PAS : A TOOL TO PROBE COMPLEX POLYMER STRUCTURES

Third Trombay Positron Meeting
Bhabha Atomic Research Centre
Mumbai
March 24, 2018

DR. S. SIVARAM
Email : s.sivaram@iiserpune.ac.in
www.swaminathansivaram.in

OUTLINE

- PAS and PALS : Basic principles
- Positronium chemistry and influence of chemical functional groups
- Concept of free volumes in polymers and determination of Tg
- Introduction to porous polymers
- Flexible and semirigid polymers
- Polymers with intrinsic porosities
- Nanoporous polymers for molecular separations
- Conclusion

PAS : BASIC PRINCIPLES

- Positron and Positronium (Ps) are preferentially localized in pre-existing defects, including free volume (0.1- 1 nm) and voids (> 1 nm) in polymeric systems.
- The positron annihilation lifetime is directly related to the integrals of positron and electron wave functions
- Trapping and tunnelling of Ps in free volumes indicate that in common polymers , Ps will spend its entire lifetime in a hole with a radius of > 0.15 nm
- Combining molecular and dynamic simulations with PAS experiments is an excellent approach to understand free volume properties of polymers

PAS is a unique tool to study sub-nanometer regime in polymers. This regime is difficult to explore using other tools such as X-ray and electron microscopy

PALS : BASIC PRINCIPLES

- Positronium (the bound state of positron and electron, Ps) is preferentially localized in the regions of low electron density sites, such as free volumes, holes, interfaces, and pores.
- The primary mechanism of annihilation of triplet positronium (*o*-Ps) in molecular substrates is by pick-off with electrons of the materials under study.
- Therefore, the intrinsic *o*-Ps lifetime (142 ns) is typically shortened to a few nanoseconds (110 ns) via two-γ annihilation processes in molecular substrates.
- According to the Ps-free volume theory, the lifetime of *o*-Ps is determined by the reciprocal of integral between the positron and the electron densities in the free volumes of molecular systems. Therefore, *o*-Ps lifetime is expected to correlate directly with the dimensions where Ps is localized.

PALS : BASIC PRINCIPLES

- A large hole, which contains a low mean electron density, results in a long *o*-Ps lifetime.
- A semi-empirical equation by fitting the measured o-Ps lifetime (τ3) in a spherical infinitive potential model with known cavity sizes is commonly used in the positron and polymeric communities because of its simplicity and with a reasonable precision to estimate a mean value of free-volume size at the atomic molecular level for most polymers.

$$\tau_3 = 0.5 \times \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1}$$

POSITRON ANNIHILATION SPECTROSCOPY IN POLYMERS

- The annihilation characteristics of positron and positronium, such as lifetime and energy, contain information about the electronic properties within molecules and solids.
- The positron thermalizes in picoseconds in polymers and exhibits lifetime in nanoseconds. Thus, PAS is considered as sub-nano to nanosecond spectroscopy
- Consequently PAS has emerged as a powerful tool to determine atomic and molecular defects and interfacial properties of a wide variety of materials
- In the case of polymers PAS has been widely used to determine quantitatively free-volume, hole (size and distribution), void and layer properties

Methodologies and applications of this tool are still in the nascent stages of development

POSITRON ANNHILATION LIFETIME SPECTROSCOPY

- PALS most widely used for polymers and has reached a certain degree of maturity
- A typical PALS spectrum of polymers can be resolved into three lifetimes; the shortest, ~0.125 ns, corresponds to the singlet state Ps annihilation; the intermediate lifetime of 0.3 to 0.5 ns due to positron annihilation and the longest lifetime due to the triplet state Ps annihilation.
- Since free-volumes in polymers is a distribution, the positron and positronium lifetimes are analyzed as a distribution.

PALS: INFLUENCE OF FUNCTIONAL GROUPS

- However, positronium (Ps) can chemically react with molecules and different functional groups by two processes, chemical quenching, which decreases o-Ps lifetime (τ_3), and chemical inhibition, which decreases the probability of o-Ps formation. Typical chemical function groups, which exhibit strong quenching are nitroaromatics, quinones, maleic anhydride, and ions with redox potential < 0.9 eV
- Some important and common materials that show no o-Ps or very small fraction of o-Ps intensity (<2%) are polyimides and materials containing only carbon.
- To overcome this problem modified correlation equation by using the second-component positron lifetime (τ_2) of PALS spectra has been proposed which is useful in the determination of the free-volume size in polymeric materials, where no *o*-Ps component is observed.

Y.C.Jean, Macromolecules. 2011

FEATURES OF PALS IN AMORPHOUS AND CRYSTALLINE POLYMERS

- Traditionally, PALS of amorphous (single phase) polymers have been analyzed in terms of three exponential components. The longest lifetime component τ_3 (in the range 2-3 ns), characteristic for the annihilation in the bound state e+-e- (a hydrogen-like *ortho* -positronium atom, *o*-Ps), is indicative of free volume in a material.

- A square box approximation for the Ps atom in free volume elements or microcavities in polymers has been proposed to relate τ_3 and the radius R_3 of free volume elements.
-
- Qualitatively, higher the τ_3 values, the larger are the radii of free-volume elements. Typical radii of free volume elements in amorphous polymers should be in the range 2.5-4 Å.

Y. P. Yampoloskii, Macromolecules, 2000

FEATURES OF PALS IN AMORPHOUS AND CRYSTALLINE POLYMERS

- However, it was shown that, at least for one amorphous glassy polymer, poly(trimethylsilyl propyne) (PTMSP), which is known for having the largest gas permeability, diffusion, and solubility coefficients among all polymeric materials, a four-component spectrum gave a far better description of the data. In this case, the difference between the two positronium components was more than 8 ns, and the splitting could not be explained, e.g., by the suggestion of a nonexponential character of the PALS. These results imply two features of free volume in PTMSP: (1) its free volume elements have much larger sizes (the radii of are in the range 6-8 Å) than those in conventional polymers; (2) the size distribution of free volume in PTMSP is bimodal, in contrast to conventional polymers, where it is supposed to be unimodal.

Y. P. Yampoloskii, Macromolecules, 2000

FEATURES OF PALS IN AMORPHOUS AND CRYSTALLINE POLYMERS

- For semi-crystalline polymers, such as polyolefins, one can expect a four component spectra since they contain two phases, crystalline and amorphous. In these materials, two positronium components of PAL spectra might characterize free volumes in crystallites and more loosely packed amorphous phases. Though in numerous PAL investigations of polyethylene and other semi-crystalline polymers three component PAL spectra have been reported, a recent detailed investigation of semi-crystalline polyethylene and poly(tetrafluoroethylene) (PTFE) showed that two long-lived components ($\tau 3$ and $\tau 4$) can be identified and attributed to o-Ps annihilation in crystalline regions interstitial cavities and in holes in the amorphous phase, respectively.
- Investigation of free volume in highly porous inorganic sorbents using the PAL method can be complicated because of an additional channel for the disappearance of o-Ps due to its reaction with molecular oxygen adsorbed on pore walls. Similar quenching effect has been described for highly permeable PTMSP, where the longest lifetime is much larger if measured in the absence of oxygen (in a nitrogen atmosphere or in a vacuum).
- The role of oxygen in quenching o-Ps has not been widely studied in other polymers

