Magnetic properties and structure of thermoresponsive polystyrene-block-poly(N-isopropylacrylamide) / iron oxide nanocomposite thin films

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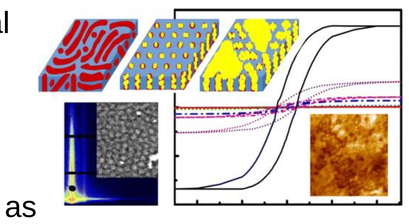
Motivation

Thermoresponsive Diblock Copolymer

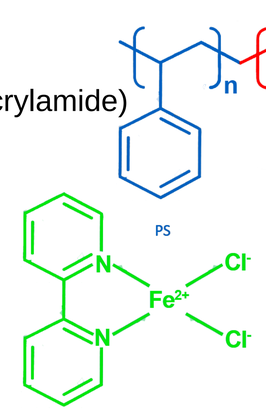
- Phase separation above the lower critical solution temperature (LCST) [1]
- Swelling / Deswelling transition
- Hydrophilic / Hydrophobic balance
- Controllable diblock copolymer structure as template [2]
- Application in sensors, catalysts, optics, targeted drugs and etc. [3].

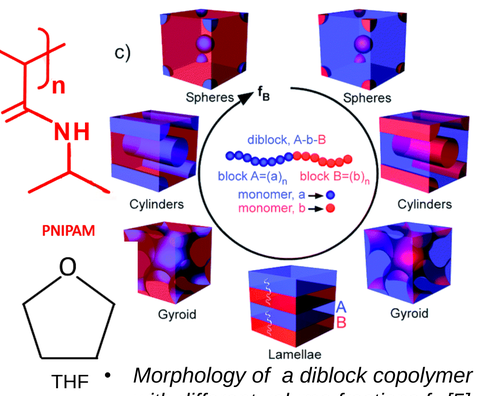


- *Superparamagnetic hybrid films composed of maghemite (γ-Fe_2O_3) nanoparticles and an asymmetric diblock copolymer (DBC) polystyrene$_{61}$-block-polyN-isopropylacrylamide$_{115}$ [4]*

Materials and Structure

- **PS-*b*-PNIPAM**
  - Polystyrene-block-Poly(N-isopropylacrylamide)
  - $PS_{(16000)}$-b-$PNIPAM_{(9500)}$, Mw/Mn:1.3
  - Dissolved in THF (Tetrahydrofuran)
- **Iron Salt**
  - $FeCl_2$(2, 2'-dipyridyl)
  - Dissolved in Methanol



