

# Investigation of Free Volume in Polymers by Positron Annihilation Lifetime Spectroscopy (PALS)

**Master Thesis**

**by M. Qasim Shaikh**

**Under supervision of**

**Prof. Reinhard Krause-Rehberg**



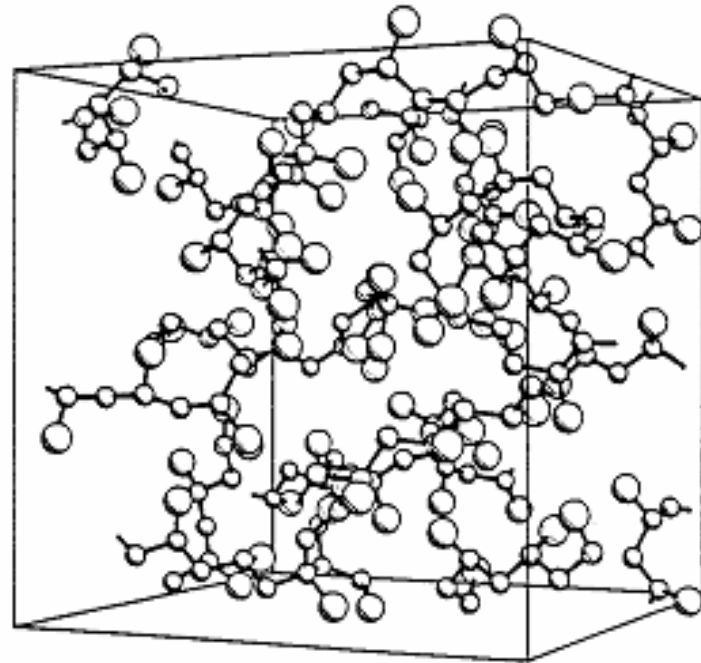
**Martin-Luther-Universität**

**Halle-Wittenberg**

**Fachbereich Physik**

# 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

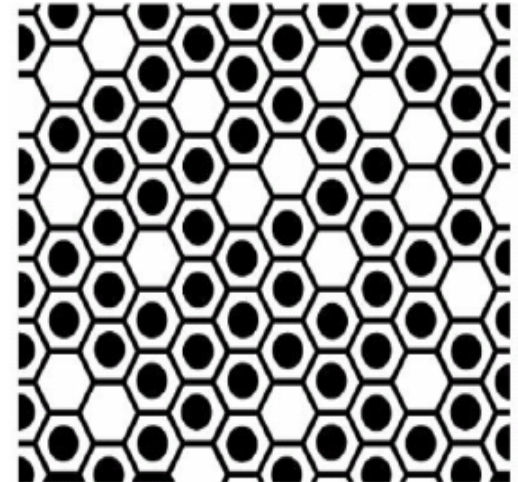


**Schematic representation of a  
single Poly (Propylene)  
microstructure (X=76)**

**(Simulation, Theodoru et al. 1985)**

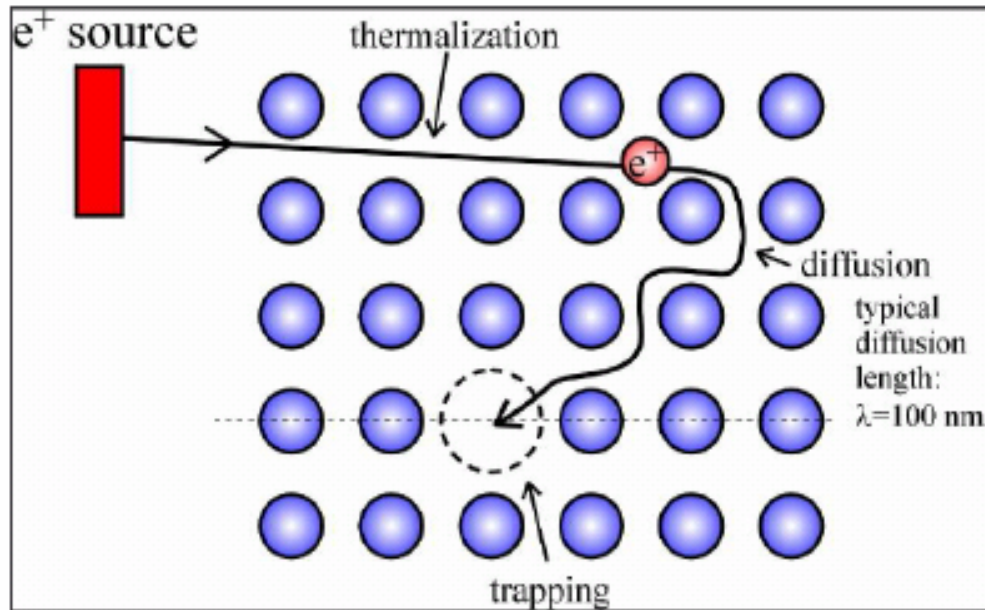
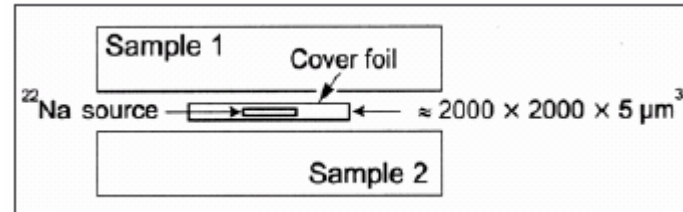
# Experimental Ways to determine Free Volume in Polymers

- **Positron Annihilation Lifetime Spectroscopy (PALS)**
  - Detection of subnanometric local free volumes (holes):  
Size distribution (mean hole volume  $\langle v_h \rangle$  and mean dispersion  $\sigma_h$ )
- **Pressure-Volume-Temperature-Experiments (PVT)**  
Analysis by Simha-Somcynsky lattice-hole model EOS
  - Fraction of vacancies  $h$ , specific hole free.  $V_f = hV$ , and occupied volumes,  $V_{occ} = (1-h)V$
- **Correlation of PALS and PVT**
  - allows estimation of PALS hole density  $V_f = N_h \langle v_h \rangle$
  - All parameters of the structure of hole free volume can be obtained from PALS and PVT