Y. P. Yampoloskii, Macromolecules, 2000

POSITRONIUM CHEMISTRY

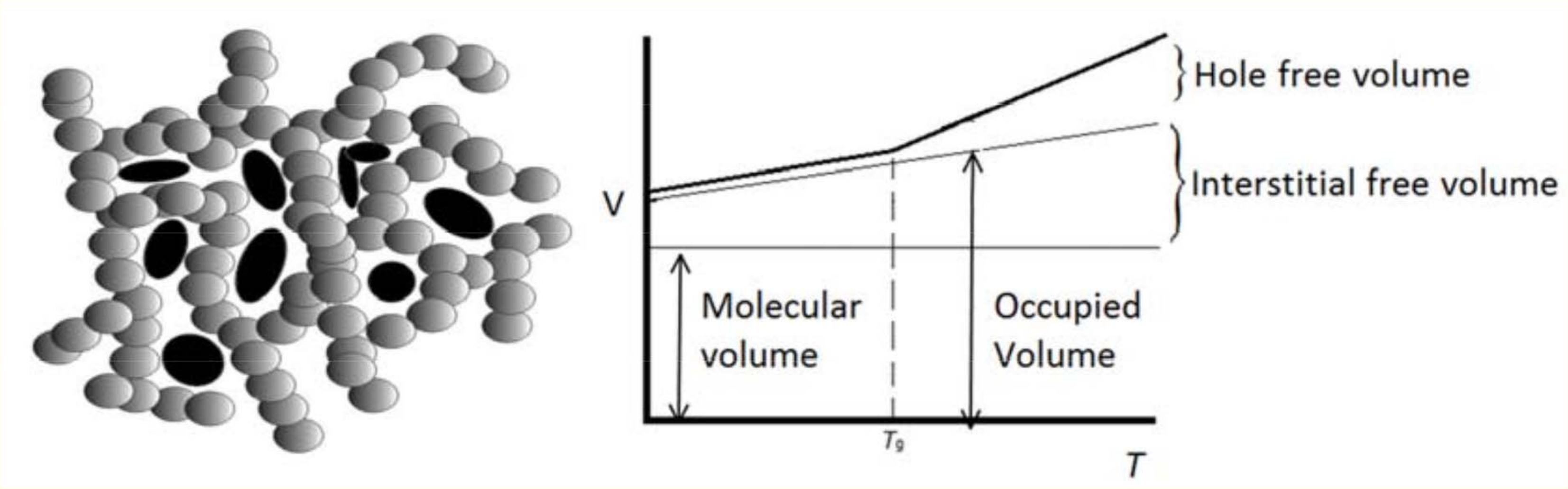
- Ps reacts with molecules and functional groups by two processes, namely, chemical quenching and chemical inhibition. The former decreases *o*-Positronium lifetime whereas the latter decreases the probability of *o*-Positronium formation
- Nitroaromatics, quinones maleic anhydride and ions with redox potential < 0.9 eV exhibit strong quenching. Polyimides exhibit strong quenching and inhibition of Ps formation
- Ps can also be quenched by water, polar organic solvents and adsorbed oxygen. Presence of trace water and polar solvents (trapped in voids) in many polymers cannot be avoided
- The potential of PAS to obtain chemical information is yet to be realized
- There is lack of systematic investigation of PAS data with different functional groups of the polymers

The modification of PAS parameters by chemical functional group on polymers is an area that need further attention since the chemical information inside the surface of free volumes or voids is essentially unknown. Positron and Positronium are uniquely sensitive to inner surface where they are localized

THE CONCEPT OF FREE VOLUME

- Molecular motions in the bulk depends on holes or voids where there are vacancies (H.Eyring, 1936)
- For chain macromolecules more than one “hole” is required in the same neighborhood since cooperative motions are involved (The Reptation Model of de Gennes). Thus for a segment of a polymer to move from one position to an adjacent site, a critical void volume must exist before the segment can jump
- These ”holes” are collectively called “free-volume”
- The free volume theory along with the kinetic and thermodynamic theories provides a comprehensive framework for understanding glass transitions in polymers
- In polymers the local free volumes and holes are at the atomic and molecular scale and directly affect the thermal, mechanical and relaxation properties of polymers. Typical radii of free volume in amorphous polymers are in the region of 2.5 to 4 Angstorm

SCHEMATIC REPRESENTATION OF a. HOLE VOLUME (BLACK ELLIPSOIDS) CONCEPT; AND b. RESPECTIVE VOLUMES.



a b

The concept of free-volume is a theoretical construct; It can be inferred only indirectly. It is both spatial and temporal and the underlying theory is based on both kinetics and thermodynamics.

Doctoral dissertation, Y.Yu, Martin-Luther Universitat, Halle-Wittenberg, October 2011

EXPERIMENTAL PROBES FOR FREE VOLUMES

- Limited probes available for experimentally measuring free volumes in view of the sub-nanometer dimensions and the short time scale for many molecular motions
- Many existing methods only measure static defects or holes
- PALS is a unique method which probes free volumes across space and time in sub-nanometer and sub-nanosecond range
- PALS can be used to determine glass transitions, physical and chemical aging, crystalline-amorphous interface studies and quantification of free volumes and their distributions.

Positron annihilation lifetime (PAL) spectroscopy can be considered as the most direct probe to estimate free volume in polymers

COMPARISON OF PAS WITH OTHER TECHNIQUES OF EXAMINING DEFECTS AND VOIDS IN MATERIALS

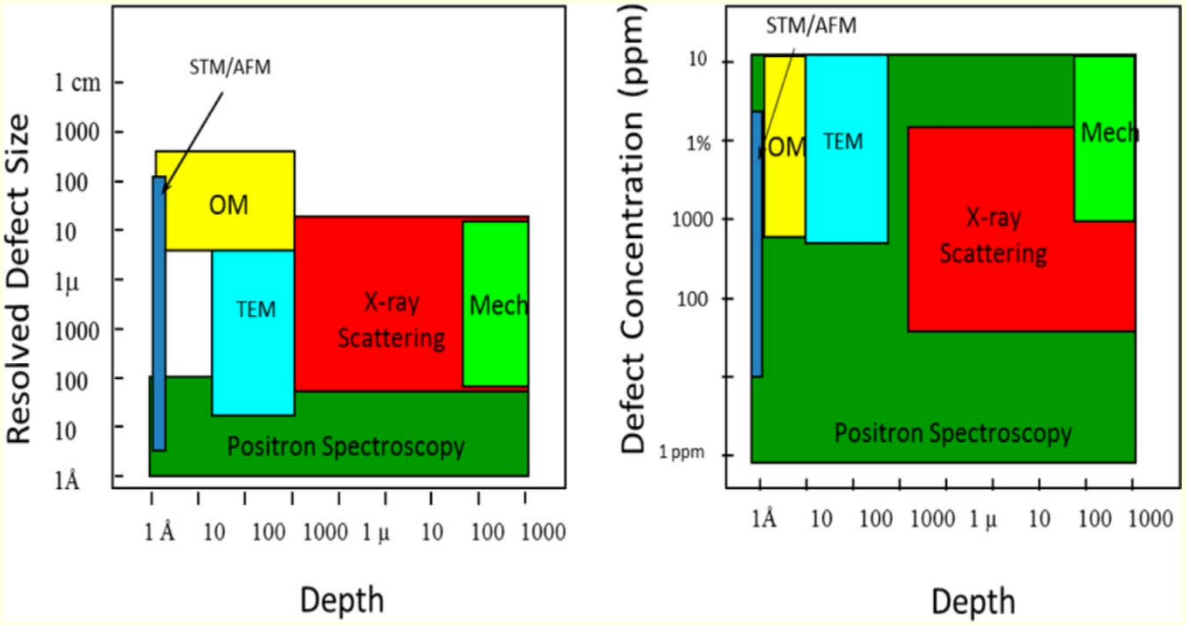


Figure 1. Comparison of PAS with various techniques for the examination of defects and voids in materials (OM, optical microscopy; TEM, transmission electron microscopy; STM, scanning tunneling microscopy; AFM, atomic force microscopy; Mech, mechanical techniques).[6]

Y.C.Jean, Macromolecules, 2013

CAN PALS MEASURE FREE VOLUME HOLE SIZE IN AMORPHOUS POLYMERS ?

