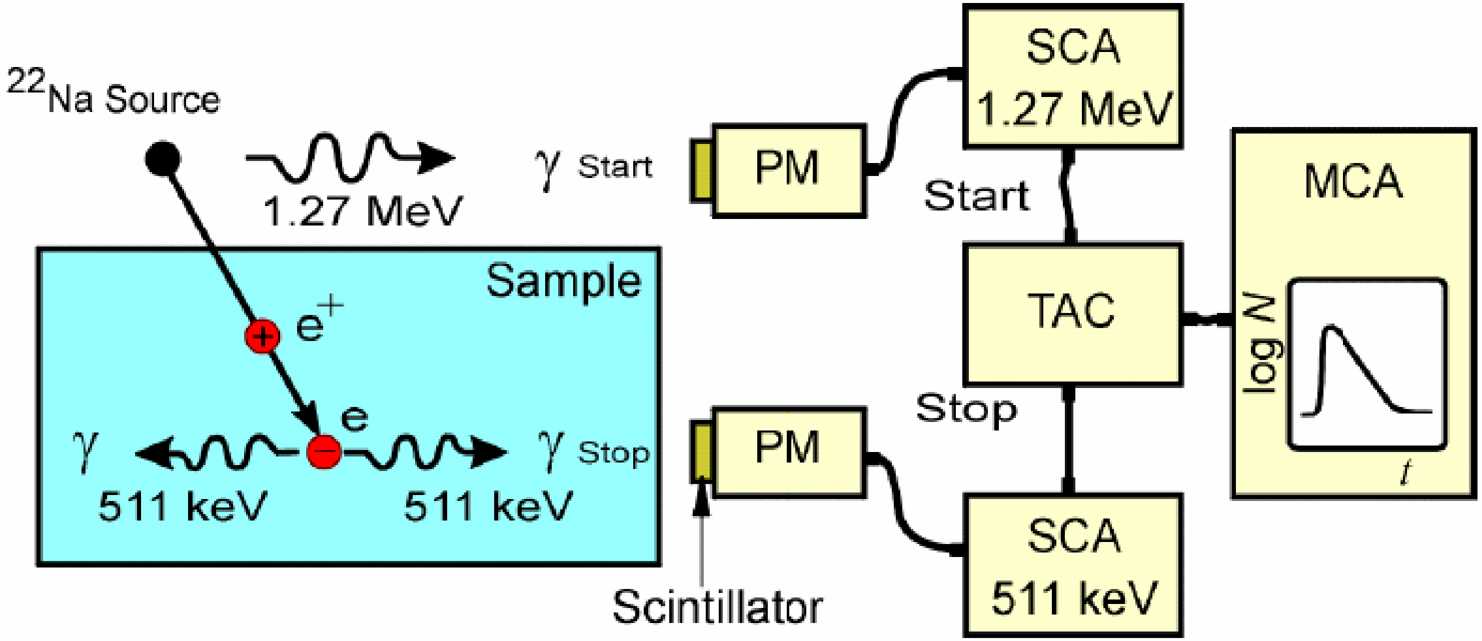
τ_2 = 0,4 ns

o-Ps (Pick-off annihilation)