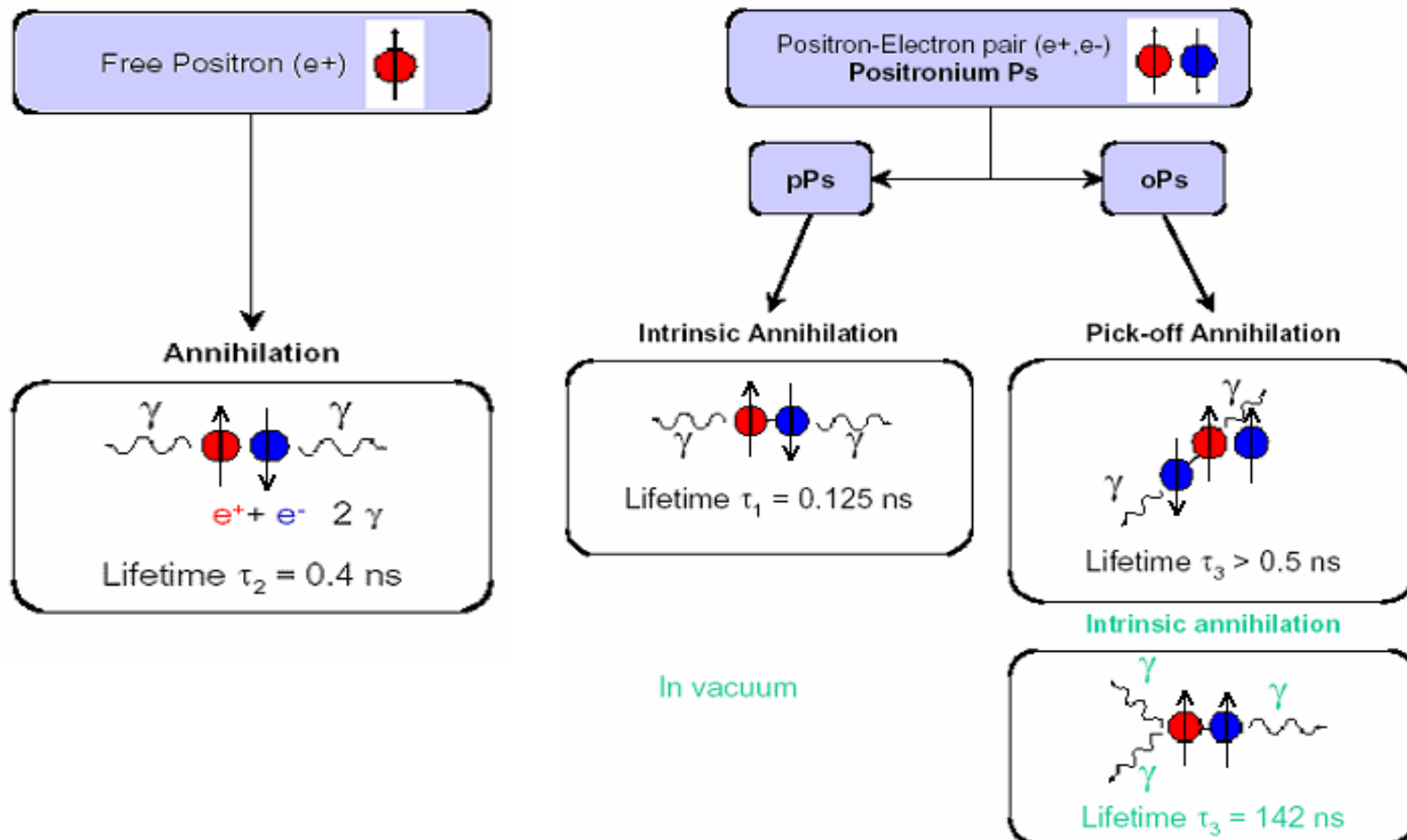
# Basics of PALS

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



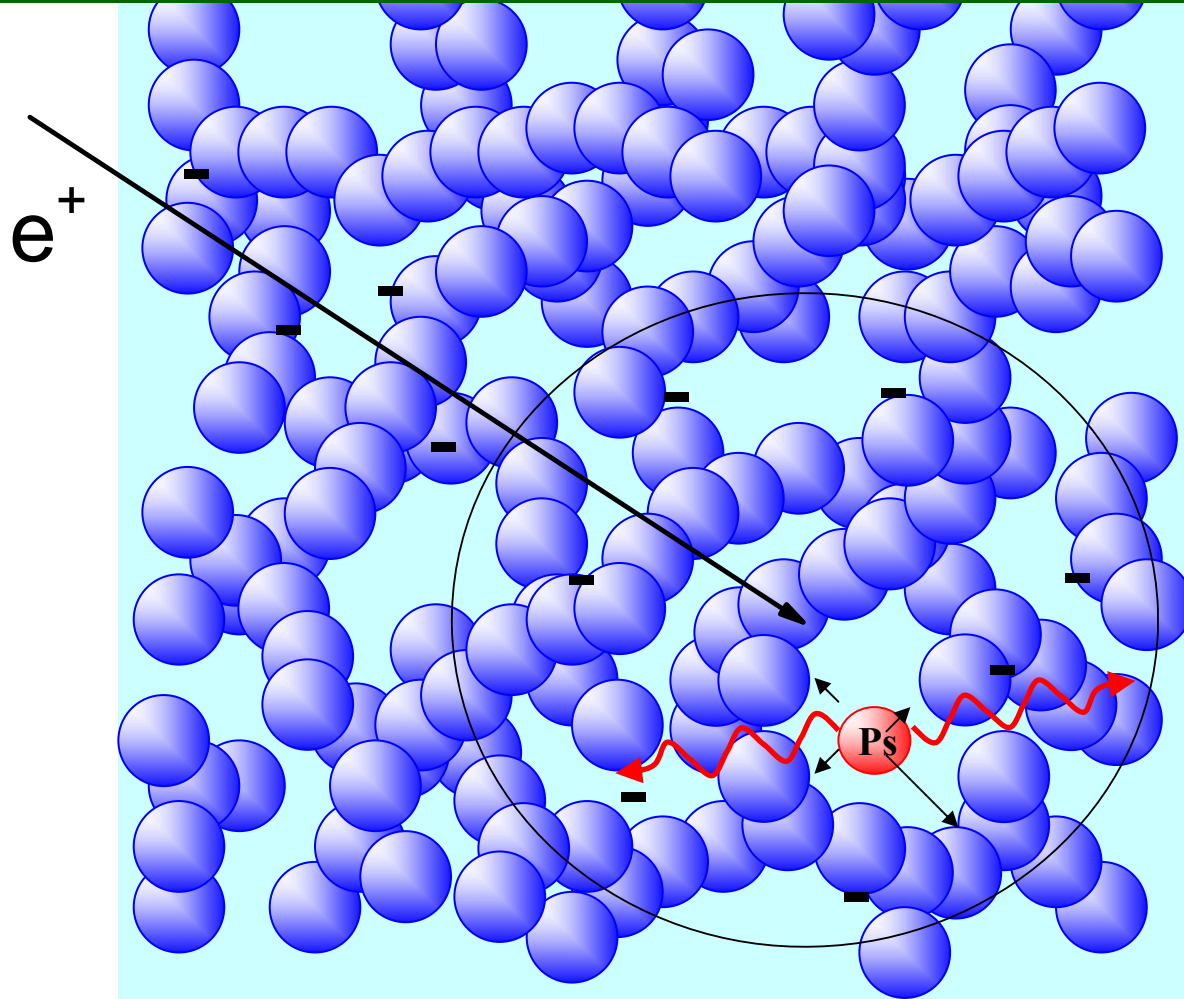
- Thermalization
- Diffusion
- Annihilation