- No clear conclusions as yet
- Positronium has a threshold for detecting free-volume holes; i.e., it can probe only holes larger than a size corresponding to the minimum for *o*-Ps localization.
- The chance for a Ps atom to remain in one particular hole for its entire lifetime is of the order of 1%;i.e., it appears that each positronium will sample a number of holes of different sizes before annihilating with a n electron.
- The lifetime of 0-Ps therefore reflects an average over the distribution of free-volume hole sizes in polymer materials
- Even if a reliable measurement of the *o*-Ps lifetime distribution has been obtained, there is no reason to believe that this lifetime distribution is a direct measure of the hole size distribution.

R. Simha, Macromolecules, 1995

DETERMINATION OF Tg OF POLYSTYRENE BY PALS

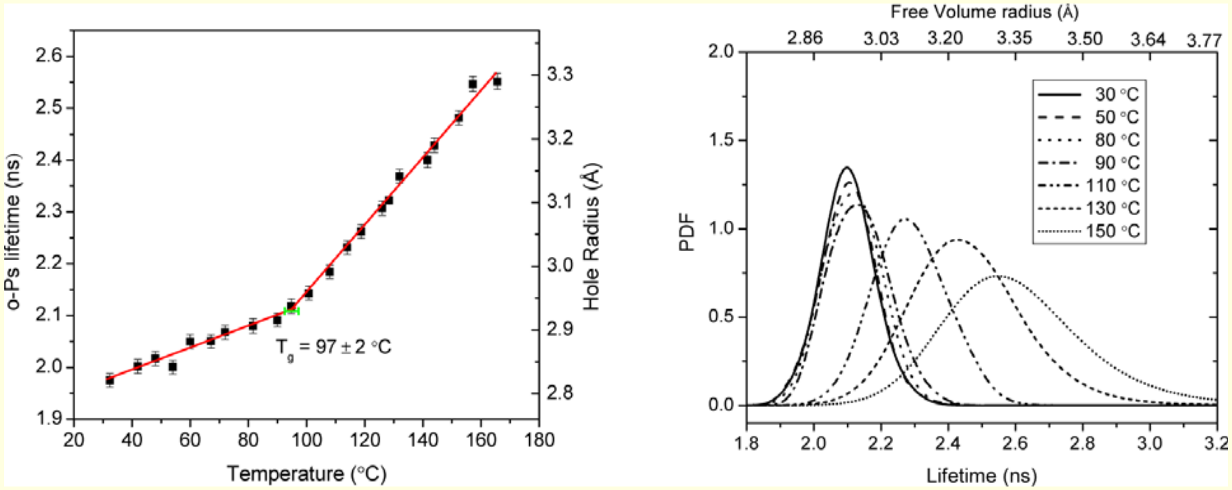


Figure 8. Determination of the glass transition in a thick polystyrene film (1 mm) from o-Ps lifetime (free-volume radius versus temperature, left). In this analysis the two linear regions are fitted with the intercept defined as T_g.[118] At right, the o-Ps lifetime distribution is plotted versus temperature.

Three useful parameters: the triplet state positronium life time, the full width at half-maximum from the distribution of triplet state positronium life time and the S parameter as a function of temperature

Y.C.Jean, Macromolecules, 2013

DEPENDENCE OF Tg of POLYSTYRENE AS A FUNCTION OF THICKNESS

(Y.C.Jean, Macromolecules, 2013)

- Tg is known to be a function of film thickness and decreases as thickness is reduced to the order of <100 nm
- PAS in combination with Variable Monoenergetic Slow Positron Beam techniques is a unique way of probing free-volume variation as function of depth from the surface or from the interface to the bulk

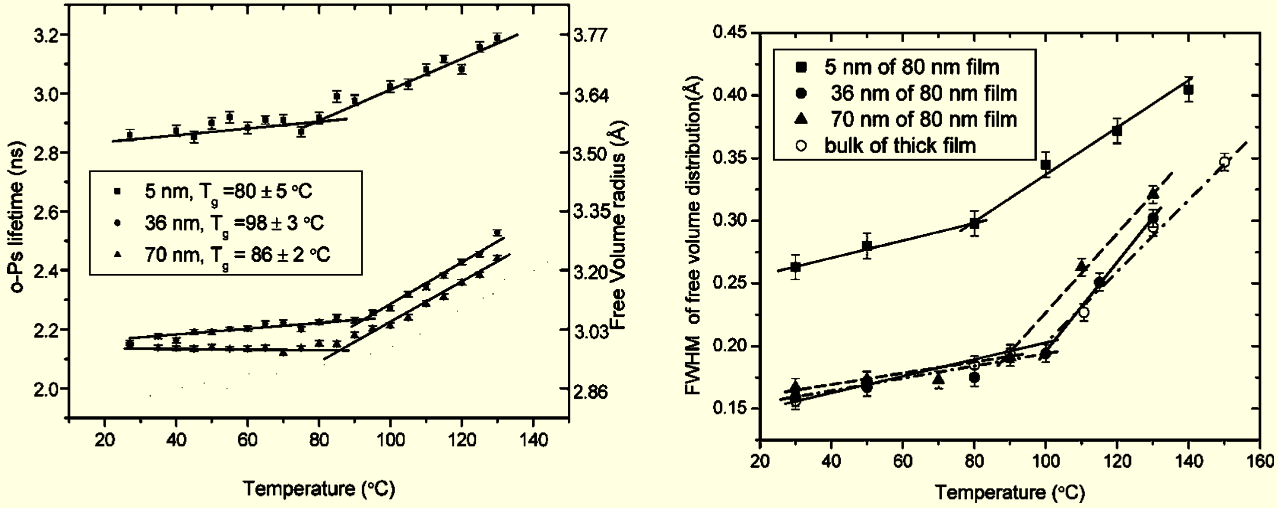
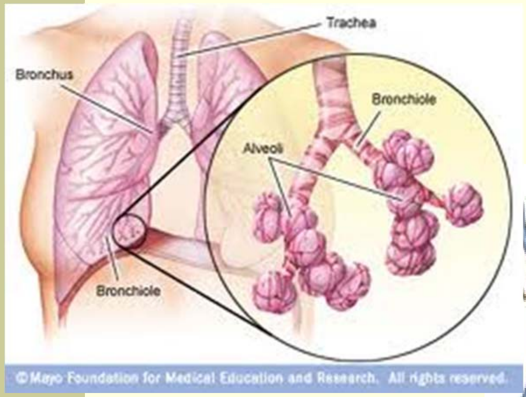
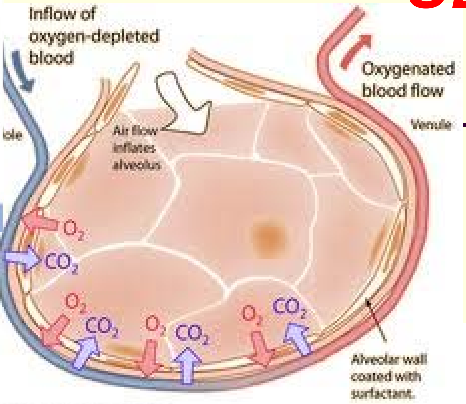


