

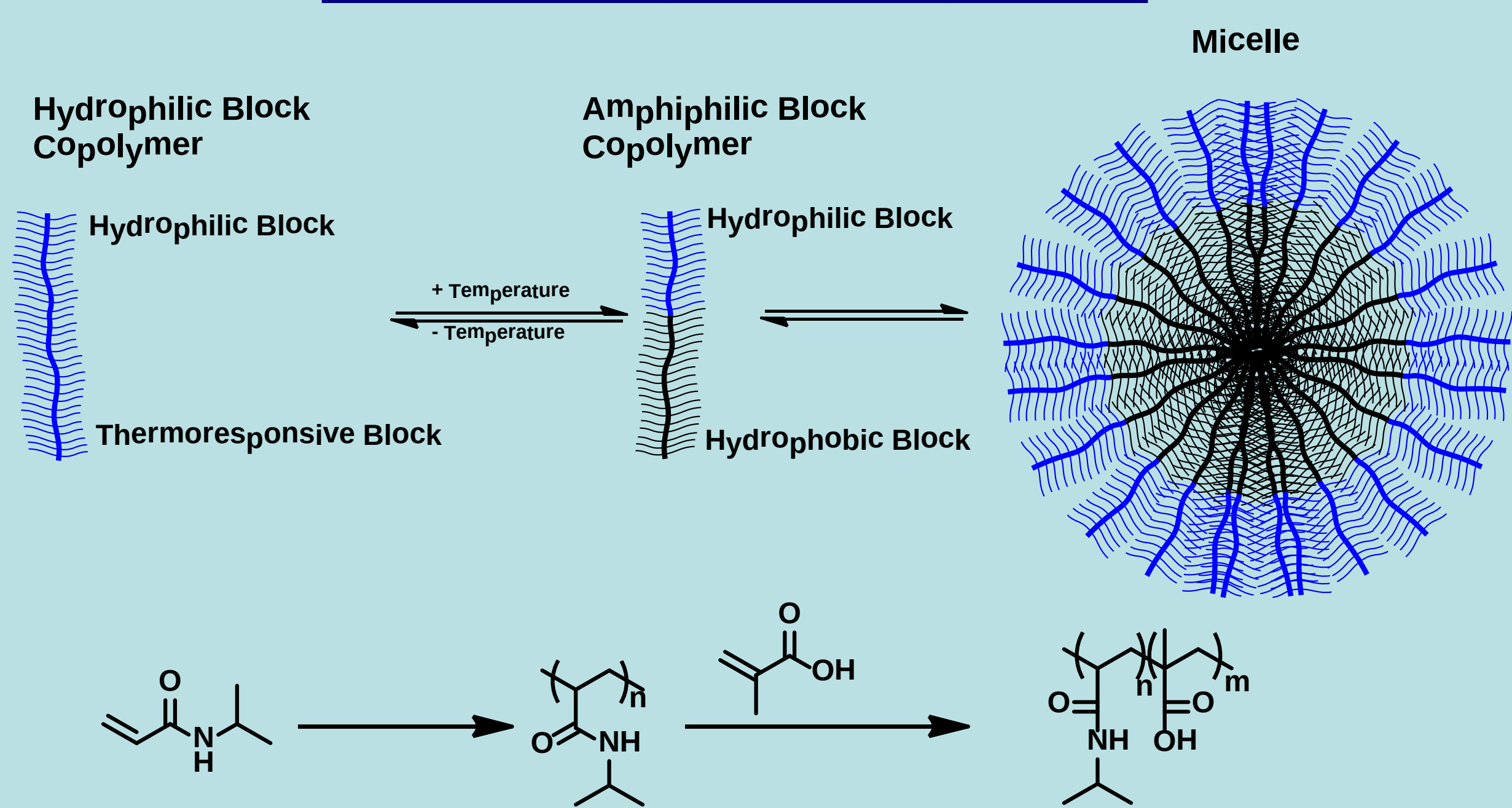
Thermo-Responsive Polymeric Materials: Norbornene NIPAM Analogues

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Due to the toxicity and solubility of many drug molecules used in the treatment of diseases it is advantageous to use a material as a carrier/delivery vehicle. Materials that form vesicles known as micelles can be used to deliver these drug molecules to the desired site. More important than the delivery itself is the extent to which scientists can manipulate the structure and activity of these micelles through changes in pH, temperature, light and biological stimuli. Here we attempt to synthesize thermo-responsive materials that can change morphology based on changes in temperature. .