# Basic Principles and Theories of Positron Annihilation in Polymers

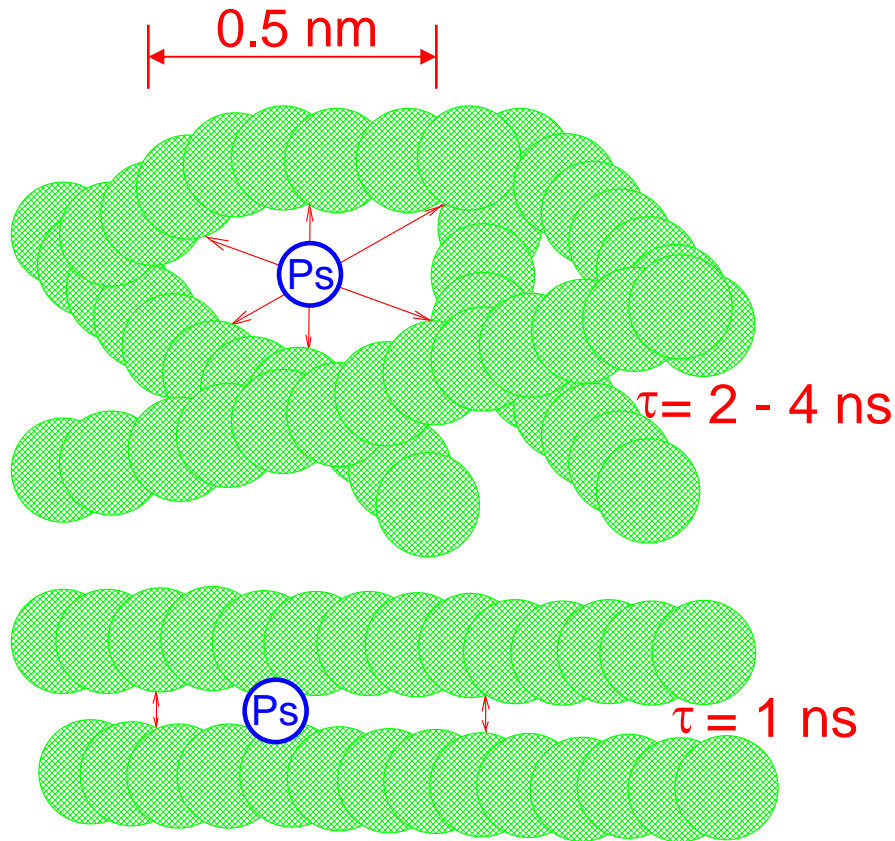


# Ps Formation in Polymers

$\beta^+$  source



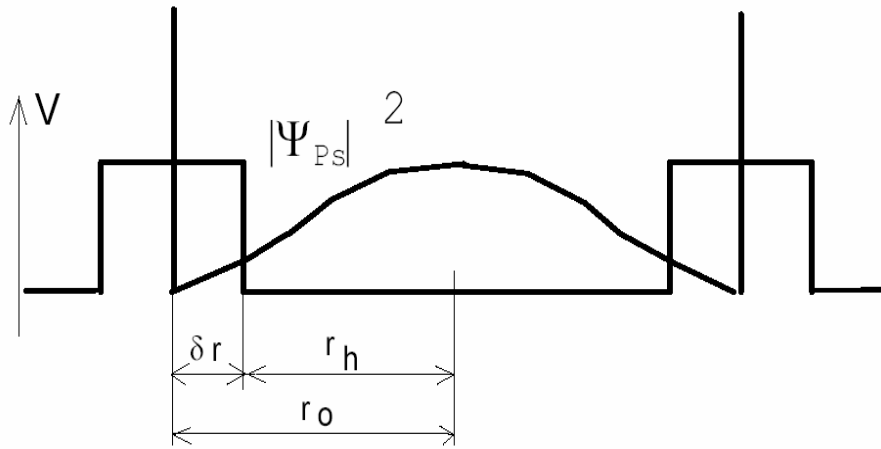
# Pick-Off Annihilation



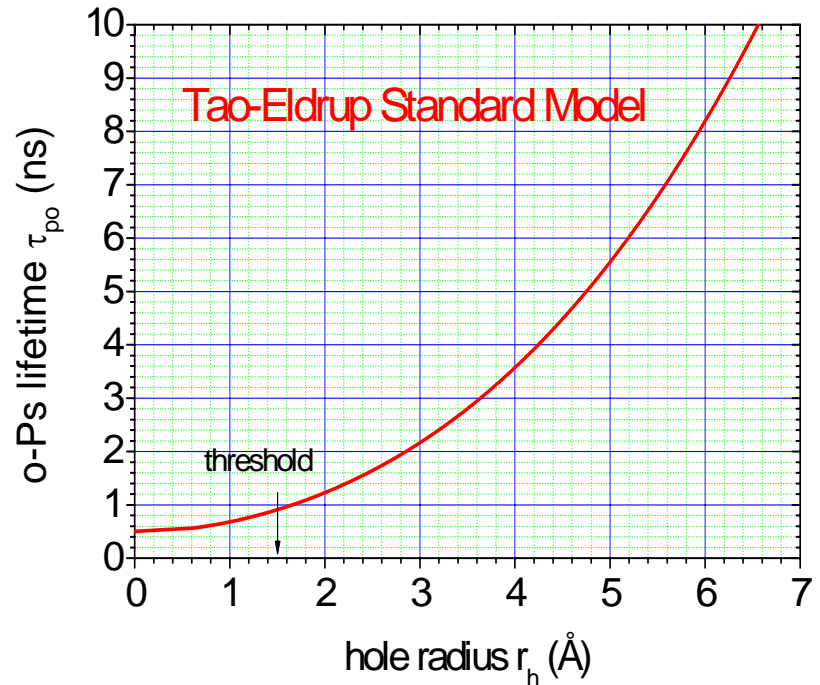
Ps localization in a hole of the (excess) free volume

Ps localization in interstitial free volume gives the packing coefficient 'C' of the crystals

# Theory of Tau-Eldrup (TE) Model



The height of the potential is infinity, and  $\delta r$  - empirical parameter  $\delta r = 0.166 \text{ nm}$



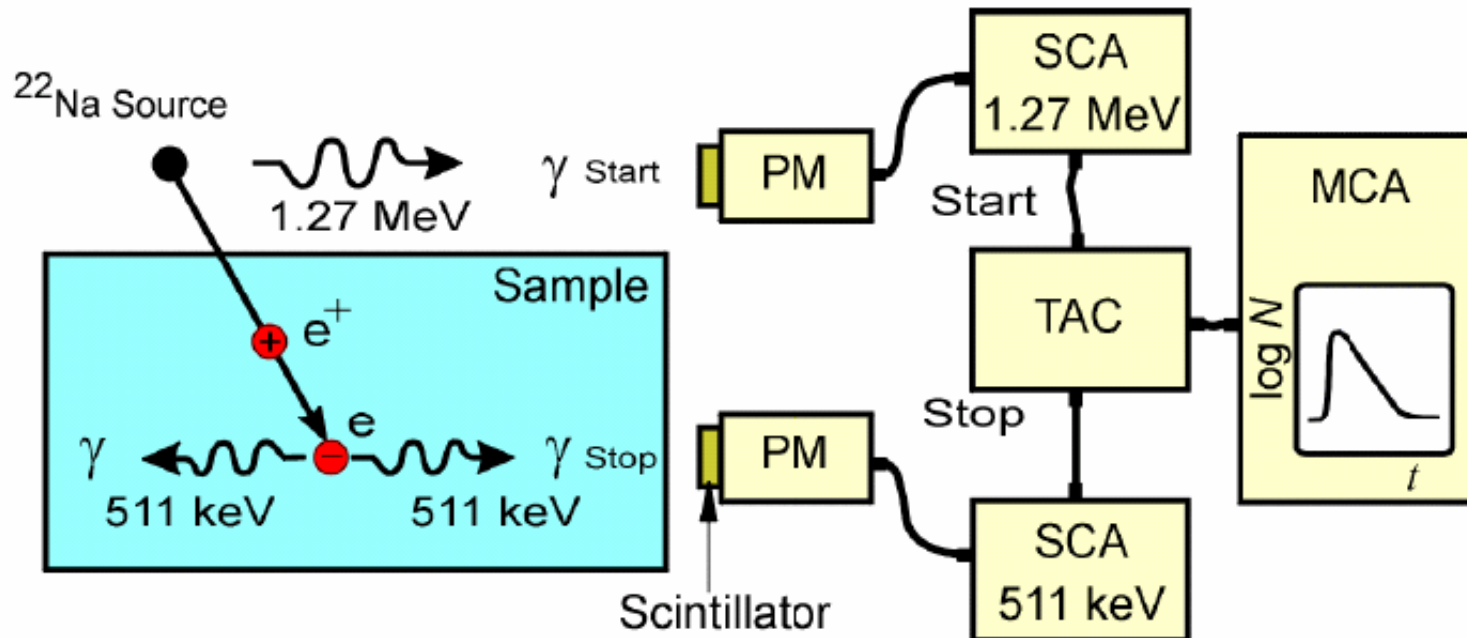
$$\tau_{o-Ps \text{ pickoff}} = \frac{0.5 \text{ ns}}{\left[ 1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi} \text{Sin} \left( \frac{2\pi r_h}{r_h + \delta r} \right) \right]}$$