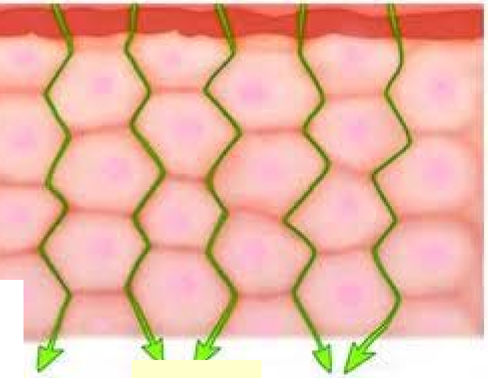
Figure 9. Determination of the glass transition in a thin polystyrene film (80 nm) from o-Ps lifetime (free-volume radius) versus temperature at three different locations in the film (left). The two linear regions are fitted with the intercept defined as T_g.[118] At right, the o-Ps lifetime distribution is plotted versus temperature.

POROUS MATERIALS ARE UBIQUITOUS !

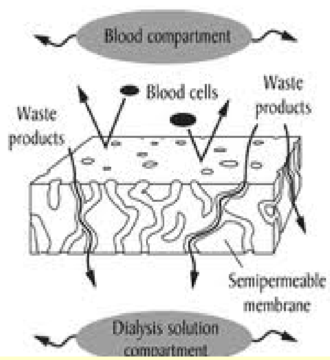




Alveoli in the lungs



Skin



Dialysis Membrane Polyacrylonitrile

Porous Carbon electrode

Max-Planck-Gesellschaft

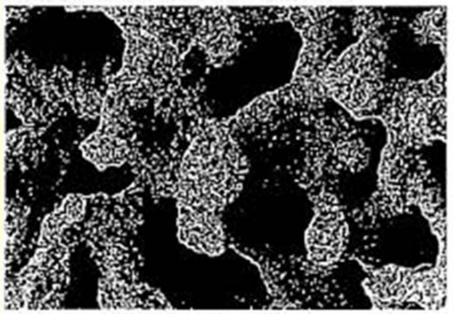
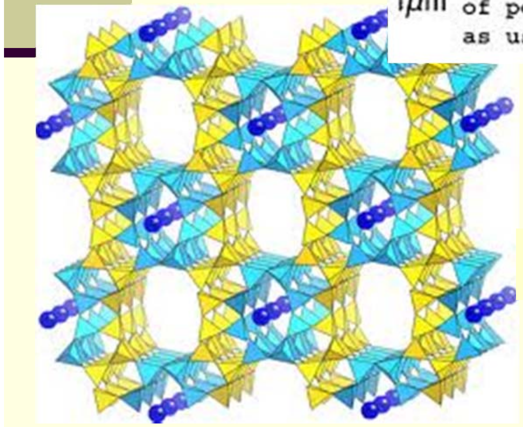