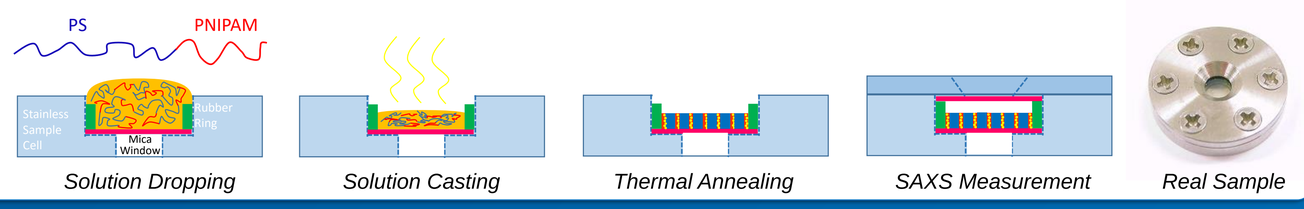


THF

- *Morphology of a diblock copolymer with different volume fractions f_B [5]*

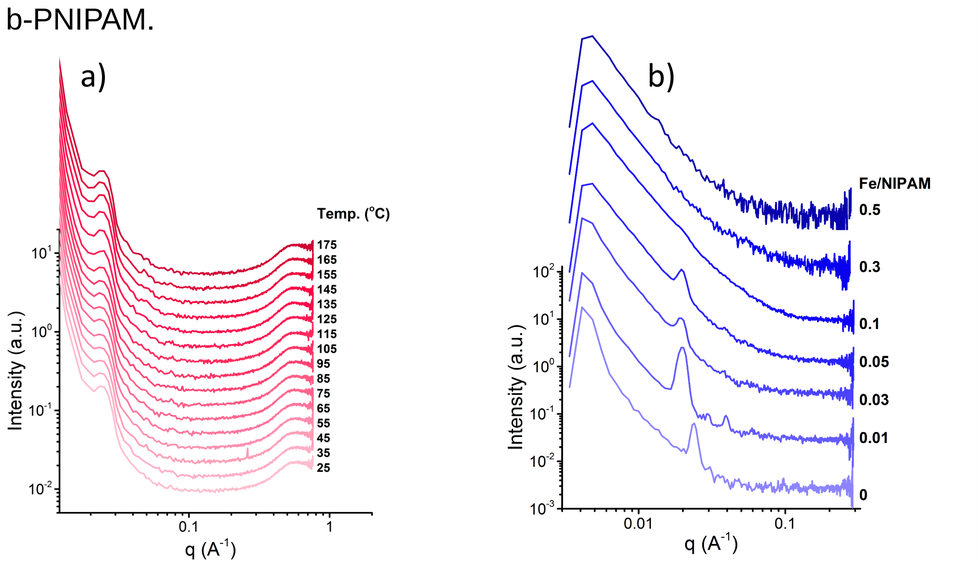
Sample Preparation

- Iron oxide/PS-b-PNIPAM hybrid bulk materials with various Fe/NIPAM molecular ratios were prepared via solution casting using THF (tetrahydrofuran) as solvent for PS-b-PNIPAM and methanol for $FeCl_2$(2, 2'-dipyridyl).
- The as-cast samples were pre-annealed in nitrogen gas atmosphere for 48 hours at the glass transition temperature of PNIPAM, which is around 130°C [1].



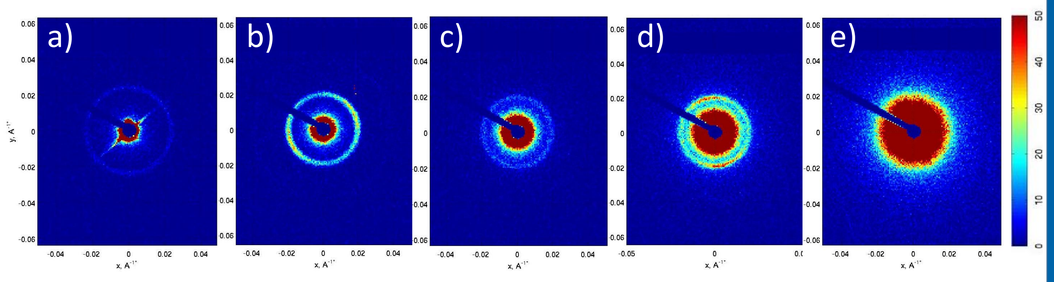
Film Structure (SAXS)

- Small angle X-ray scattering (SAXS) measurements were carried out to analyze the inner morphology of the iron-polymer hybrid materials.
- Compared with pure polymer, additional Fe oxide can change the diblock polymer structure significantly thus a shift on q vector can be observed.
- When the molecular ratio of Fe/NIPAM is as low as 0.01, the contrast of the structure gets improved, thus even second scattering peak can be observed. While the ratio increased above 0.1, the diblock copolymer structure disappeared because of the saturation of Fe oxide inside PS-b-PNIPAM.



a) *In-situ temperature dependent SAXS measurement profiles of PS-b-PNIPAM DBC that pre-annealed at 130°C during the heating up from 25°C to 175°C. The curves are shifted along the y axis for clarity of the presentation.*