**mean hole volume**

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

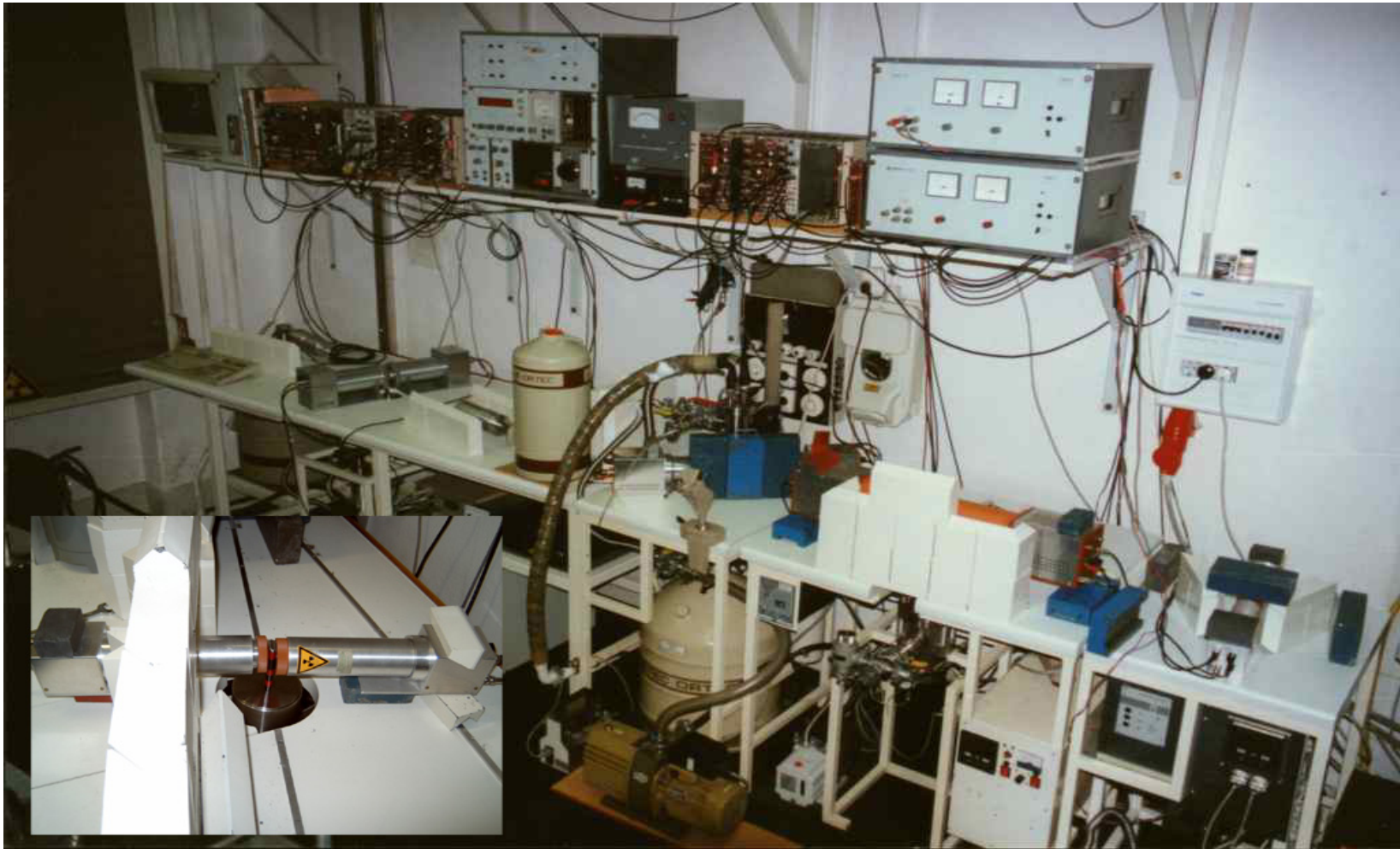


# The Positron Lifetime Measurement

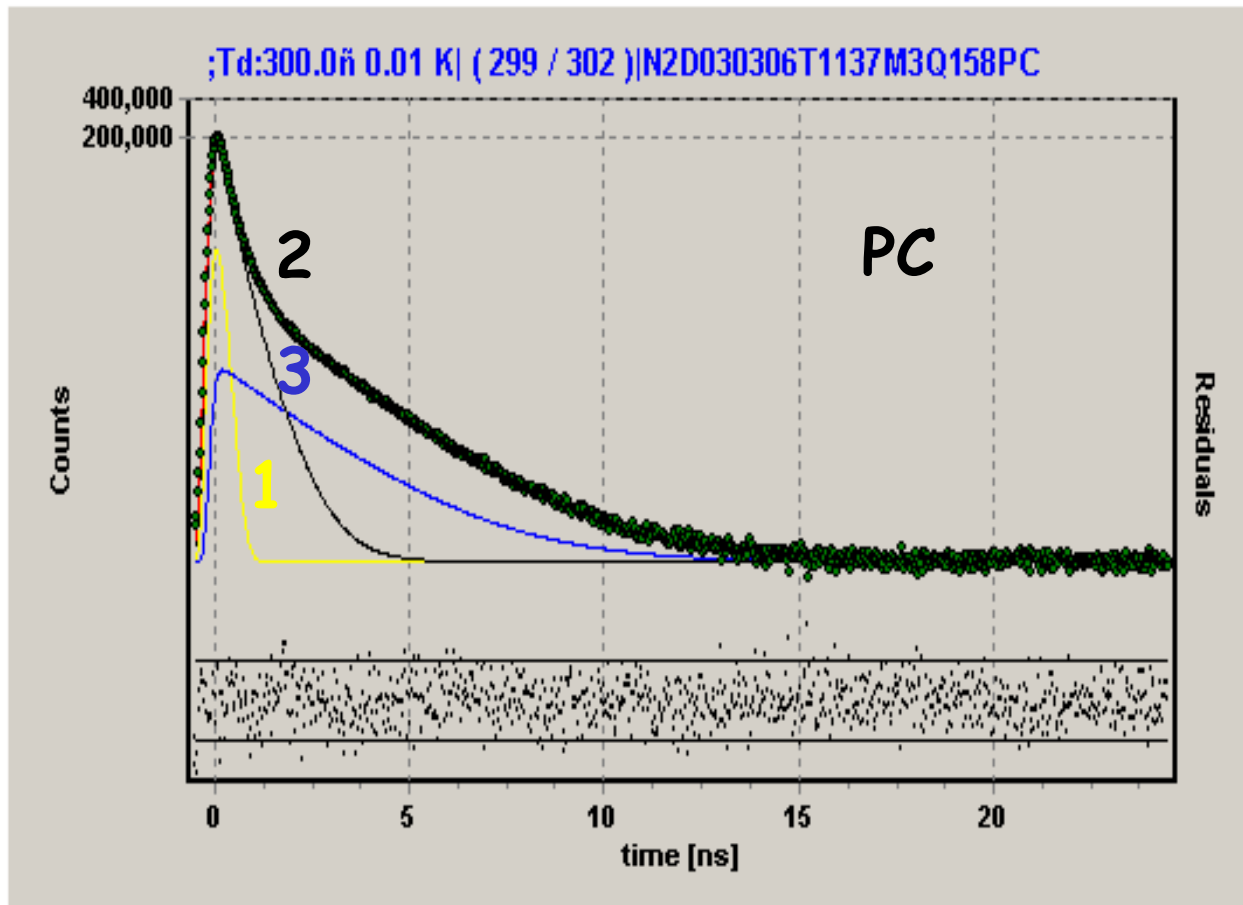


- Positron lifetime is measured as time difference between  $1.27\text{ MeV}$  quantum ( $\beta^+$  decay) and  $0.511\text{ MeV}$  quanta (annihilation process)
- PM=photomultiplier; SCA=single channel analyzer (constant-fraction type); TAC=time to amplitude converter; MCA= multi channel analyzer

