Effect of block composition on structure in mesoporous block polymers

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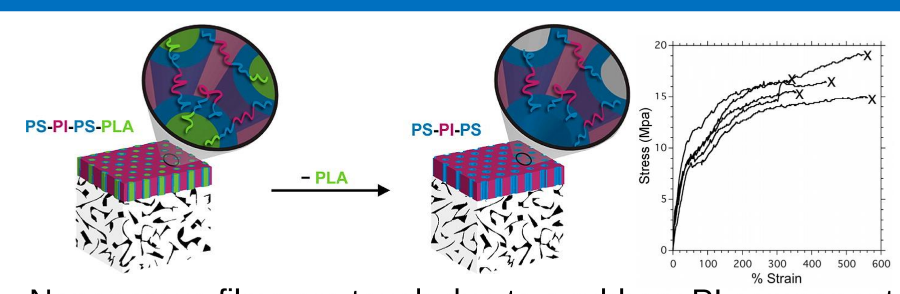
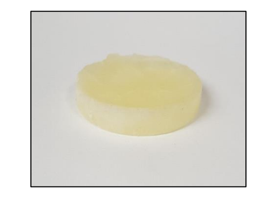
Background and motivation

Mesoporous monoliths are desirable for separations
– Mesopores (2 – 50 nm diameter) can provide high surface area and enhanced selectivity



Nanoporous films are tough due to a rubbery PI component
Jackson, E. A.; Lee, Y.; Hillmyer, M.A. *Macromolecules* **2013**, *46*, 1484-1491.

Polymerization-induced microphase separation: an attractive route towards mesoporous materials
– Dissimilar polymer blocks microphase separate during polymerization, creating chemically distinct domains
– In-situ chemical crosslinking traps resulting structure
– Polymerization is amenable to both monoliths and thin-films, and yields materials with percolating mesopores



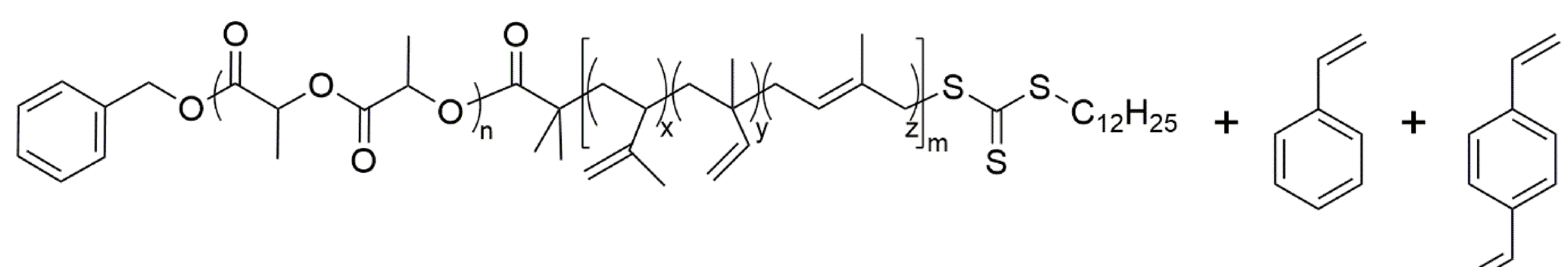
Mesoporous polymer monolith (diameter = 25 mm)

Challenge: obtaining tougher monoliths

Why: Previously studied materials have focused on glassy matrices, which are brittle

Approach: integrate rubbery domains into existing glassy mesoporous polymer systems

Facile synthesis of nanoporous monoliths



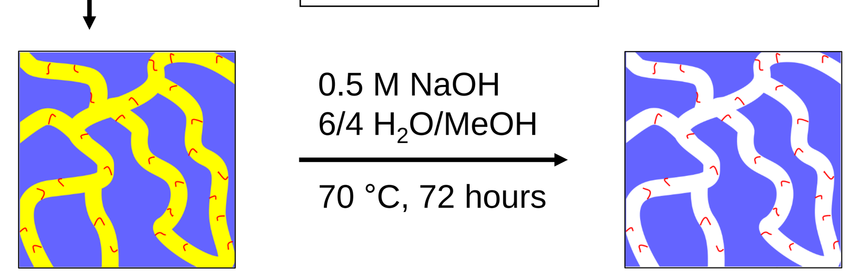
Poly(lactide)-*block*-poly(isoprene) (PLA-*b*-PI) macro-chain transfer agent
15, 33, or 45 wt% loading