FIG. 3B SEM micrographs of porous carbon material as used for an electrode

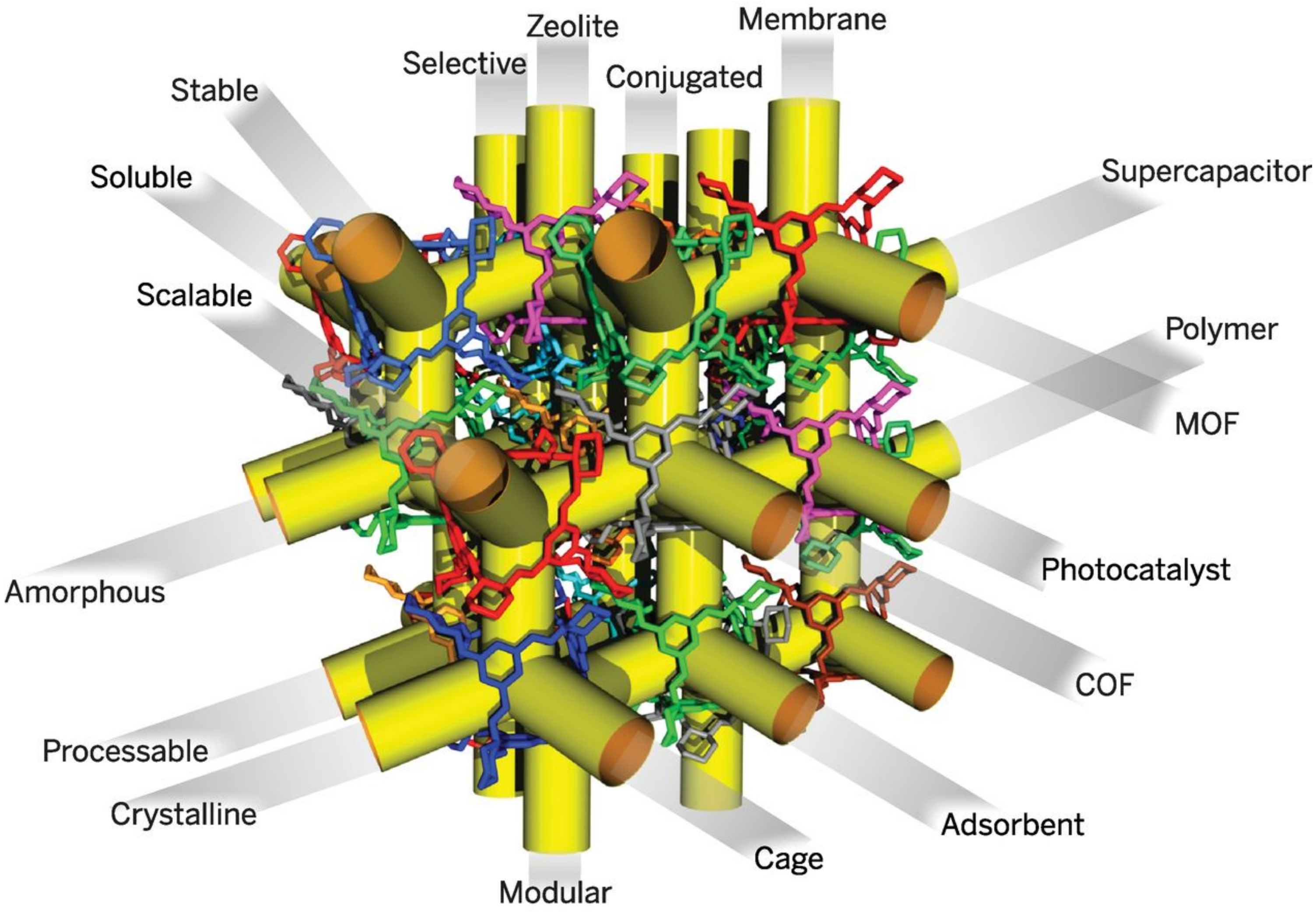


Zeolite 4A

Polystyrene foam cup

Polyurethane Floor mop

POROUS MATERIALS DEFINED BY TYPE OR BY FUNCTION,



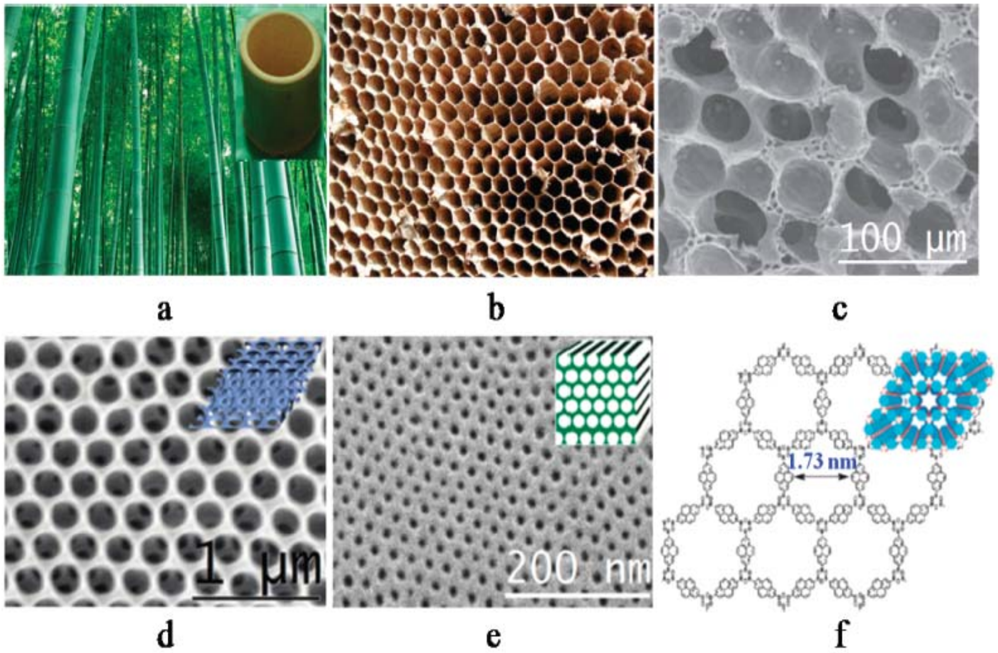
Anna G. Slater, and Andrew I. Cooper, Science 2015, 348, 6238

POROUS POLYMERS

Porous polymers are polymeric materials, which have pores in the structure of polymers. They are classified as :

Microporous < 2 nm.
Mesoporous = 2 to 50 nm.
Macroporous > 50 nm

Qiu, S.; Ben, T. ed. Porous Polymers, RSC, UK, 2015; Silverstein, M. S,;Cameron, M.R.; Hillmeyer, M.A. ed, Porous Polymers, Wiley, 2011 Wa et al,. Chemical Reviews, 2012; A.G. Slater and A.I.Cooper, Science, 348, 6238, 2015; Zhang et al., J. Mat. Chem.,A 5, 8795, 2017



SYNTHESIS

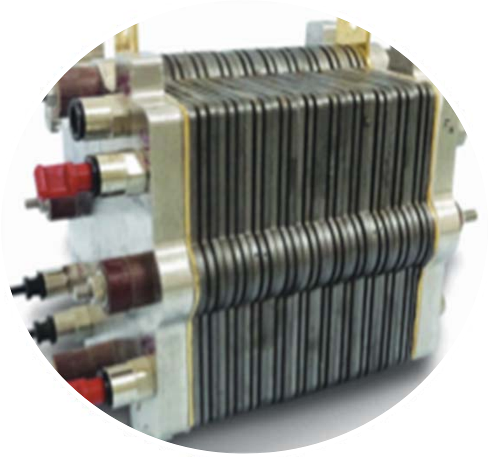
- Porogen incorporation and phase inversion
- Polymers with intrinsic porosity
- Thermal rearrangement
- Porous polymers with self assembled structures
- Colloidal templating
- High internal phase emulsion polymerization (Emulsion templated)

Applications of porous polymers

- Separation membranes (NF, OSN)
- Gas storage (adsorption) and separation membranes
- Catalysis
- Tissue engineering and scaffolds
- Biomedical devices
- High performance microelectronics
- Templates for porous ceramics and carbon
- Selective proton and lithium ion transport membranes

FUNCTIONAL POROUS POLYMERS IN ENERGY APPLICATIONS

- Energy Storage : Separator membranes for selective lithium ion transport



- Energy Generation : Proton conducting membranes for polymer electrolyte fuel cells

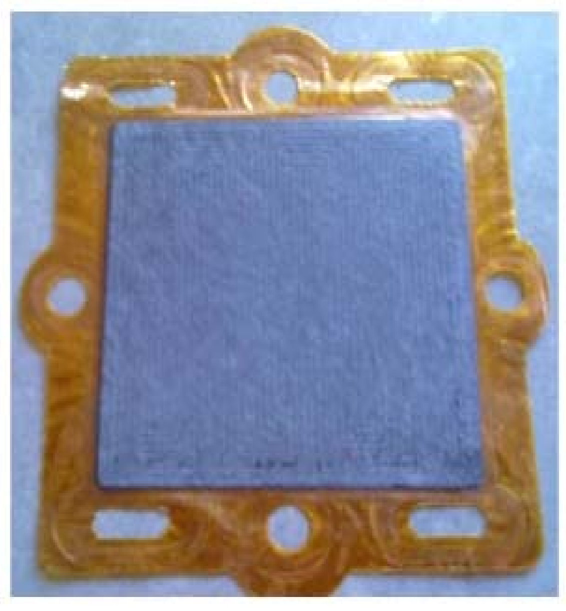
POLYMER STRUCTURE

- Ring substitution
  electronic/ steric
- Co-monomers
  flelxible / rigid
- Porosity
- **Crosslinking**

POROSITY

PROPERTY

- Molecular weight
- Tg / free volume
- Crystalline/amorphous
- Acid binding sites
- Water retention
- Tensile strength and elongation



PERFORMANCE

- Chemical stability
- Thermal stability
- Proton conductivity
- Gas permeability

STRUCTURE – PROPERTY – PERFORMANCE MATRIX FOR FUEL CELL MEMBRANES

FLEXIBLE AND SEMI RIGID POLYMERS

Flexible Polymers	Semi-rigid Polymers
• A distribution of penetrant scale voids or holes occur constantly within the material due to segmental motions. • Entropic factor is negligible; Lack of entropic factor reflects the difficulty in controlling the penetrant rotational and vibrational modes in the diffusion transition state due to imprecisely controlled segmental motions. • In such material there is a trade off between lower permeability of desired component A with higher A/B selectivity. • Additionally, in presence of sorbents, segmental mobility is increased due to plasticization which results in reduced selectivity	• Materials with intermediate rigidity, occupying the space between flexible polymers and crystalline molecular sieve type materials. • These polymers possess micropores and sub-nano range of pores. • Exhibit small scale motions at critical points along the backbone • PIMs and TR Polymers belong to this class of materials. • These materials have redefined the so-called polymer upper bound for solution processable polymers of some gas pairs.