# Positron Laboratory at MLU



# Typical PALS Spectrum



p-Ps

$$\tau_1 = 0,125 \text{ ns}$$

Free Annihilation

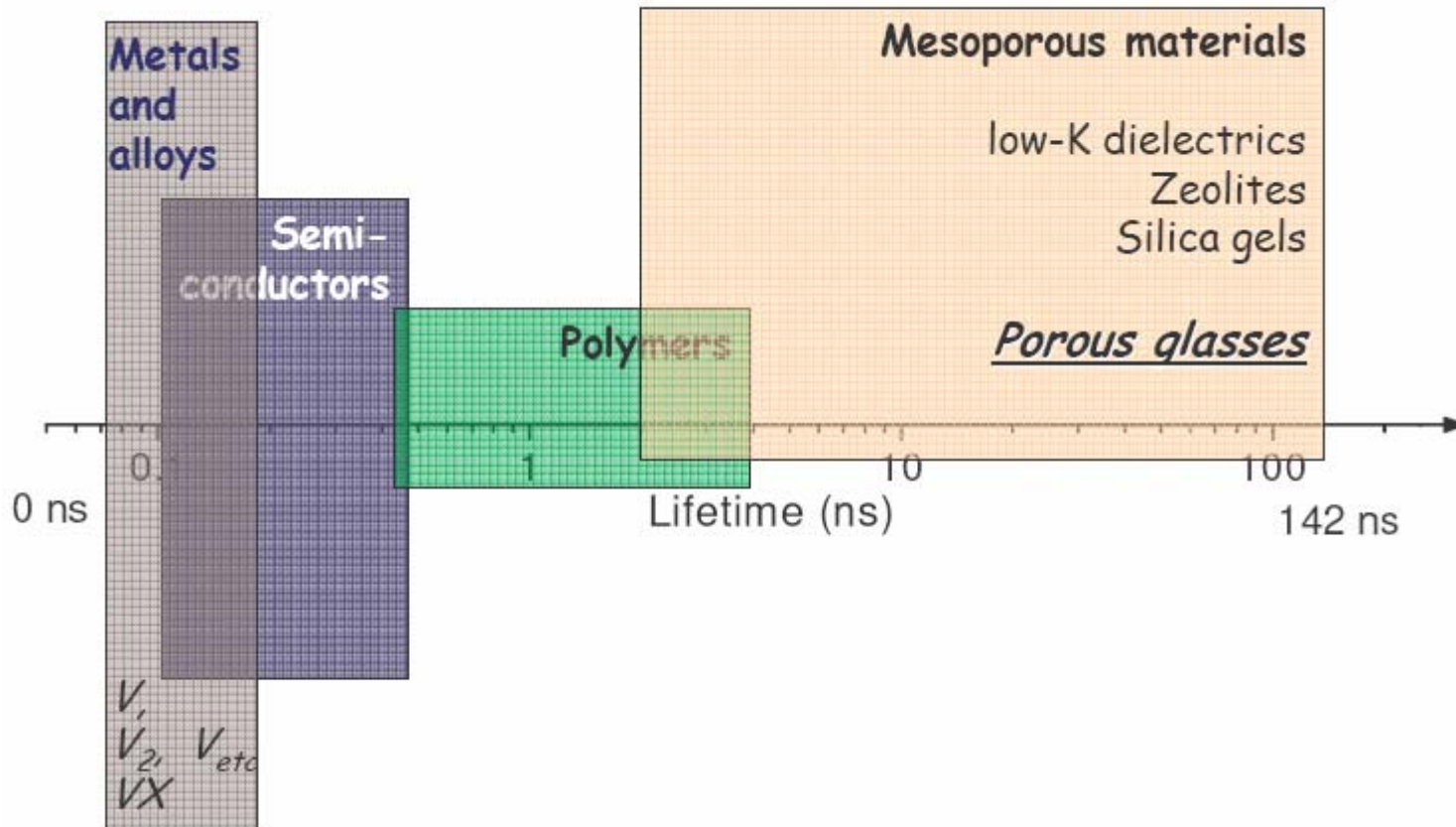
$$\tau_2 = 0,4 \text{ ns}$$

o-Ps (Pick-off  
annihilation)

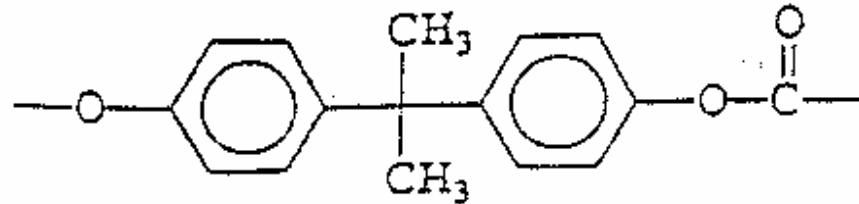
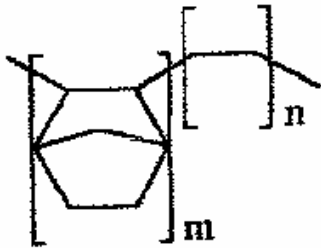
$$\tau_3 > 0,5 \text{ ns}$$

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

# Typical Lifetimes in Holes of:



# Analysis of COC and PC



Cyclo Olefin Copolymer (COC)

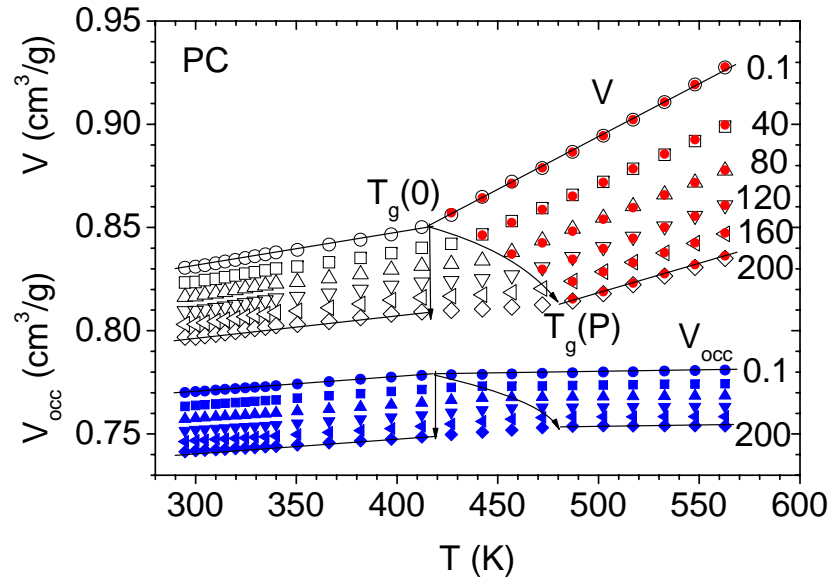
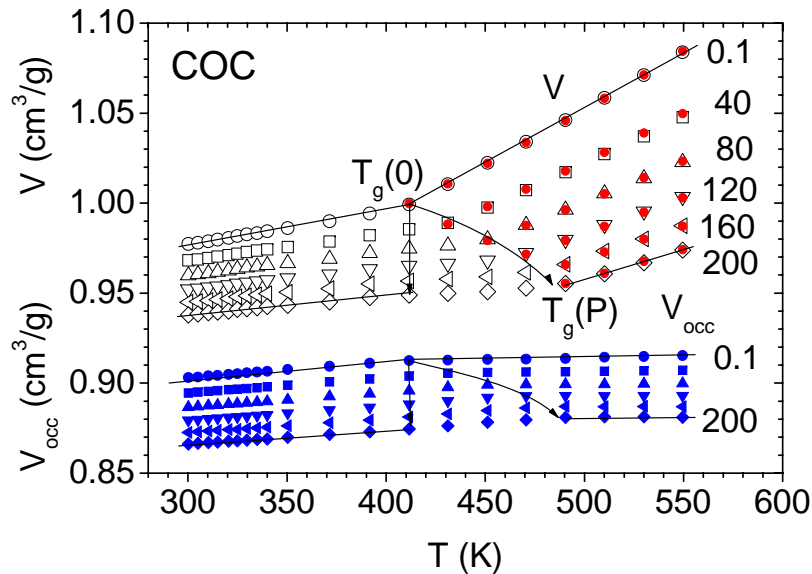
Poly Carbonate (PC)



- Un-treated,
- Pressure Densified, and
- Gas Exposed.