Styrene (S) and Divinylbenzene (DVB)

Macro-CTA M_n(PLA)-M_n(PI) (kg mol^{-1})
15-0 (control)
26-0 (control)
28-0 (control)
26-11
15-15
32-5.5
27-7
27-15

AIBN, 120 °C, 20 hours

PLA
PI
P(S-*co*-DVB)

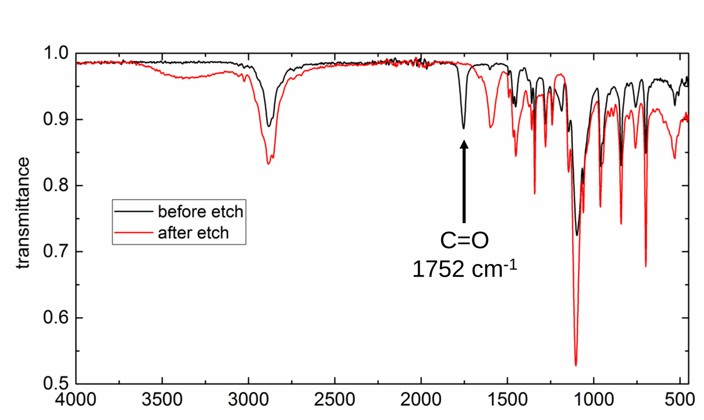


Polymerization-induced microphase separation

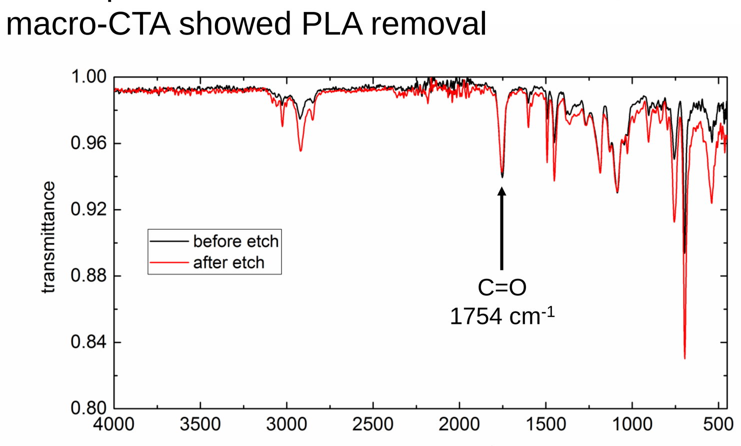
Well-defined mesoporous network with PI-lined pore walls

Determination of PLA accessibility in precursor monoliths

Complete etching of PLA in monoliths derived from 33, 45 wt% macro-CTA
– Confirmed with FT-IR
– PLA domains accessible to aqueous etch solution



