Porosity Analysis in Soft Microporous Matter

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Microporous Polymers
• found interest in gas separation/storage; catalysis applications
• can be synthesized by a large number of ways
• are amorphous, light weight and chemically stable
but:
their porosity is far less understood (compared to inorganics)

Intrinsically Microporous Polymers
are based on hindered packing of contorted, still polymers
(ultra-high free volume is obtained and accessible – measurable microporosity)

H₂ sorption at 77.3K revealed the presence of microporosity for almost all materials (precipitated)
However: still some unusual isotherms (strong hysteresis upon desorption)
H₂ sorption: Irena Senkovska, Stefan Kaskel (TU Dresden)

Carbon dioxide sorption at 273K: all materials adsorb CO₂ – even in the solvent cast state (no H₂ adsorption for cast films)
Solubility effects? Temperature effect?

Preliminary experiments show that solubility could most probably be ruled out!
(no significant difference in adsorption enthalpy between differently processed samples)
Influence of polymer chain dynamics at the different measurement temperatures seems more important (see scheme below)

Conclusions
when analyzing microporous polymers one has to pay attention to:

Analysis Temperature
Polymeric structures exhibit significant differences in mobility at 77K and 273K, respectively
Impact on pore accessibility

Processing History
Polymer precipitation/ freeze drying can yield metastable states
Difference to film casting/ evaporative drying
Impact on pore accessibility and size

Intra/Intermolecular Interactions
Interactions (e.g. hydrogen-bonding) can close pores of soft porous matter!
Switchable porosity

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