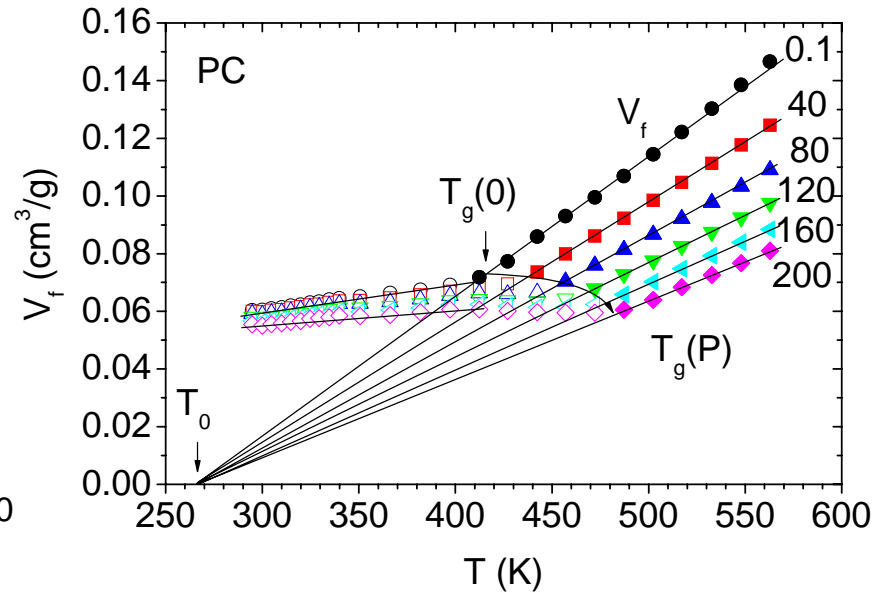
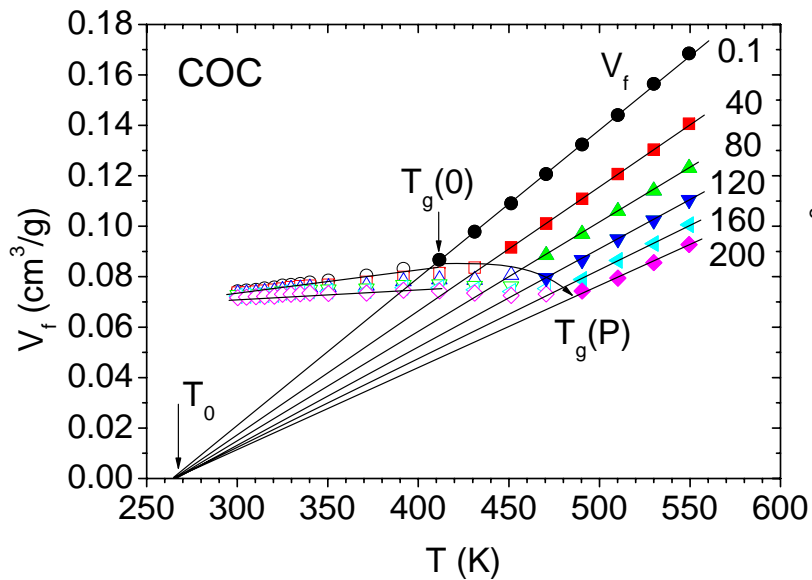


# V and $V_{occ}$ vs T (K) [PVT]



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.

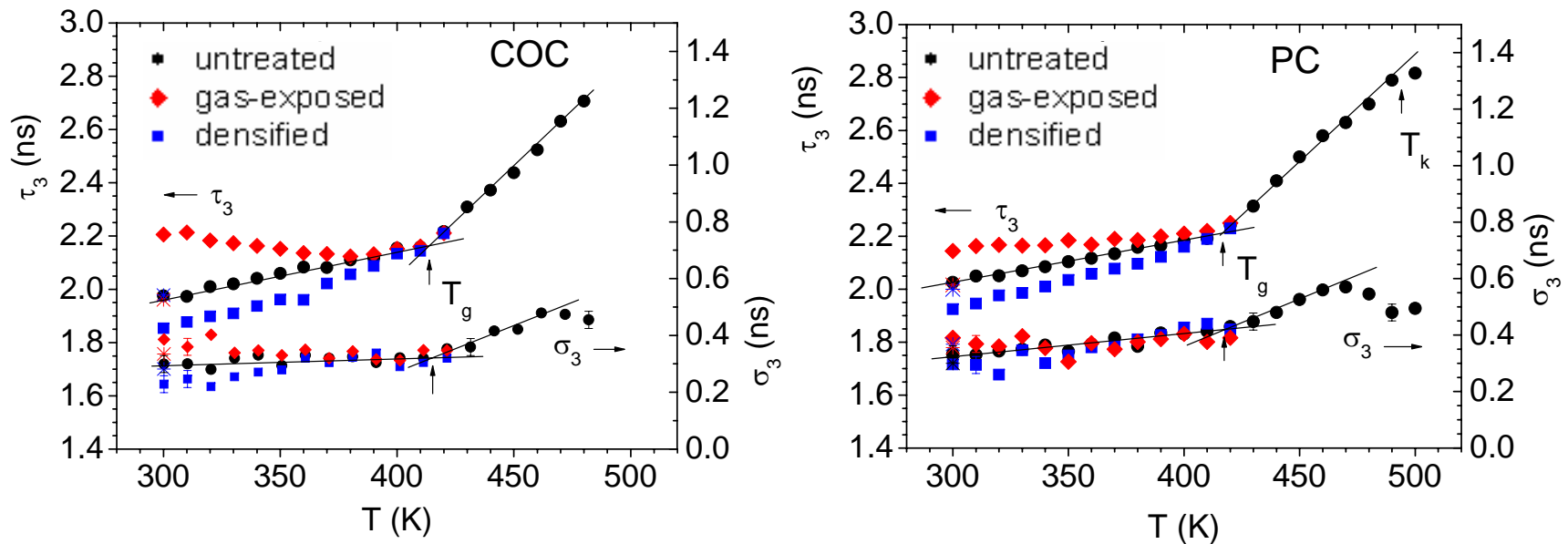
# $V_f$ vs $T(K)$



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.



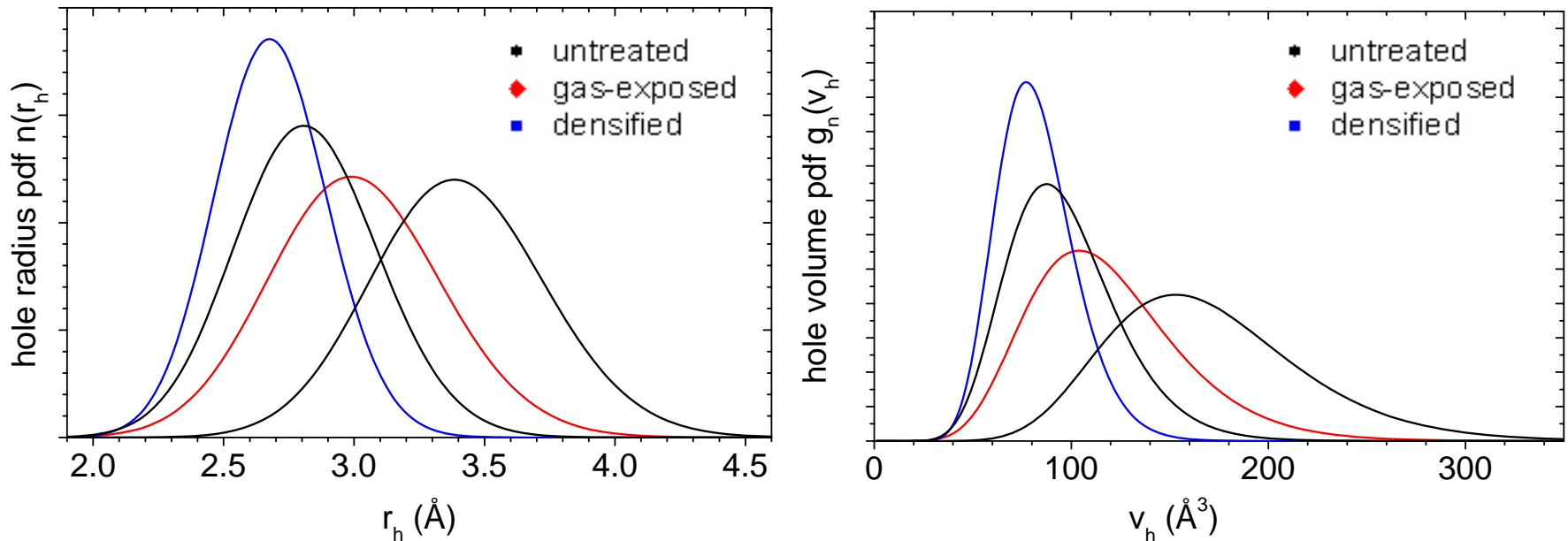
# $\tau_3$ and $\sigma_3$ vs $T$ (K) [PALS]



The mean,  $\tau_3$ , and the mean dispersion,  $\sigma_3$ , of o-Ps lifetimes as a function of temperature  $T$  for densified at 200 MPa (blue), gas-exposed (read) and untreated (black) COC and PC.