RIGID POROUS SOLIDS, SEMI-RIGID AND FLEXIBLE POLYMERS

Rigid Pores

Connected and permanent porosity

Transient porosity based on segmental motion

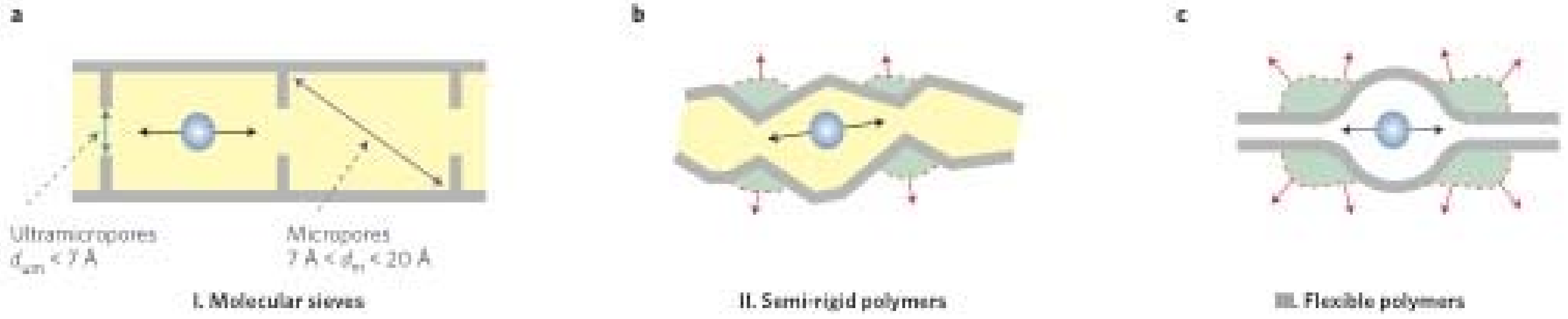
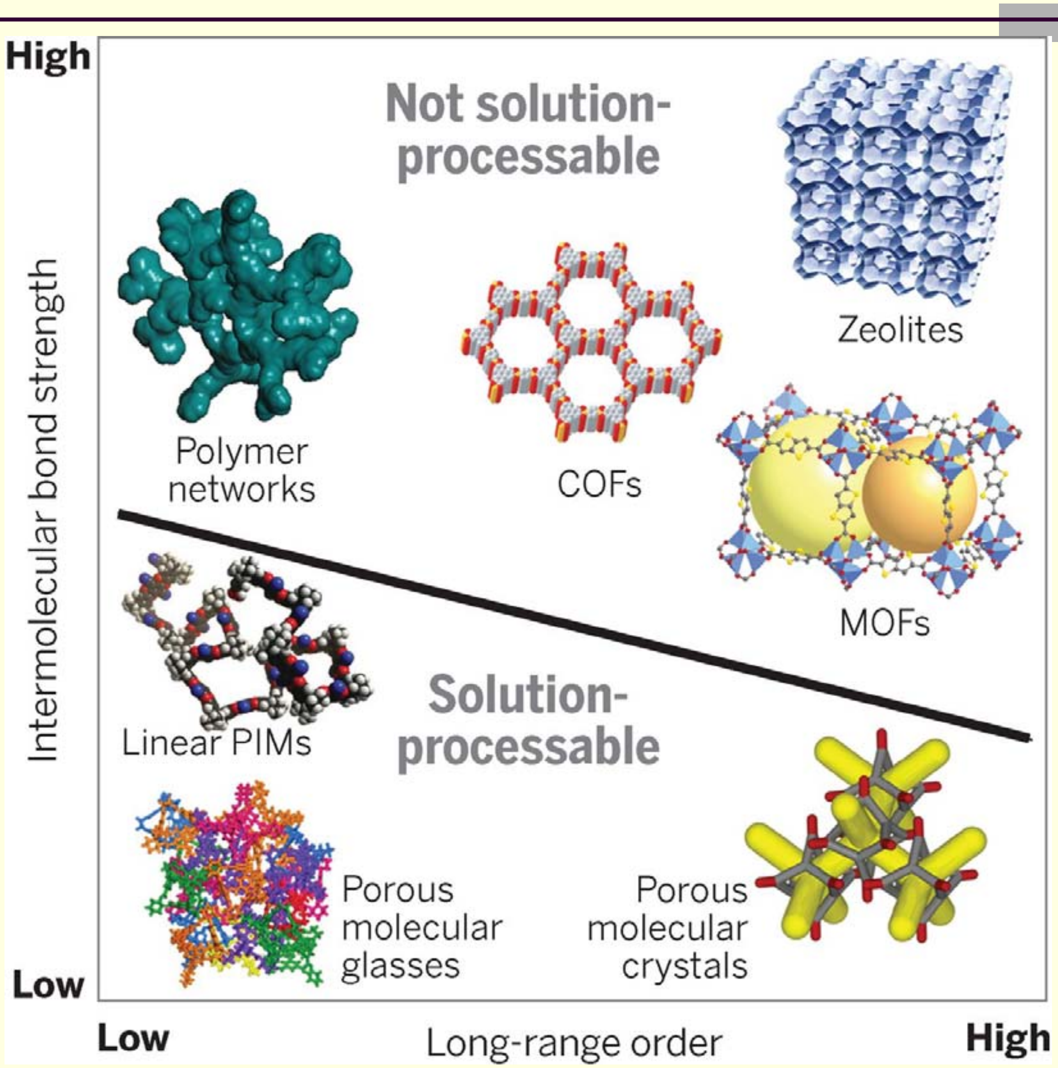


Figure 1 | Molecular diffusion selective media. a, Molecular sieves (type I), with rigid ultramicropore and micropore morphology. **b**, Semi-rigid polymers (type II), with connected porosity distribution created by segmental packing. **c**, Flexible polymers (type III), with transient gap distribution created by segmental packing and motion. In the case of molecular sieves (**a**) and semi-rigid polymers (**b**), the yellow shaded areas represent permanent porosity, which is not present in flexible polymers (**c**). The green shaded areas represent motion-enabled zones of activation needed for diffusion.