τ_3 > 0,5 ns

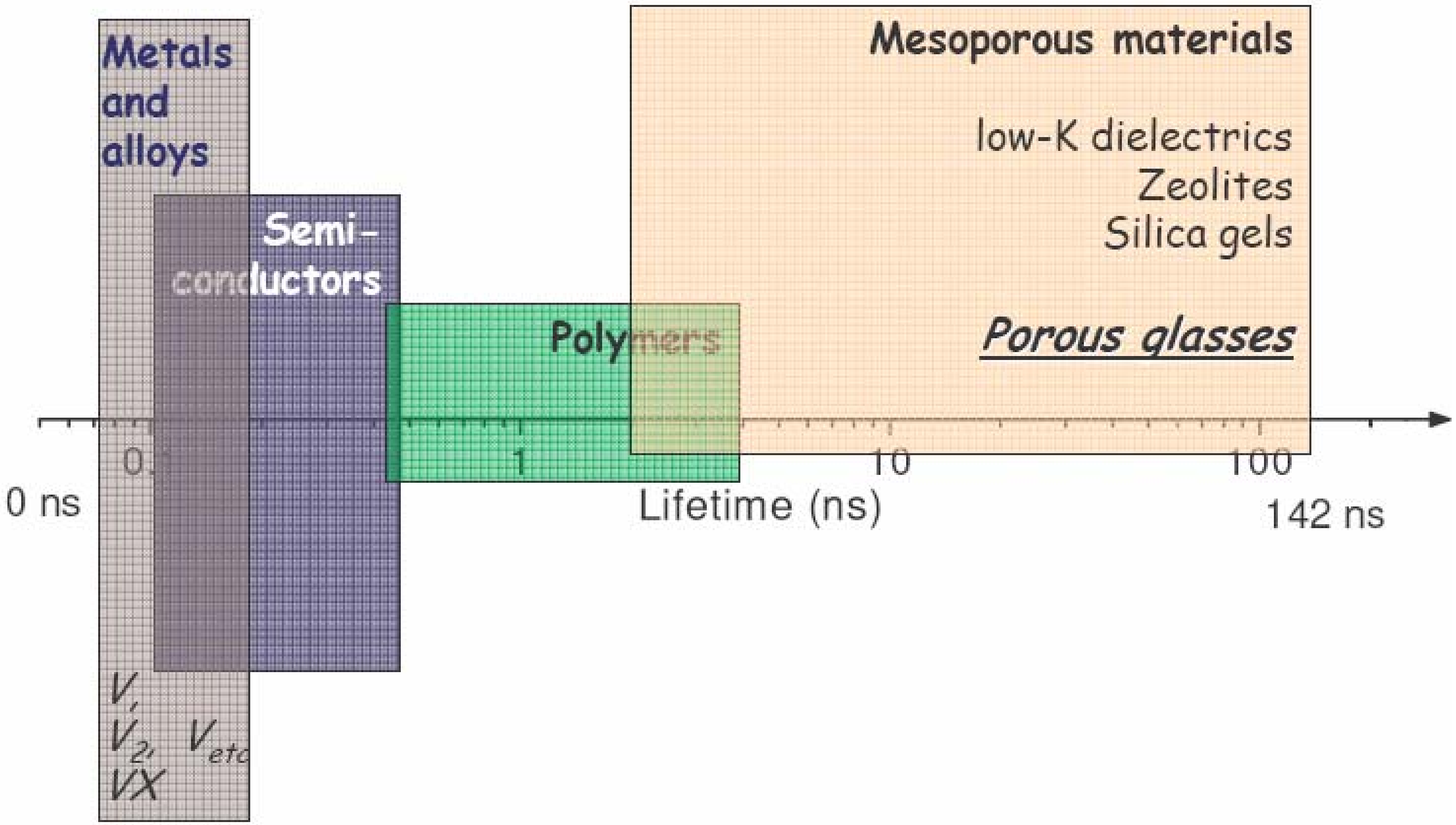
$$n(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) + I_3 \exp(-t/\tau_3)$$