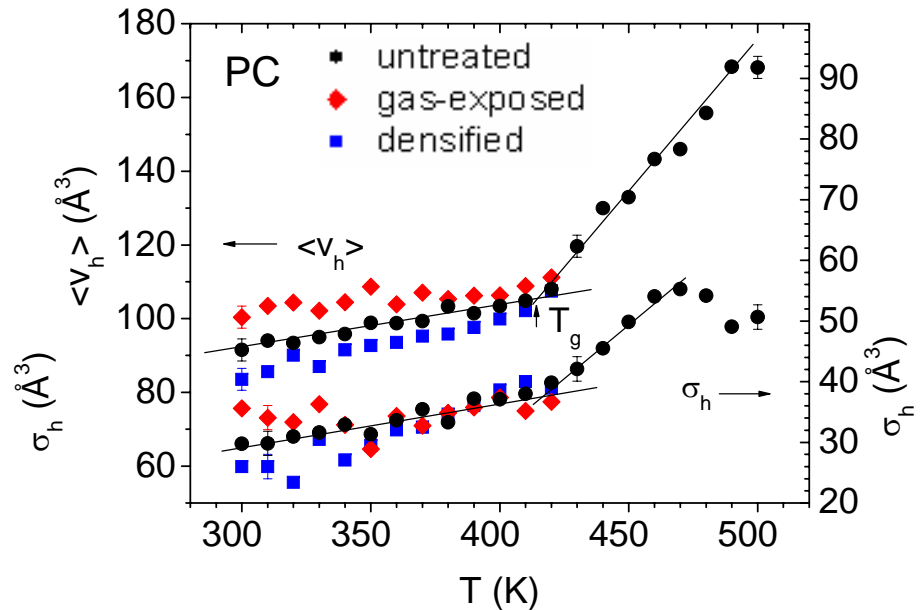
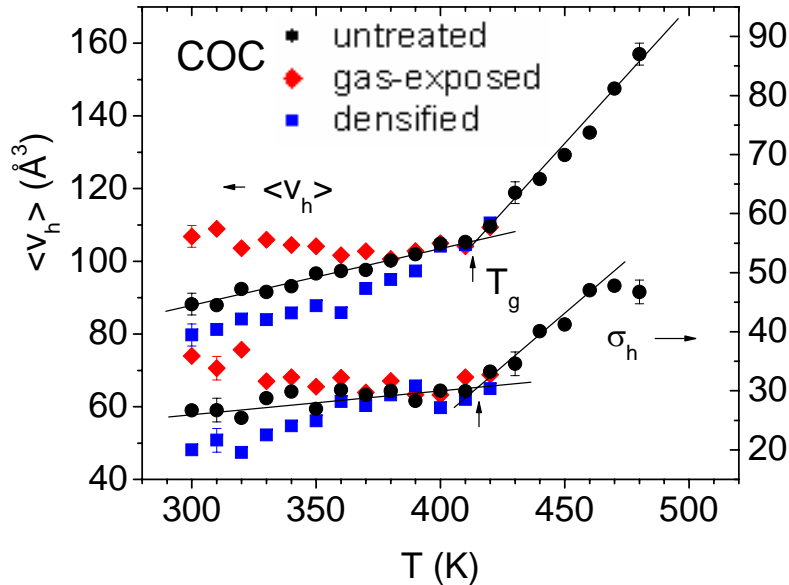


# Probability density function (pdf) [COC]



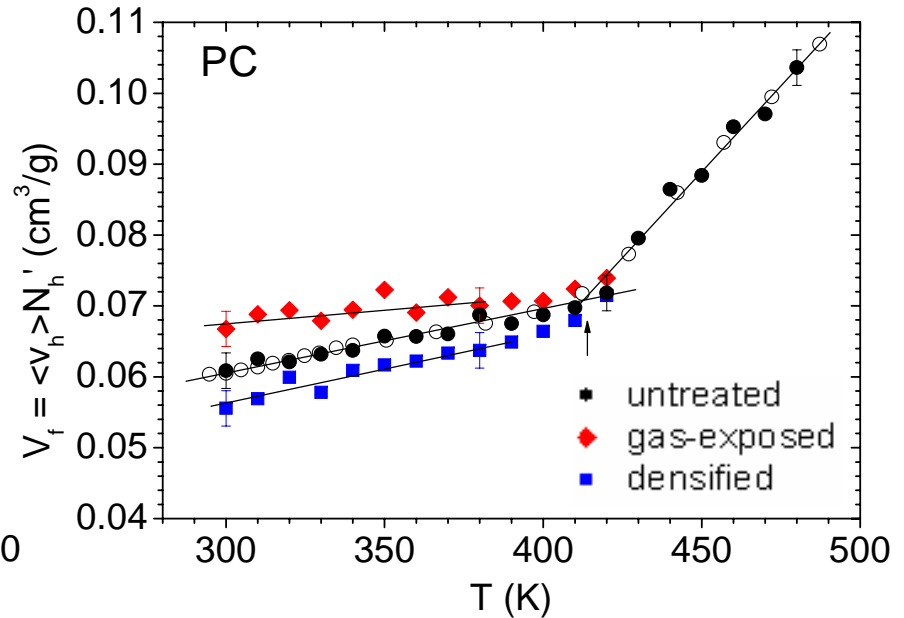
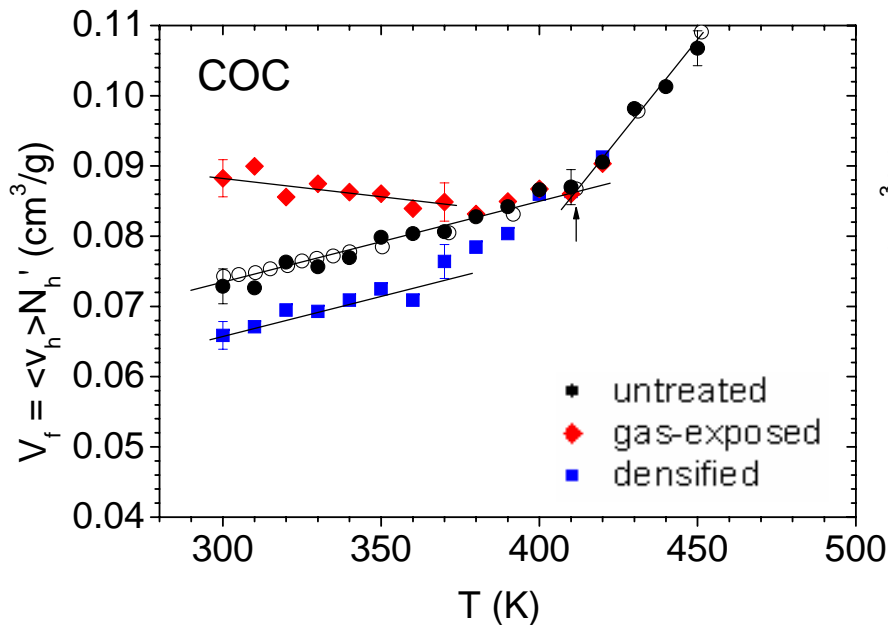
**Probability density function (pdf) of the hole radius,  $n(r_h)$ , and hole volume,  $g_n(v_h)$ , for COC. Blue: densified, red: gas-exposed, black: untreated samples at 300 K (lower curve) and 480 K (upper curve).**