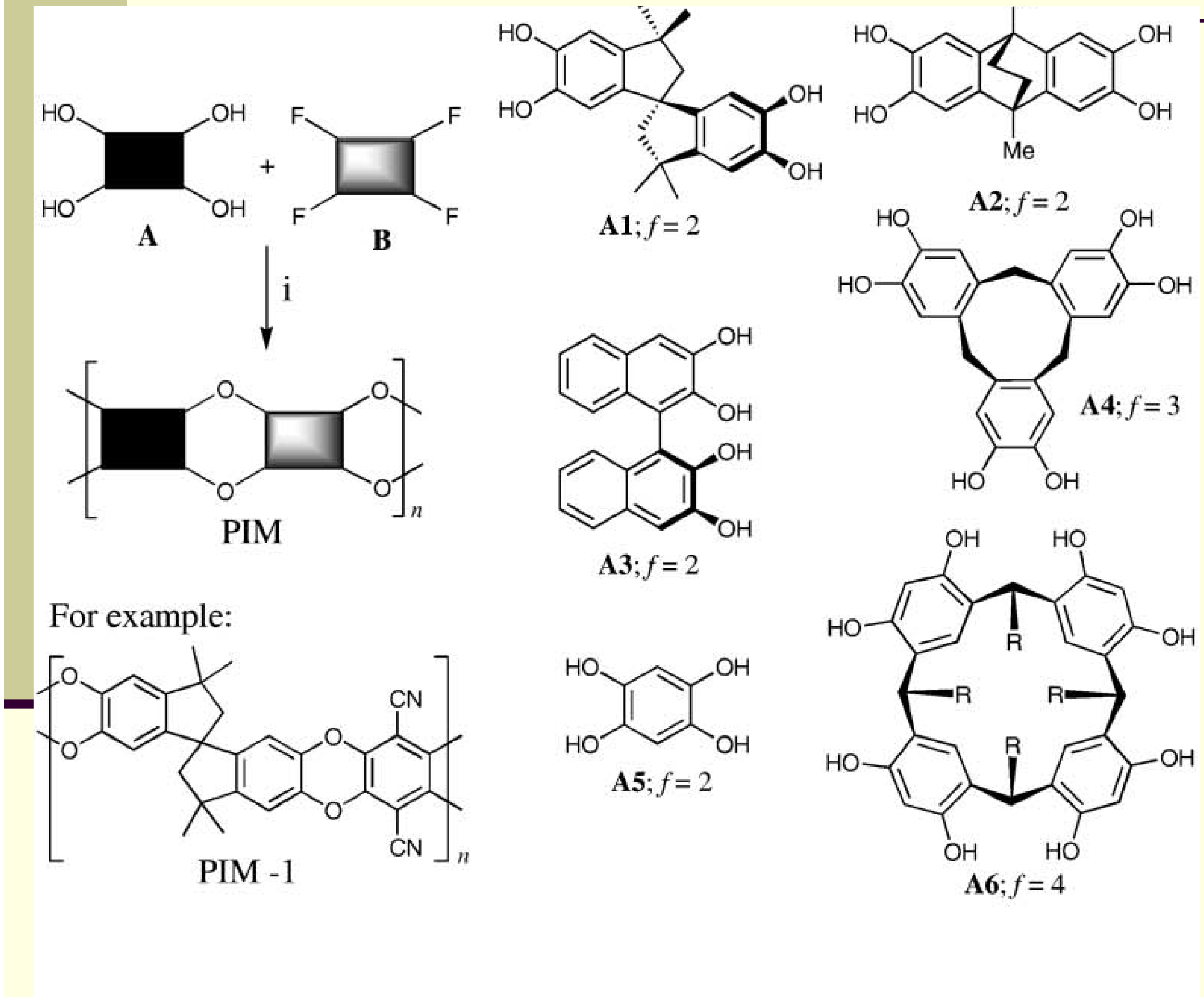
W.J. Koros, Nature Materials, 2017

FUNCTIONAL CLASSIFICATION OF POROUS SOLIDS

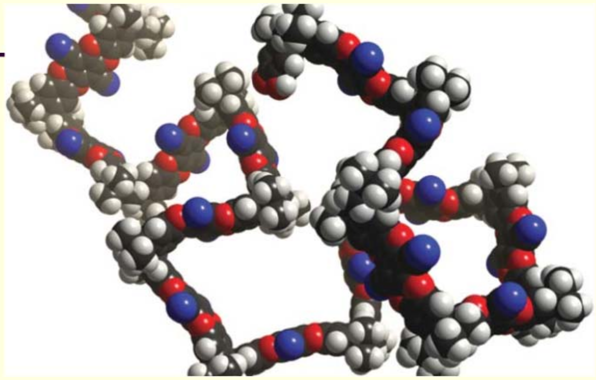
Anna G. Slater, and Andrew I. Cooper Science 2015;348: 6238



POLYMERS WITH INTRINSIC MICROPOROSITY : USE OF CONTORTED MONOMERS

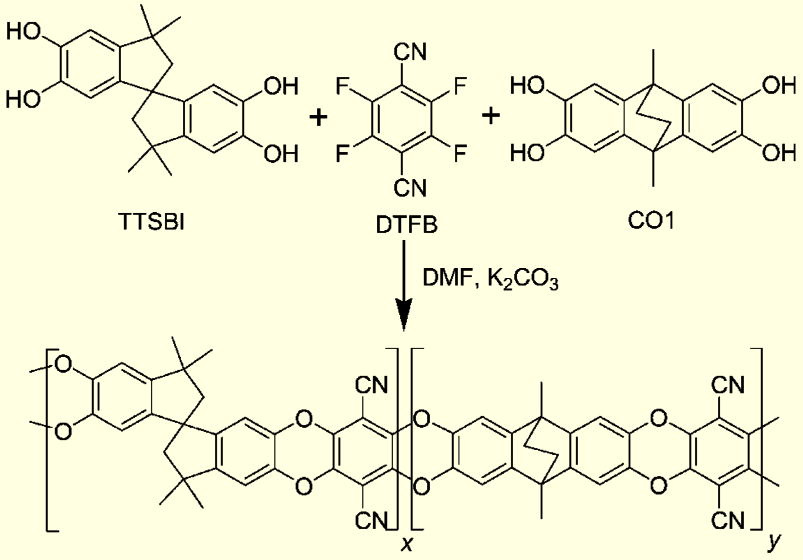


Chem. Soc. Rev., 35, 675, 2006



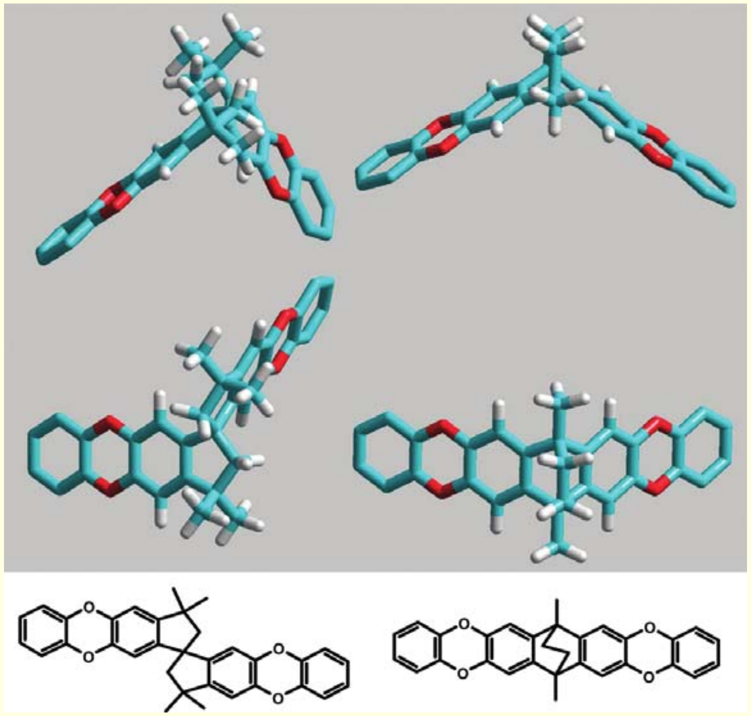
- Ladder like non-planar structures with sites of contortion
- Hindered chain packing leading to large free volumes
- Limited rotational freedom
- Typical pore sizes of 5 to15Å and surface area of 500 to 1500 m^2/g