The Positron Lifetime Measurement

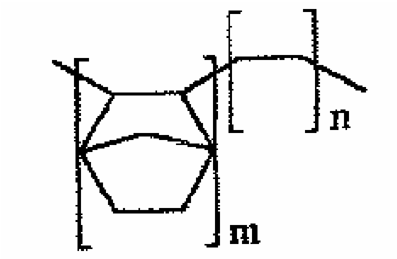


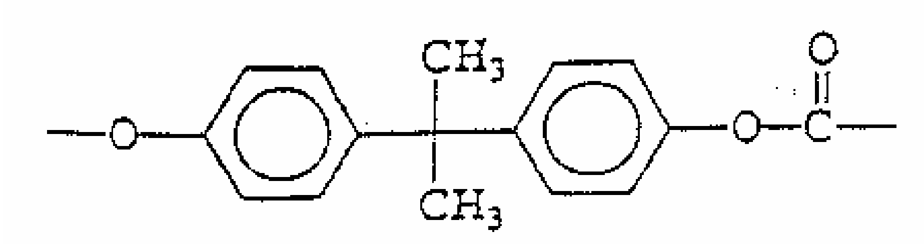
- Positron lifetime is measured as time difference between 1.27 MeV quantum (β^+ decay) and 0.511 MeV quanta (annihilation process)
- PM=photomultiplier; SCA=single channel analyzer (constant-fraction type); TAC=time to amplitude converter; MCA= multi channel analyzer

Typical Lifetimes in Holes of:



Analysis of COC and PC by PALS

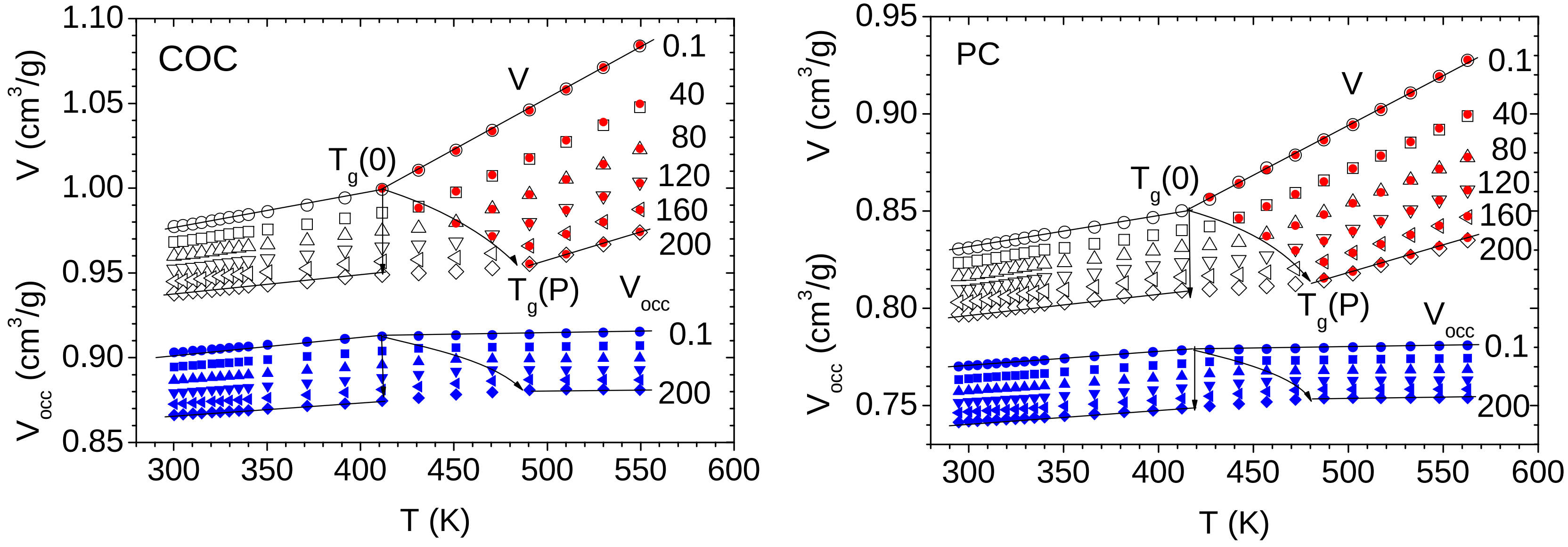




Cyclic Olefin Copolymer (COC)