# $V_h$ and $\sigma_h$ vs $T(K)$



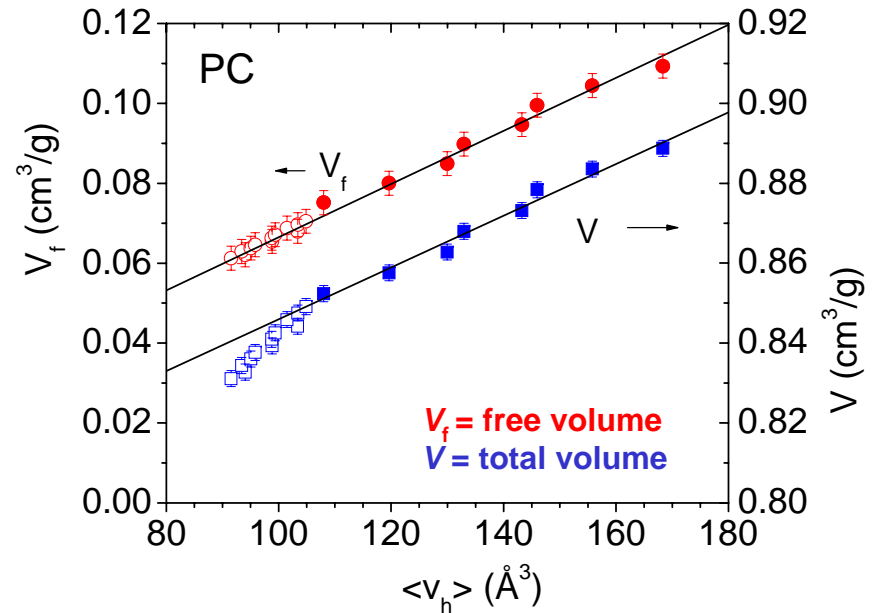
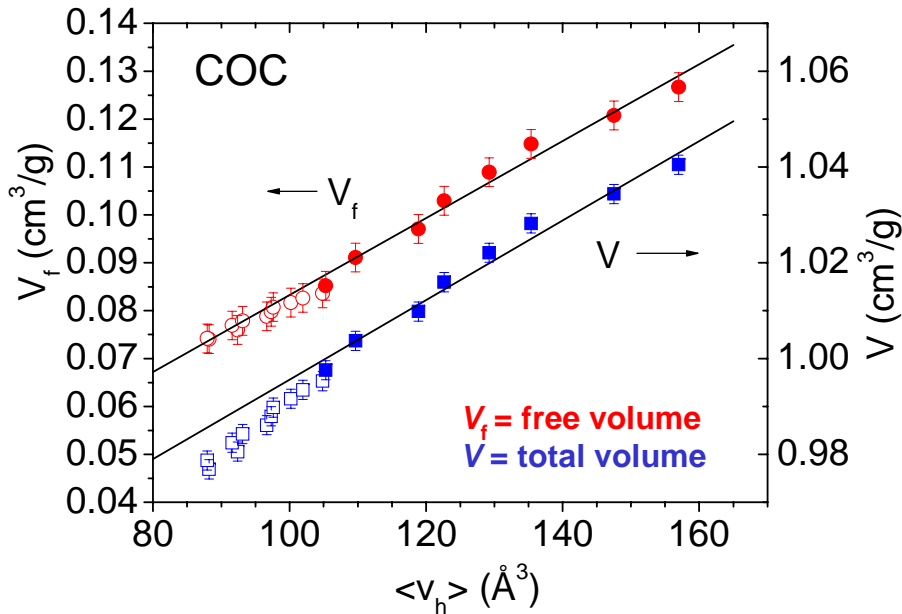
The mean,  $\langle v_h \rangle$ , and the mean dispersion,  $\sigma_h$ , of the hole volume as a function of temperature  $T$  for densified at 200 MPa (blue), gas-exposed (red) and untreated (black) COC and PC.

# Hole density $N_h'$

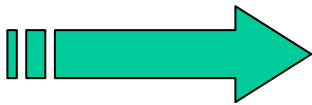


The specific free volume  $V_f = \langle v_h \rangle N_h'$  from PALS at  $10^{-5}$  Pa as a function of temperature for untreated (black filled circles), densified at 200 MPa (blue squares), and gas-exposed (red diamonds) COC and PC. The black empty circles show 0.1 MPa isobars from PVT experiments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

# $(V_f \text{ and } V) \text{ vs } V_h$



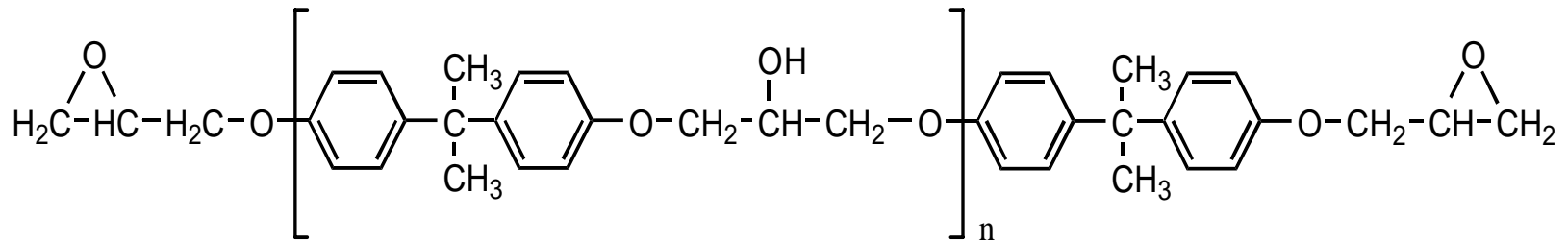
Plots of the **specific free,  $V_f(T)$  (red)**, and **total,  $V(T)$  (blue)** volume vs. the mean hole volume  $\langle v_h(T) \rangle$  for COC and PC. Data from above  $T_g$  are shown by filled symbols, those from below by empty symbols.



$$V_f = hV = N_h' \langle v_h \rangle$$

$$V = V_{\text{occ}} + N_h' \langle v_h \rangle$$

# Epoxy Resin (DGEBA)

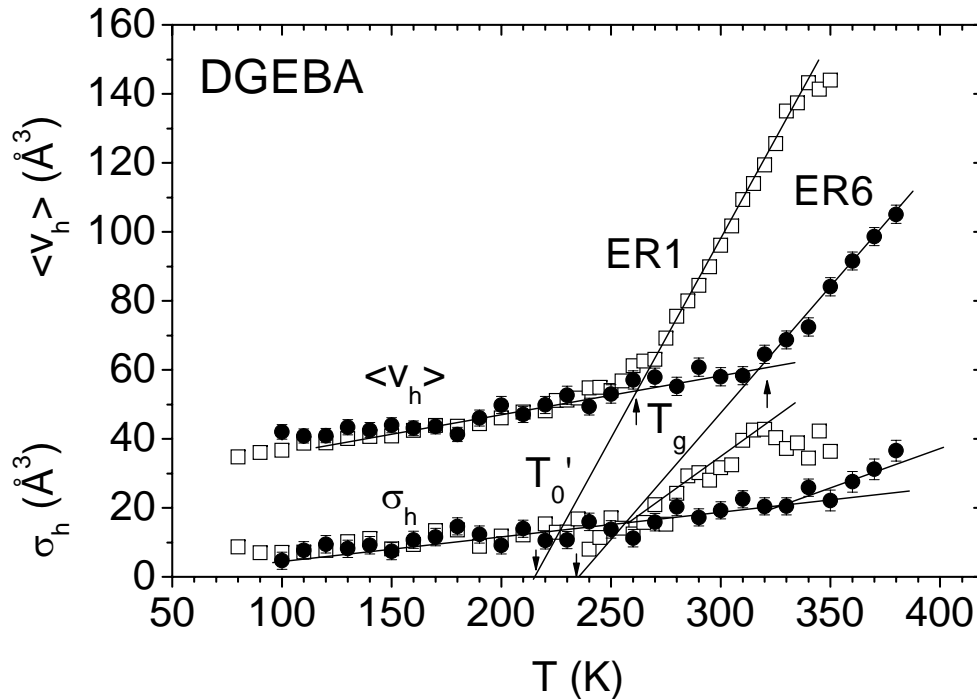


**Resin of diglycidyl ether of  
bisphenol-A (DGEBA)**

**V<sub>f</sub> = free volume**

**V = total volume**

# Epoxy Resin (DGEBA)



ER1 - monomer of  
DGEBA ( $n \approx 0.18 = 1$  unit)

ER6 - oligomer of  
DGEBA ( $n \approx 5 = 6$  units)

The mean hole volume,  $\langle v_h \rangle$ , and the mean hole volume dispersion,  $\sigma_h$ , as a function of the temperature  $T$  for ER6 (filled symbols) and ER1 (empty symbols).



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