POLYMERS WITH INTRINSIC MICROPOROSITY : USE OF CONTORTED MONOMERS



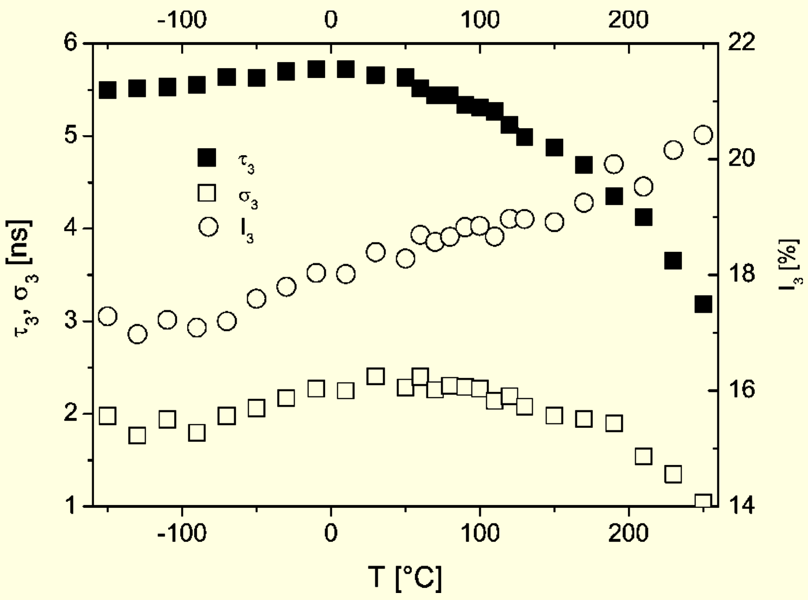
PIM-1: *x*:*y*=100:0

PIM1-CO1-40: *x*:*y*=60:40



Surface area > 750 m^2/ g

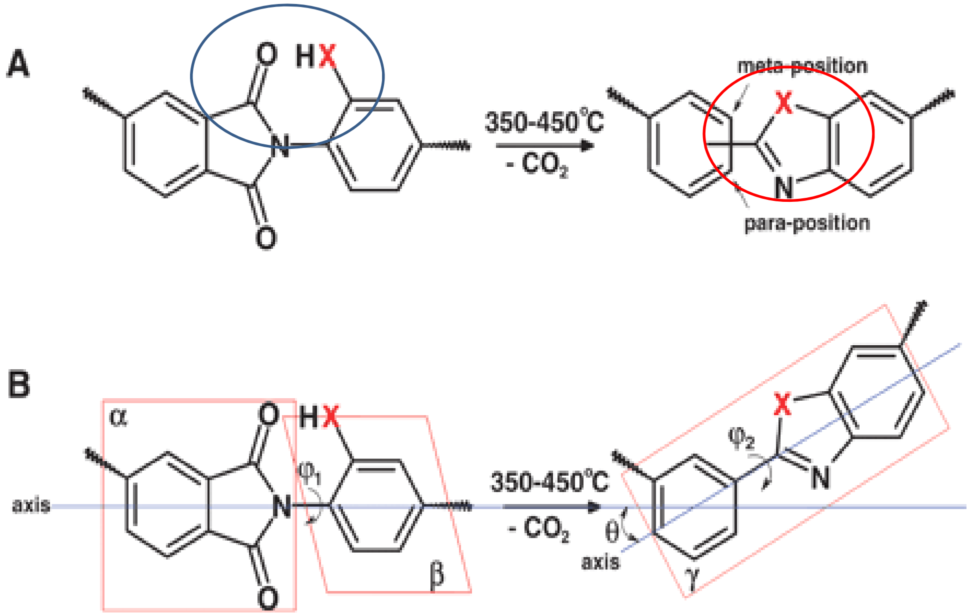
TEMPERATURE DEPENDENCE OF O-PS LIFETIME, DISPERSION AND INTENSITY OF PIM1-CO1-40.

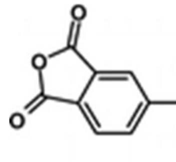


Maximum in τ_3 at approximately 0

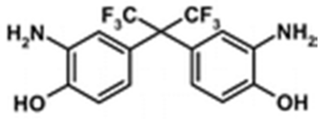
T, C	*o-ps lifetime, ns*	*Spherical hole diameter, A*
-150	5.47	9.93
-25	5.81	10.22
+25	5.92	10.31
+50	5.92	10.31
+100	5.86	10.26
+250	4.92	9.43

THERMALLY REARRNAGEMENT : A ROUTE TO POLYMERS WITH INTRINSIC MICROPOROSITY

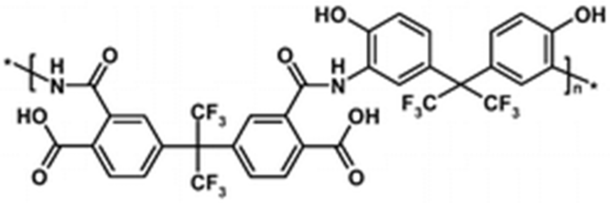




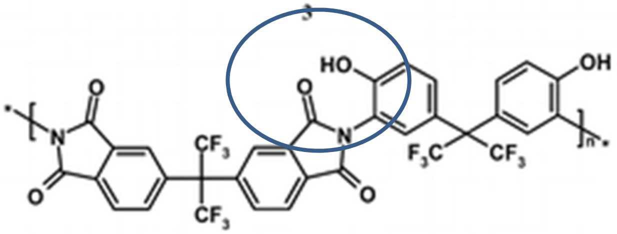
1



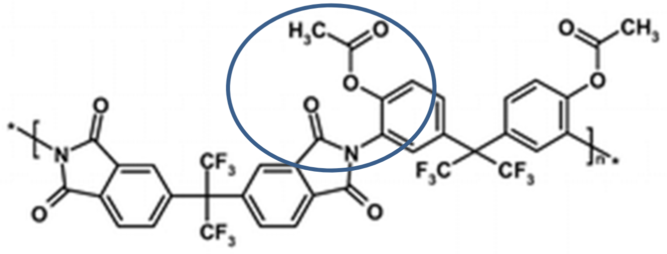
2



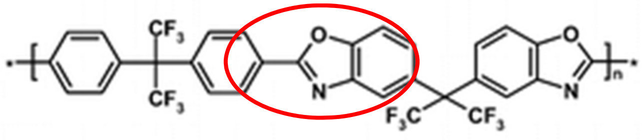
3



4a (tHPI), 4b (aHPI)



4c (cAcPI), 4d (sAcPI)



5a (tPBO), 5b (aPBO), 5c (cPBO), 5d (sPBO)

- *Change of chain conformation: meta- and para-linked chains can be created*
- *Spatial relocation due to chain rearrangement in confinement, leading to generation of free volume elements*
- *Cavity radius about 3.6 to 3,8 Angstorm as determined by o-Ps lifetime*

CONCLUSION

- Bottoms up approach in chemical synthesis is enabling synthesis of diverse nano- , micro – and meso-porous polymers with a variety of pore size, pore morphology and pore surface functionality
- There is a need to understand many fine features of such structures to tailor useful applications. Examples are transient and permanent voids, pore geometry, depth dependent pore structure, connectivity between pores, tortuosity and in thin film composites, the nature of pores at interface
- No single tool is capable of providing all the information
- PAS is fast emerging as a valuable tool in the armory of polymer chemists to examine such polymers and to better understand structure- property–performance relationship.

THANK YOU FOR YOUR PATIENT LISTENING

IISER PUNE