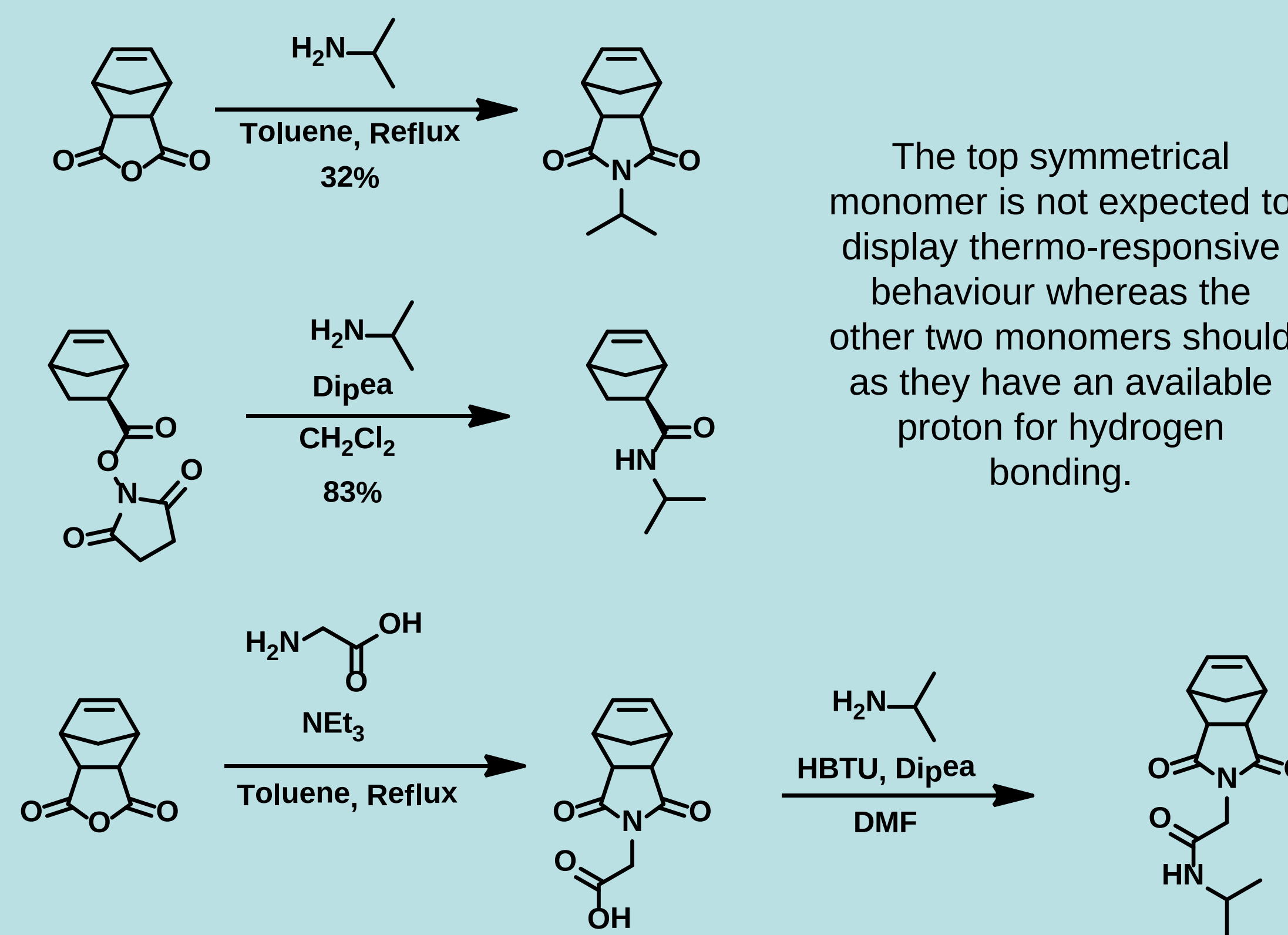
Thermo-Responsive Systems



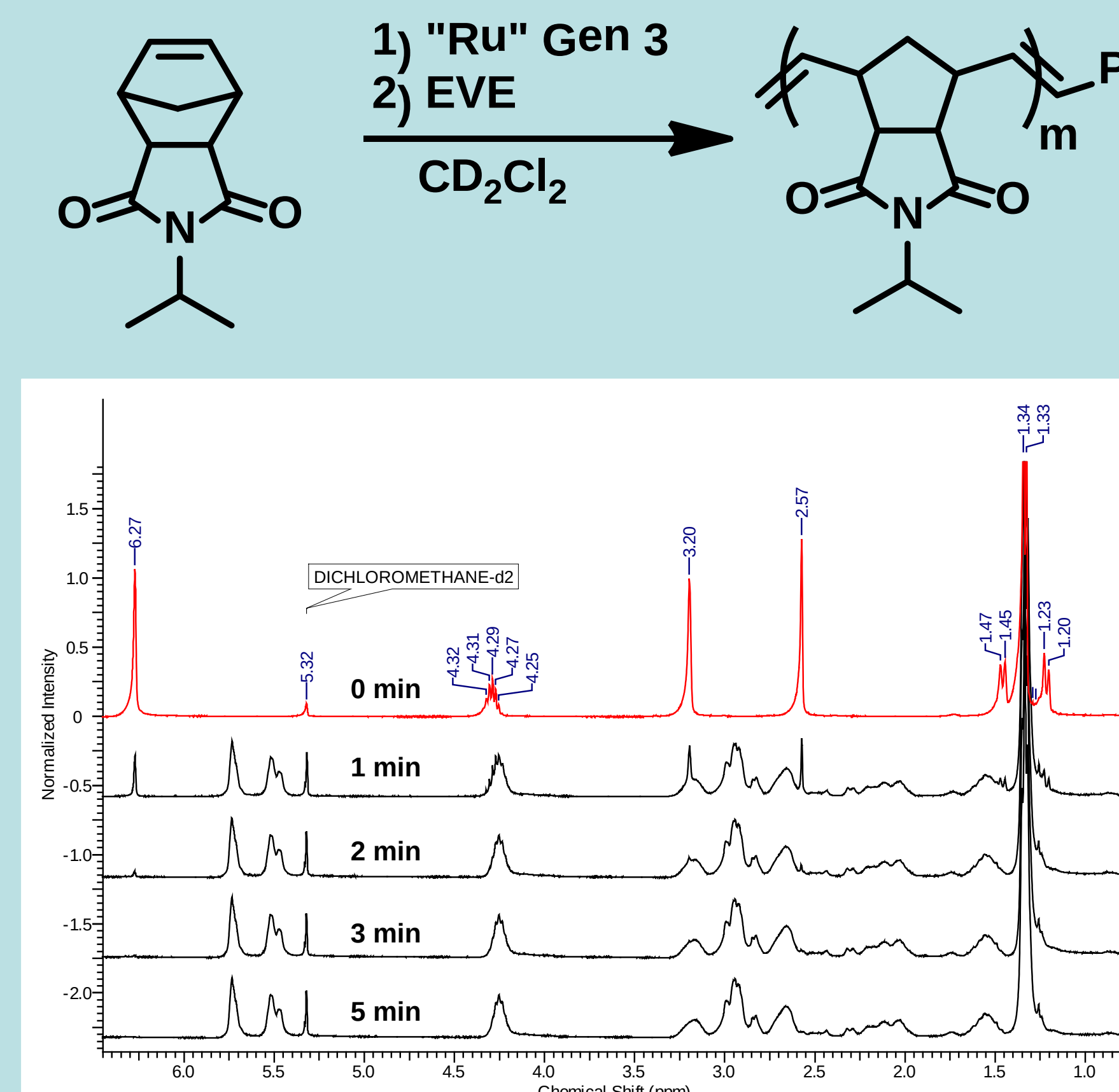
NIPAM homopolymer

Above 32°C LCST phase transition where it goes from a swollen hydrated state to a shrunken dehydrated state. Copolymers can reversibly form aggregates upon heating above the LCST. Will a norbornene NIPAM analogue show similar behaviour?