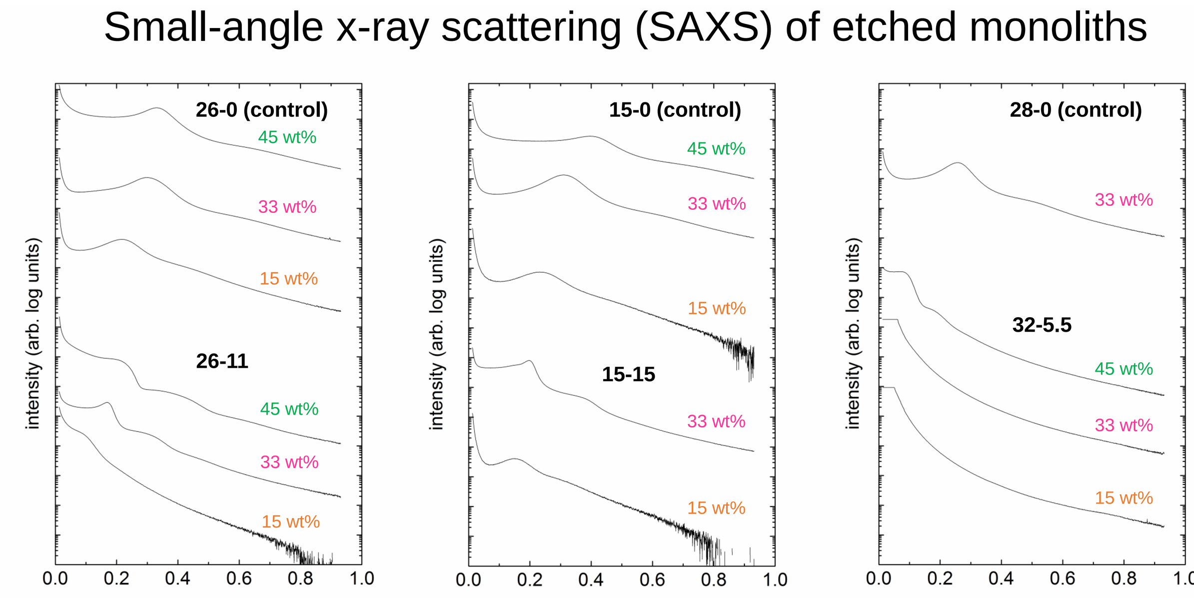
PLA domains isolated from etch solution in monoliths derived from 15 wt% macro-CTA
– Carbonyl functionality observed after etch
– Exception: monolith derived from 32-5.5, 15 wt% macro-CTA showed PLA removal



Disordered mesoporous structures with high surface areas

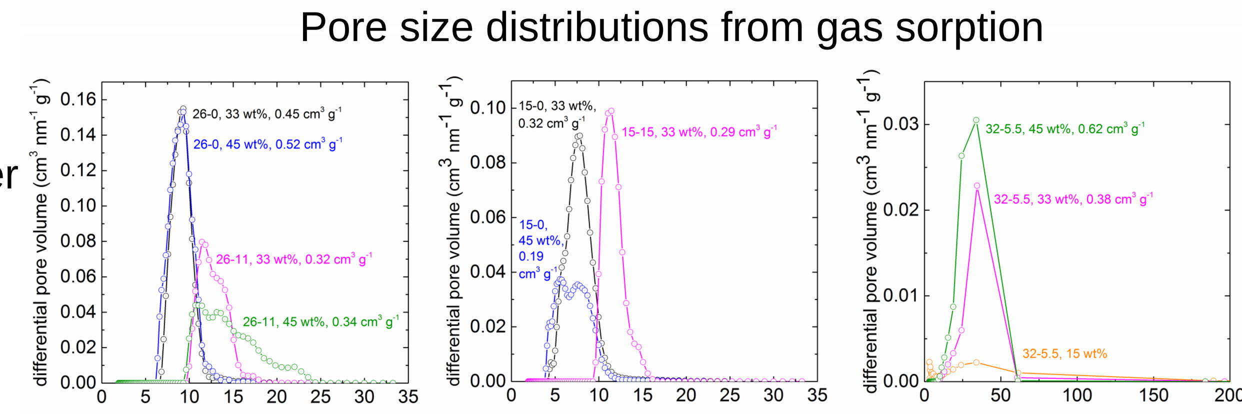
Monoliths derived from PLA-*b*-PI-CTA exhibit disordered microphase-separated structure
– Domain spacings of 30 – 75 nm determined by SAXS
– Comparison with SAXS profiles prior to etching suggests structural integrity (data not shown)
– Domain spacing decreases with increasing diblock loading
– Second order peaks suggest local ordering in 33, 45 wt% macro-CTA systems

Small-angle x-ray scattering (SAXS) of etched monoliths

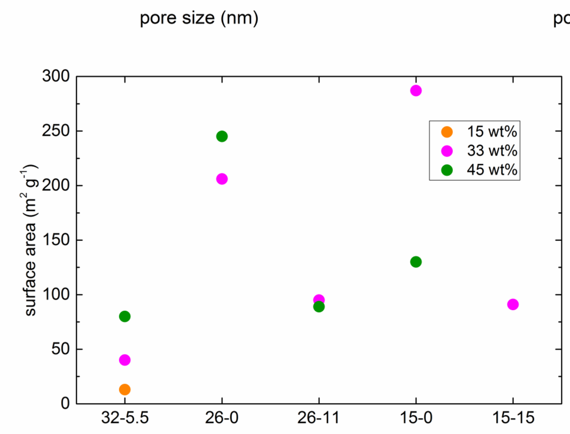


Pore size distributions from gas sorption

Monoliths derived from PLA-*b*-PI-CTA have larger pore diameters, smaller pore volumes when compared to monoliths derived from PLA-CTA