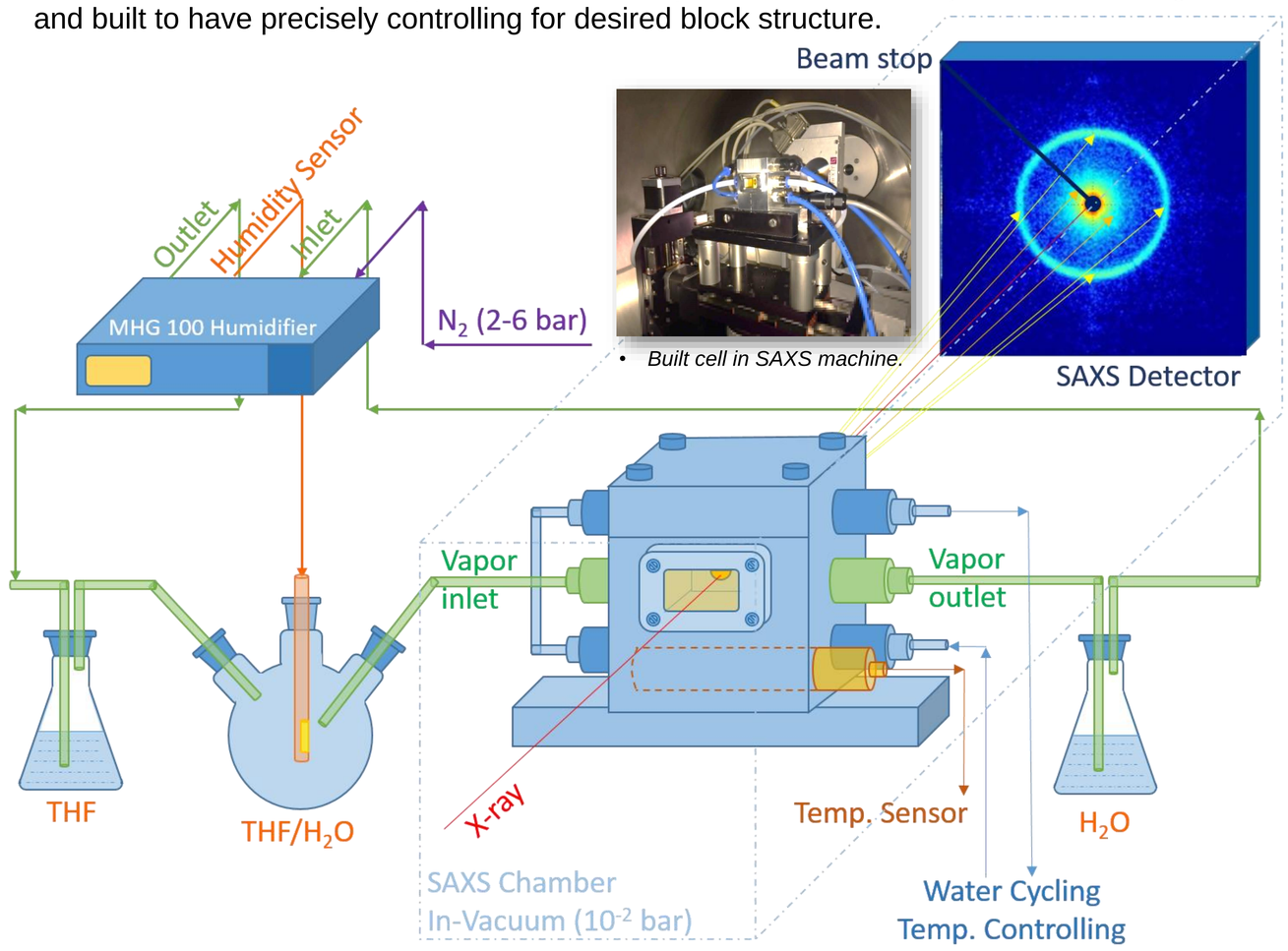
b) *The SAXS measurement profiles of iron oxide/PS-b-PNIPAM diblock copolymer hybrid bulk materials with different Fe/NIPAM molecular ratios from 0 to 0.5. The curves are shifted along the y axis for clarity of the presentation.*



- *The SAXS 2D interference patterns of iron oxide/PS-b-PNIPAM diblock copolymer hybrid bulk materials with different Fe/NIPAM molecular ratios, viz: (a) 0, (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.1.*

Temperature and Humidity Controlling Cell

- Since PNIPAM domain is responsive to both temperature and humidity, a cell was designed and built to have precisely controlling for desired block structure.

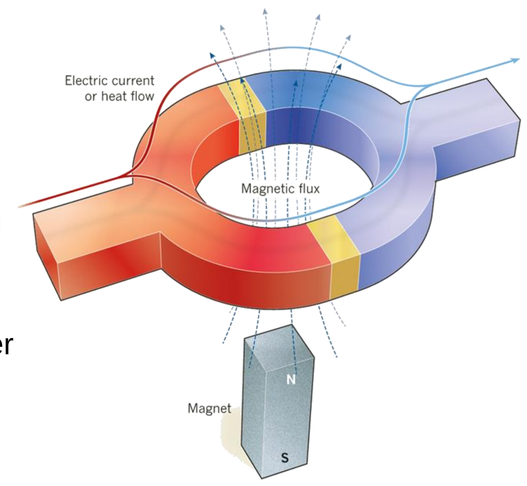


- *Built cell in SAXS machine.*

- *Configuration of temperature and humidity controlling cell for thermoresponsive iron oxide/PS-b-PNIPAM hybrid materials.*

Magnetic Properties (SQUID)

- Superconducting quantum interference device (SQUID) are employed to investigate the magnetic properties of the iron oxide/PS-b-PNIPAM hybrid materials.
- SQUIDs are sensitive enough to measure fields as low as 5 aT (5×10^{-18} T) [7].
- The iron salt is diamagnetic, after thermal annealing it becomes Iron (II) and Iron (III) which can be paramagnetic.
- The magnetic properties are strongly depended on the arrangement of iron oxide domain which is formed by diblock copolymer template [4,8].



- *In d.c.-SQUIDs, a superconducting loop contains two Josephson junctions — thin insulating barriers (yellow) sandwiched between the two superconductors (red and blue).[6]*

Outlook

- Investigate the iron oxide/PS-b-PNIPAM hybrid materials with built temperature and humidity controlling cell.
- Use PNIPAM dominated PS-b-PNIPAM to have thermoresponsive PNIPAM framework.
- Study the influence of iron oxide/PS-b-PNIPAM hybrid structures on its magnetic properties.

References

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