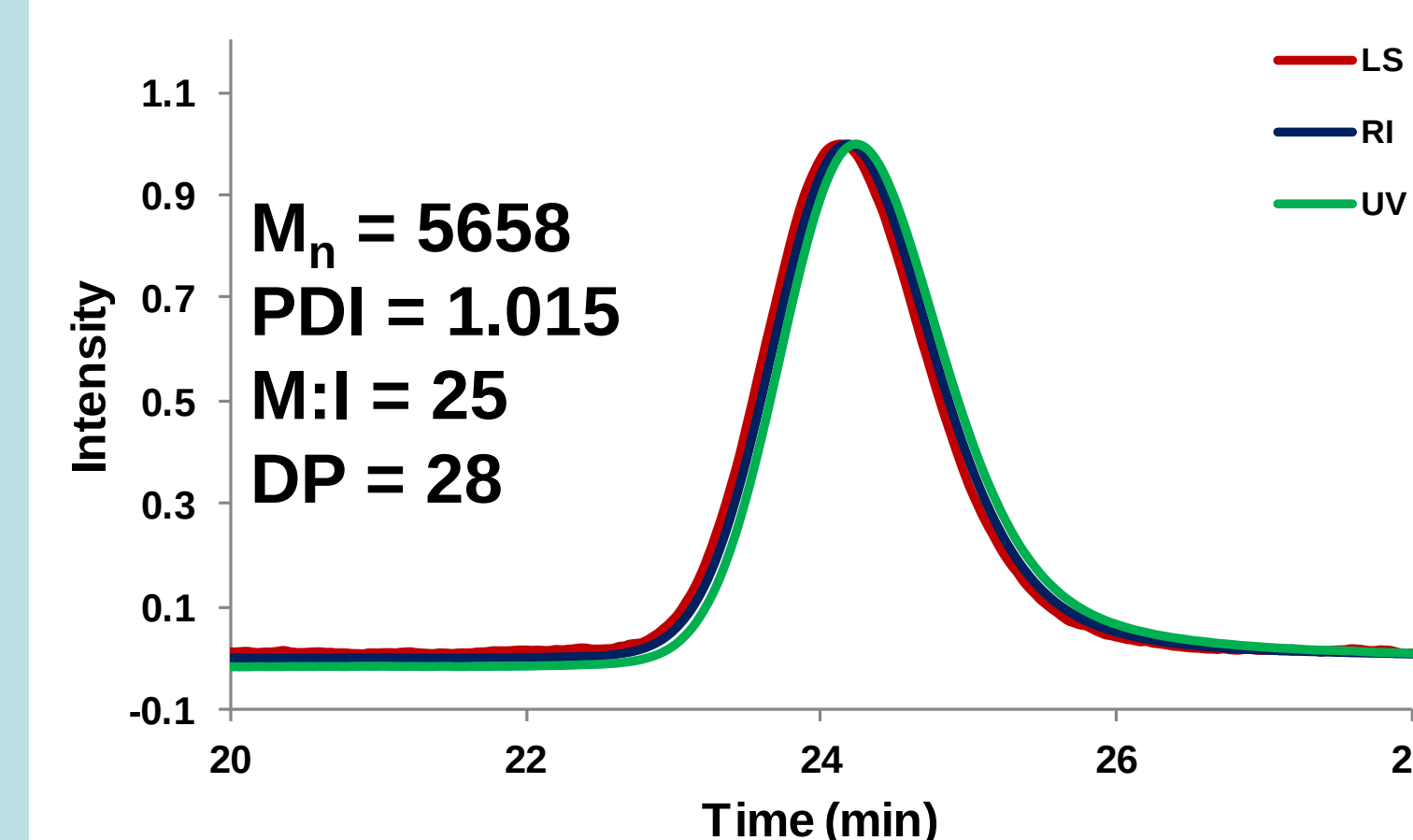
NIPN: Monomer Synthesis



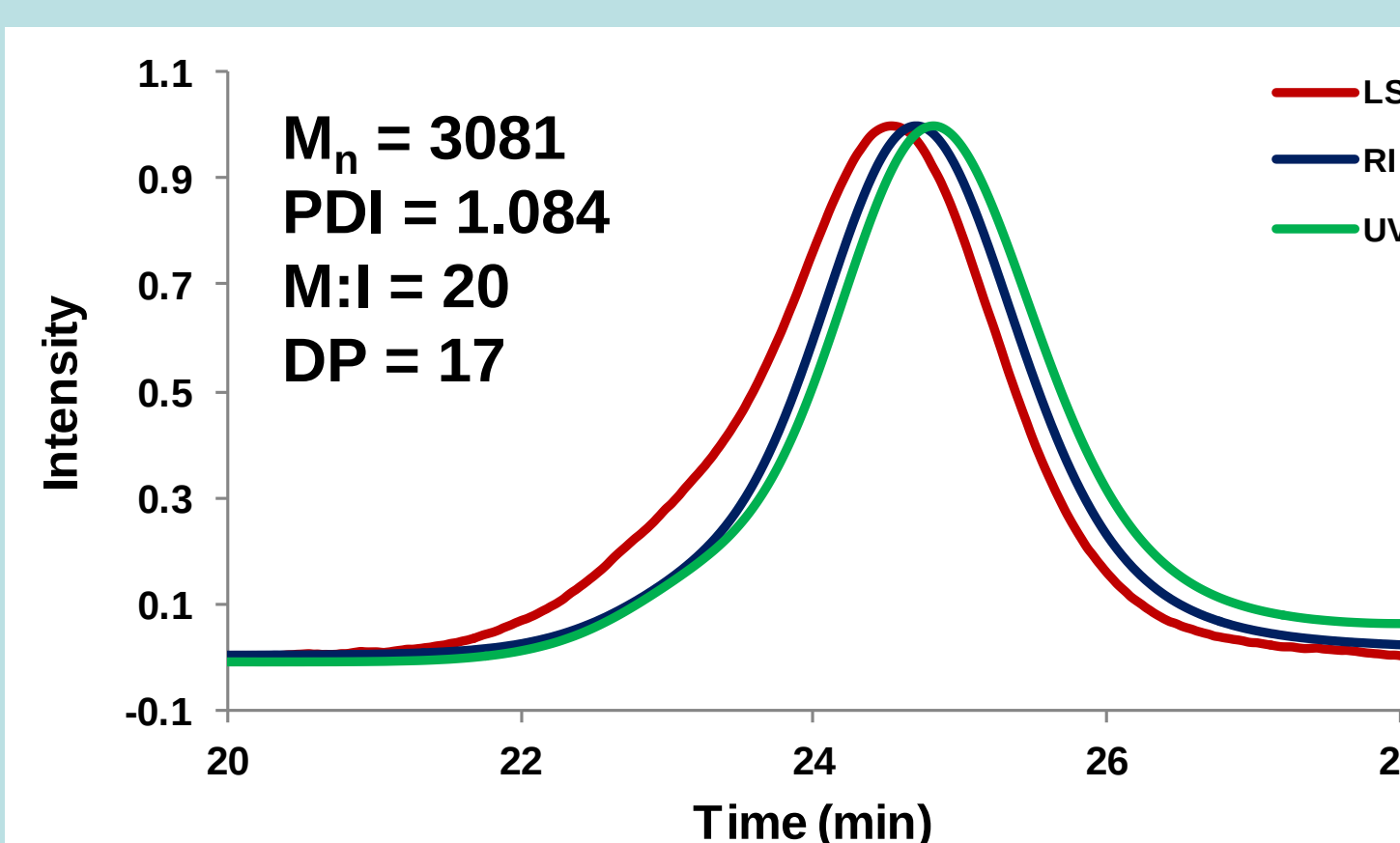
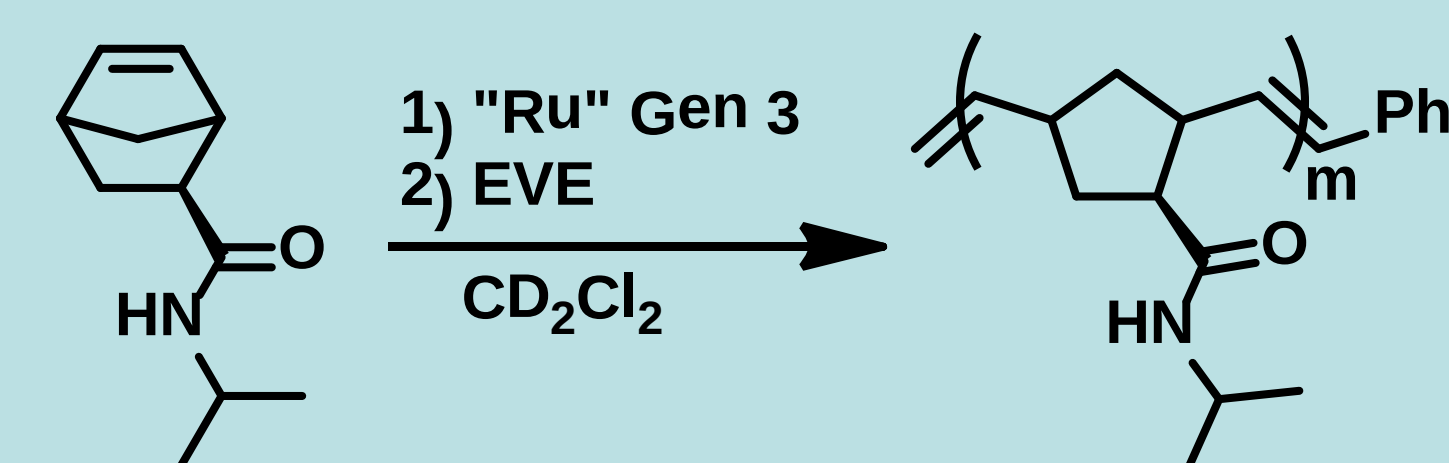