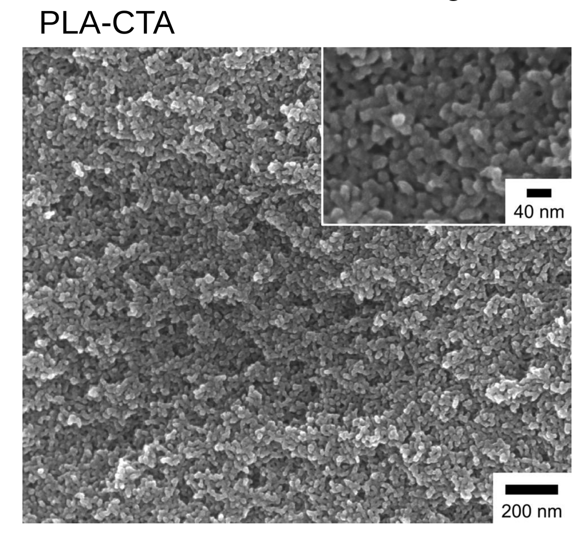
High surface area monoliths
– Surface areas are 13 – 95 m^2 g^{-1} determined by BET analysis
– Surface area decreases when compared to analogous systems that do not contain PI



Disordered morphology comparable to monoliths that do not contain PI

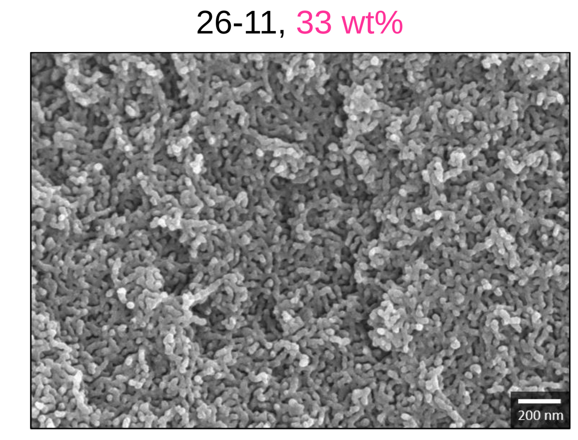
Mesoporous structures observed in scanning electron microscopy

Monolith obtained from 22 kg mol^{-1} PLA-CTA

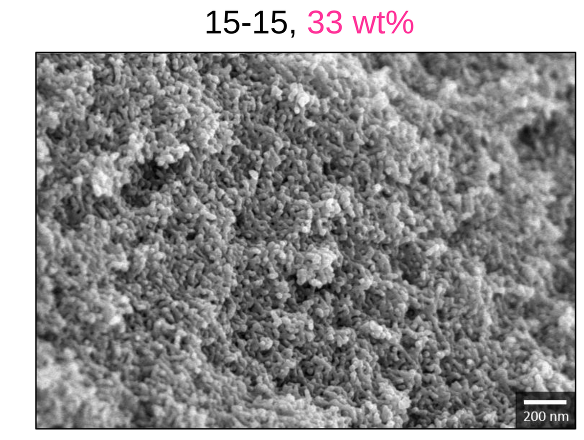


Seo, M.; Hillmyer, M. A. *Science* **2012**, *336*, 1422-1425.