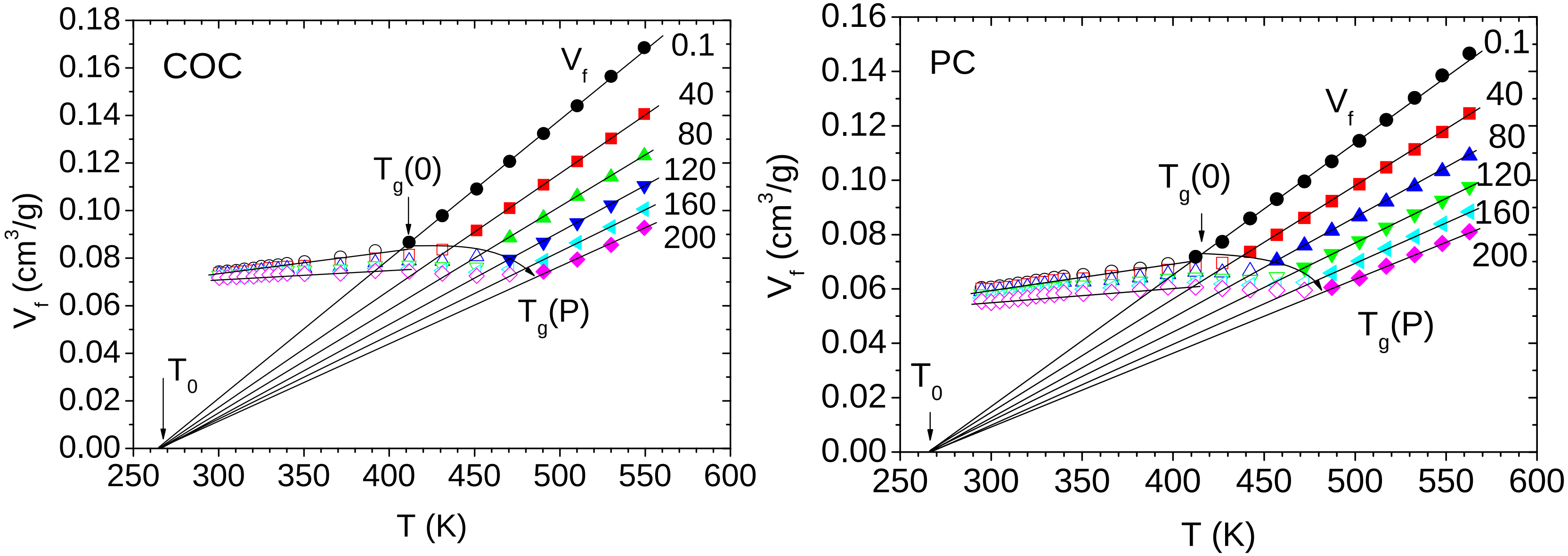
Poly Carbonate (PC)

V and V_{occ} vs T (K) [PVT]



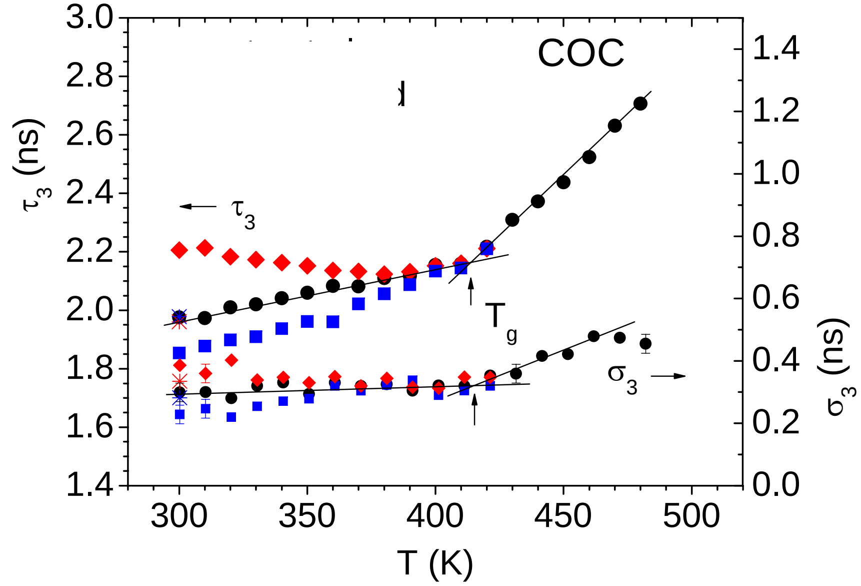
The specific total, *V*, (black open symbols), and occupied, $V_{occ} = (1 - h)V$ (blue symbols) volume as a function of temperature *T* and as selection of isobars (*P* in MPa) for COC and PC.