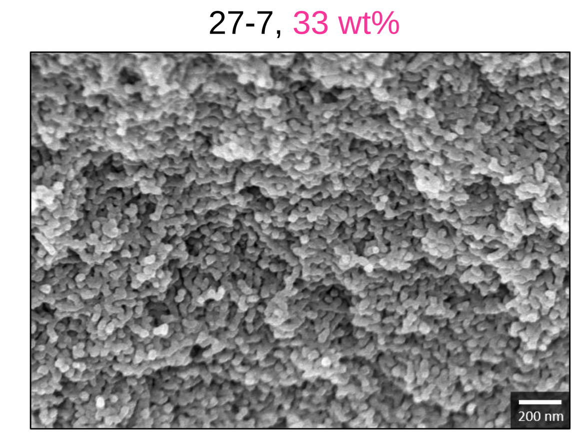
26-11, 33 wt%



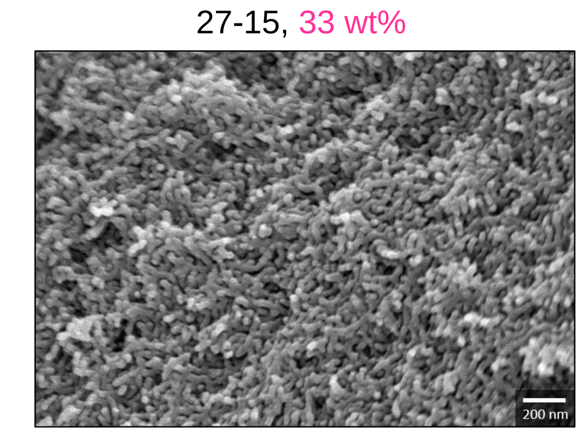
15-15, 33 wt%



27-7, 33 wt%

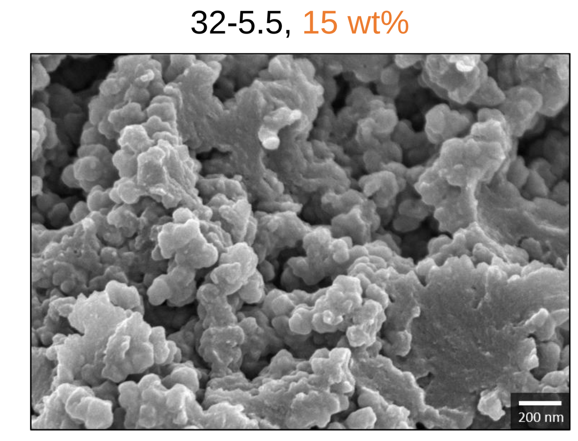


27-15, 33 wt%

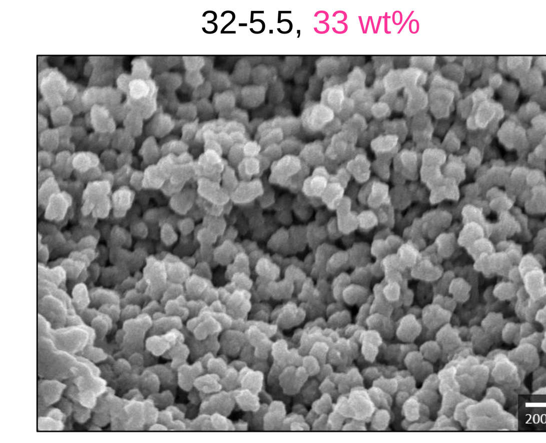


Monoliths derived from 32-5.5 PLA-*b*-PI exhibit structures observed in related systems
– Diblock composition and loading greatly influences nanostructure formation