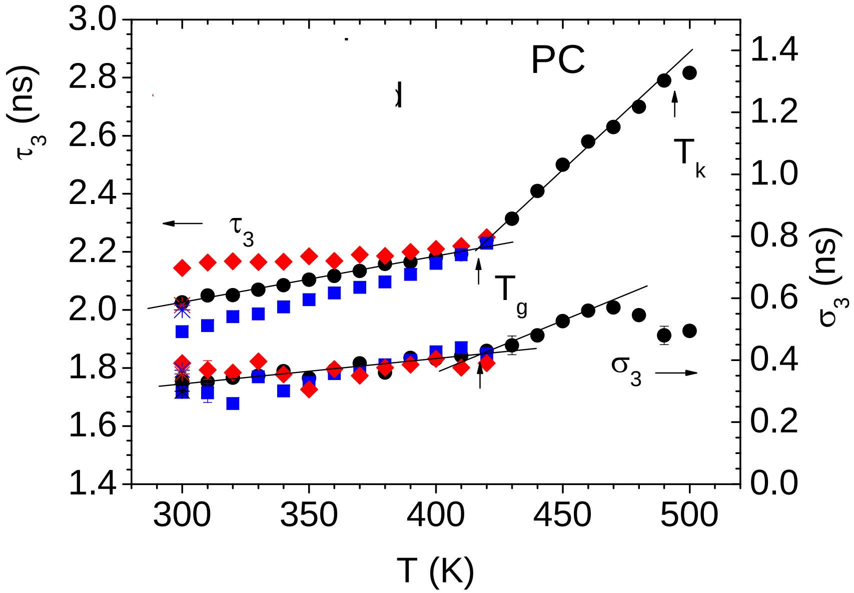
V_f vs T(K)



The specific hole free volume $V_f = hV$ as a function of temperature T and as selection of isobars (P in MPa) for COC and PC.

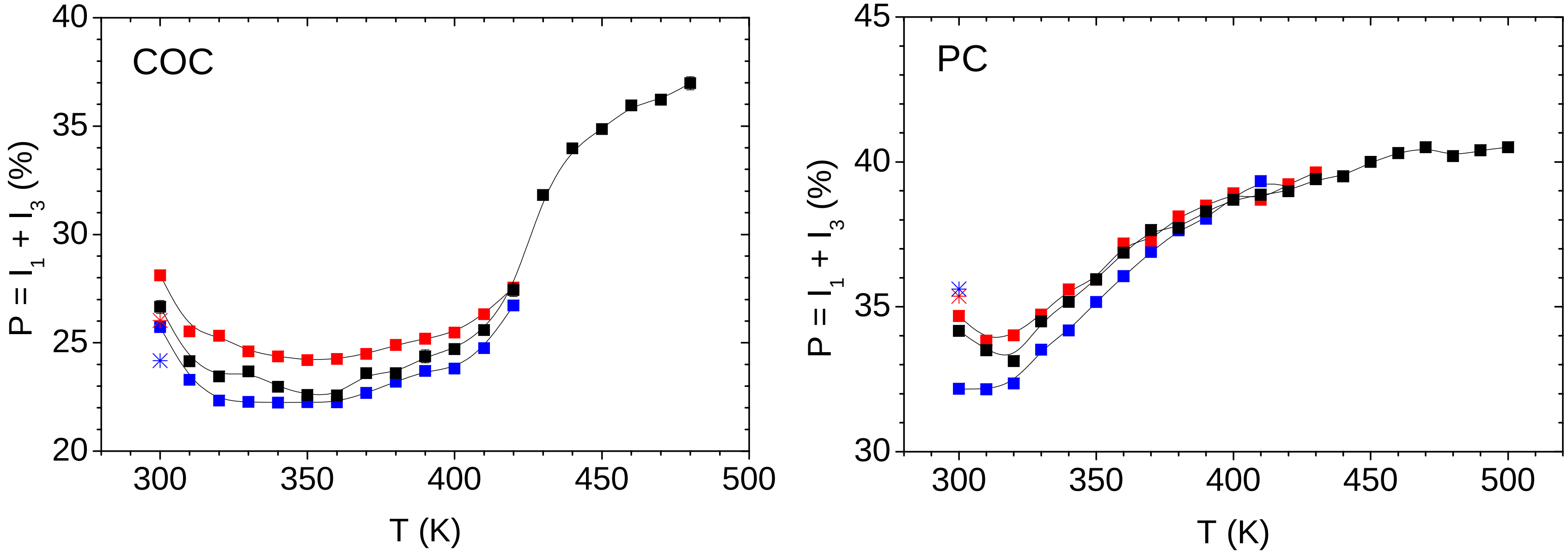
τ_3 and σ_3 vs T (K) [PALS]





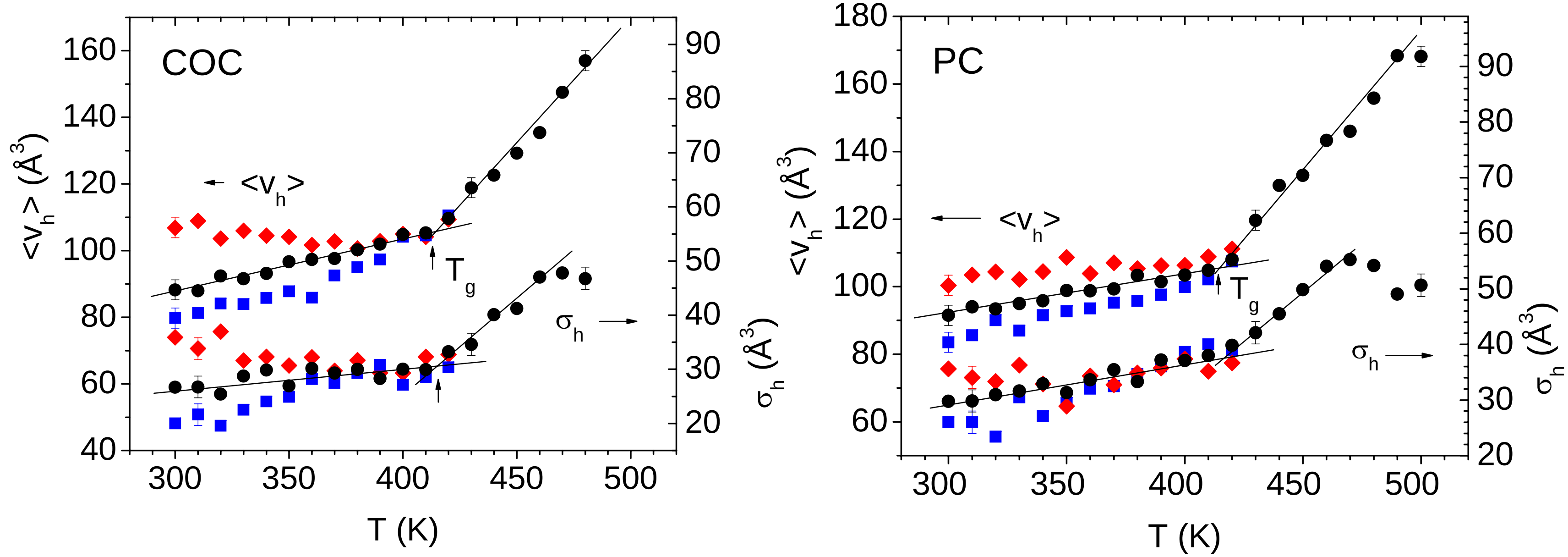
The mean, τ_3, and the mean dispersion, σ_3, of *o*-Ps lifetimes as a function of temperature *T* for densified at 200 Map (blue), gas-exposed (read) and untreated (black) COC and PC.