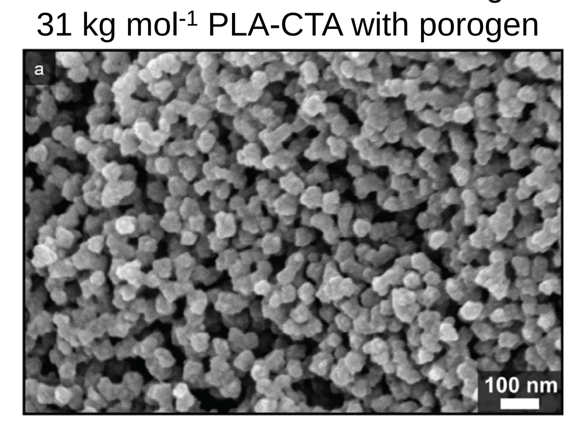
32-5.5, 15 wt%



32-5.5, 33 wt%

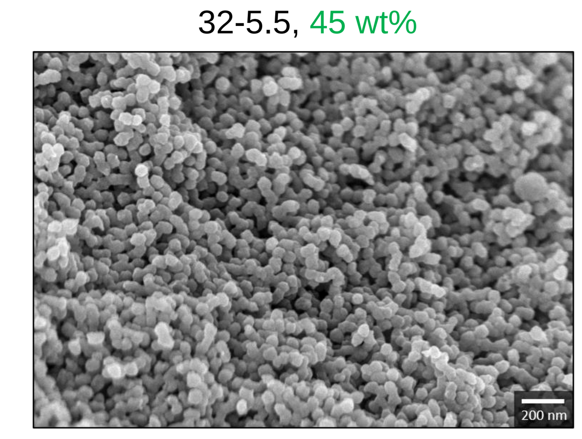


Monolith obtained from blending 31 kg mol^{-1} PLA-CTA with porogen



Saba, S. A.; Mousavi, M. P. S.; Bühlmann, P.; Hillmyer, M. A. *J. Am. Chem. Soc.*, **2015**, *137*, 8896-8899.

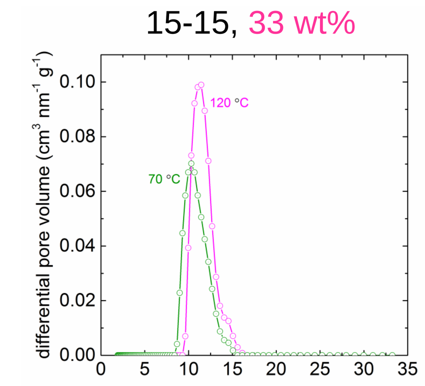
32-5.5, 45 wt%



Modifying reaction temperature and set-up

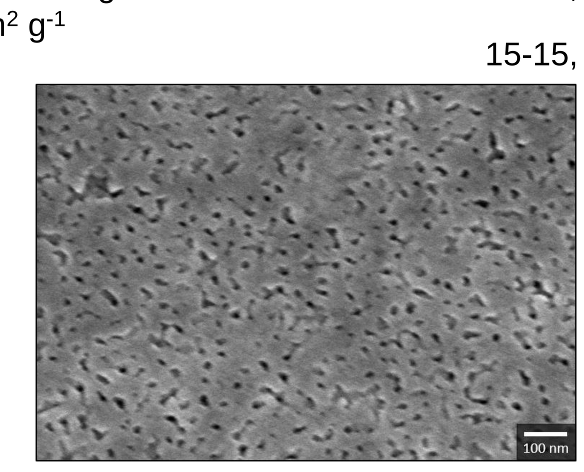
Lower reaction temperature
– Ran at 70 °C for 20 hours
– Minimal effects on pore diameter
– Decreases pore volume from 0.29 to 0.22 cm^3 g^{-1}
– Decreases surface area from 91 to 78 m^2 g^{-1}

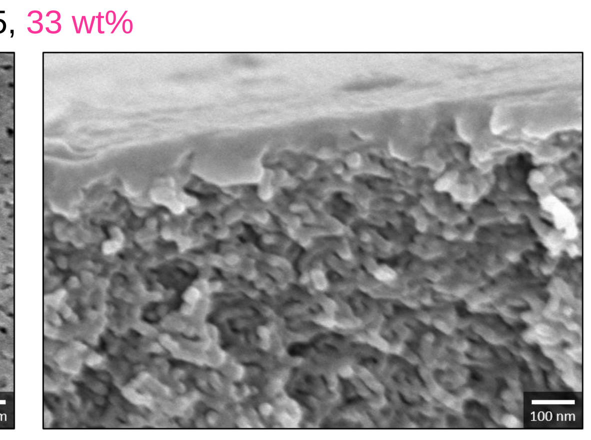
15-15, 33 wt%



Thin-film analog
– Modified reaction set-up to fabricate a 250 μm film
– Retains disordered morphology
– Surface effects visible, suggests limited pore access

15-15, 33 wt%





Conclusions and future work

– Mesoporous materials with good control over pore size are readily obtainable from PLA-*b*-PI-CTA
– System is versatile and allows for thin-film fabrication
– Chemically functionalizing pore walls for tailored applications will be explored
– Effect of PI on mechanical properties will be elucidated

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