Ps yield vs T(K)



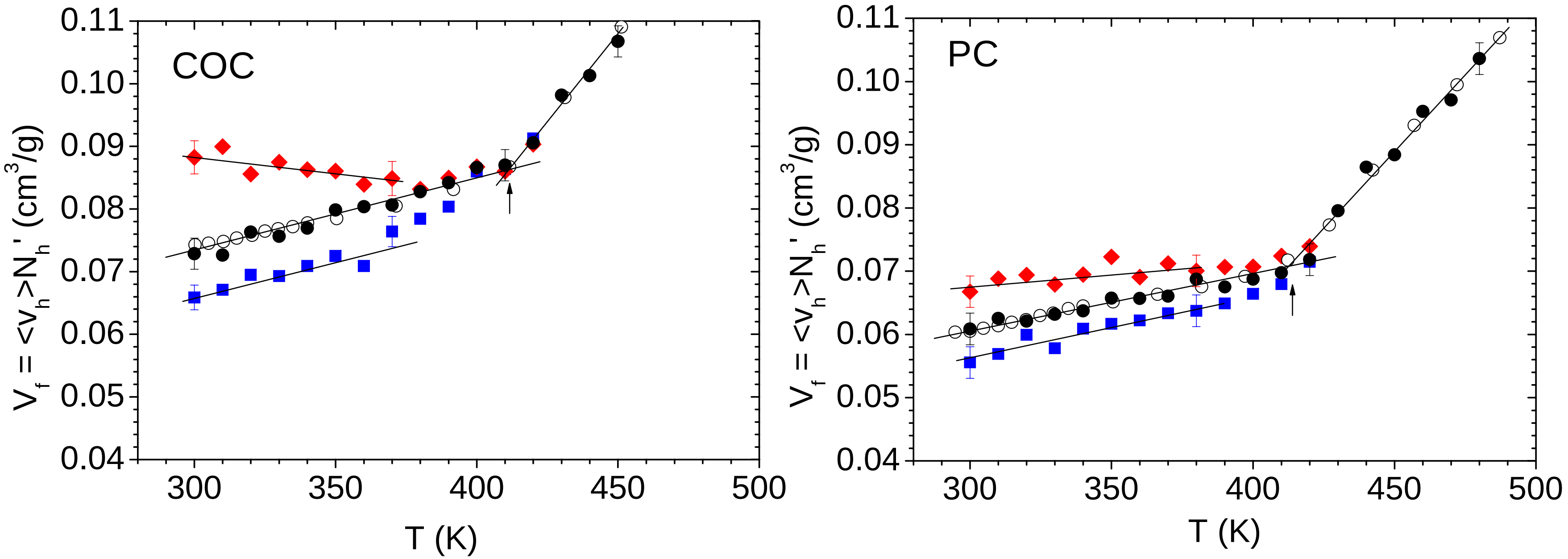
The Ps yield $P = I_1 + I_3$ with $I_1/I_3 = 1/3$ as a function of temperature *T* for densified at 200 Map (blue), gas-exposed (read) and untreated (black) COC and PC.

V_h and σ_h vs T(K)



The mean, <v_h>, and the mean dispersion, σ_h, of the hole volume as a function of temperature *T* for densified at 200 MPa (blue), gas-exposed (red) and untreated (black) COC and PC.

V_f vs T(K)



The specific free volume $V_f = \langle v_h \rangle N_h'$ from PALS at 10^{-5} Pa as a function of temperature for untreated (black filled circles), densified at 200 MPa (blue squares), and gas-exposed (read diamonds) COC and PC. The black empty circles show 0.1 MPa isobars from PVT experiments for the untreated polymers, $V_f = hV$.

Thanks for your time and patience!