Polymerization - Homopolymer



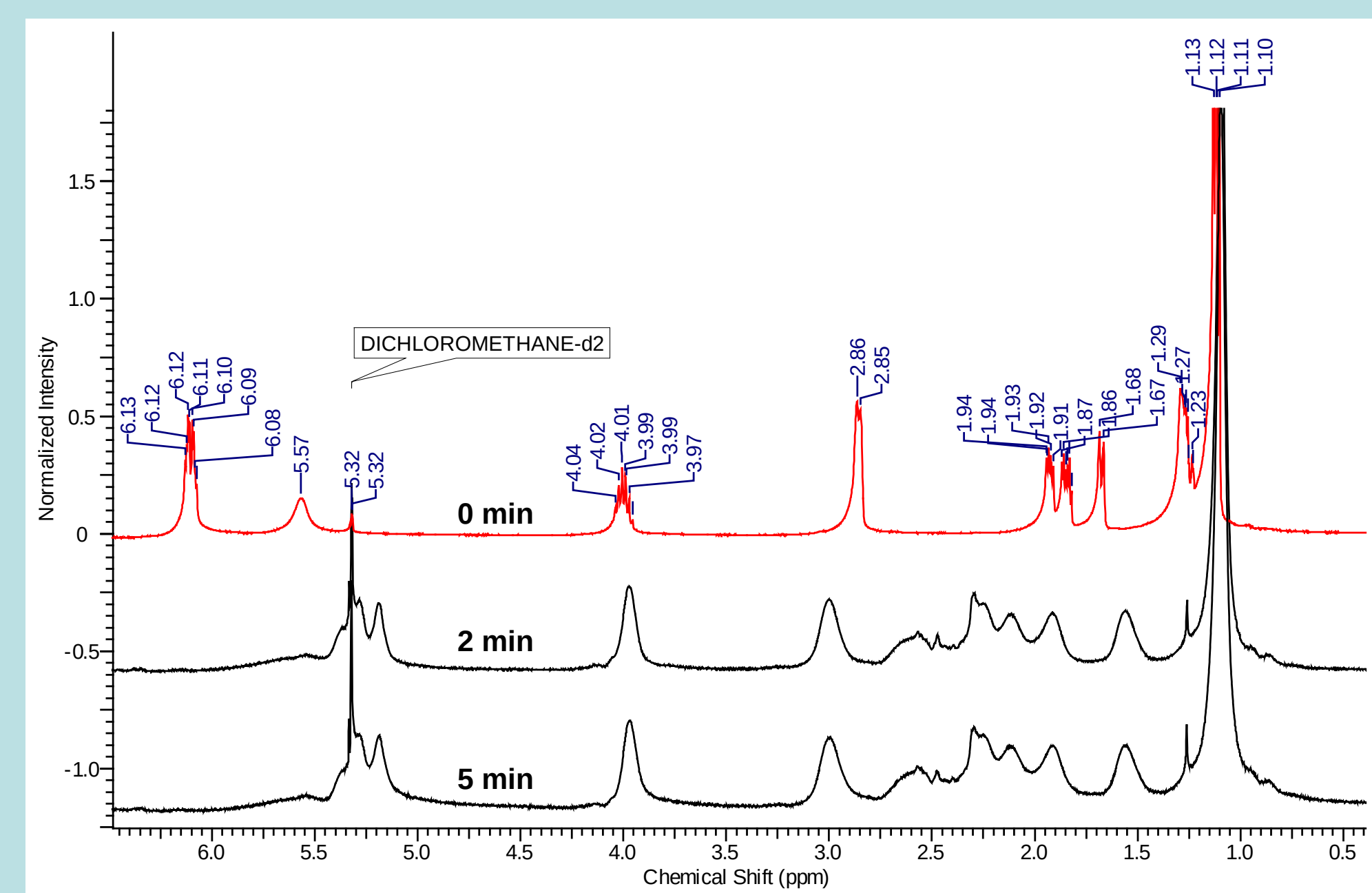
Monomer undergoes complete polymerization in 5 minutes as seen by the disappearance of monomer olefin ^1H NMR signal (6.27 ppm). Polymer molecular weight was determined using size-exclusion chromatography coupled with multi-angle light scattering.



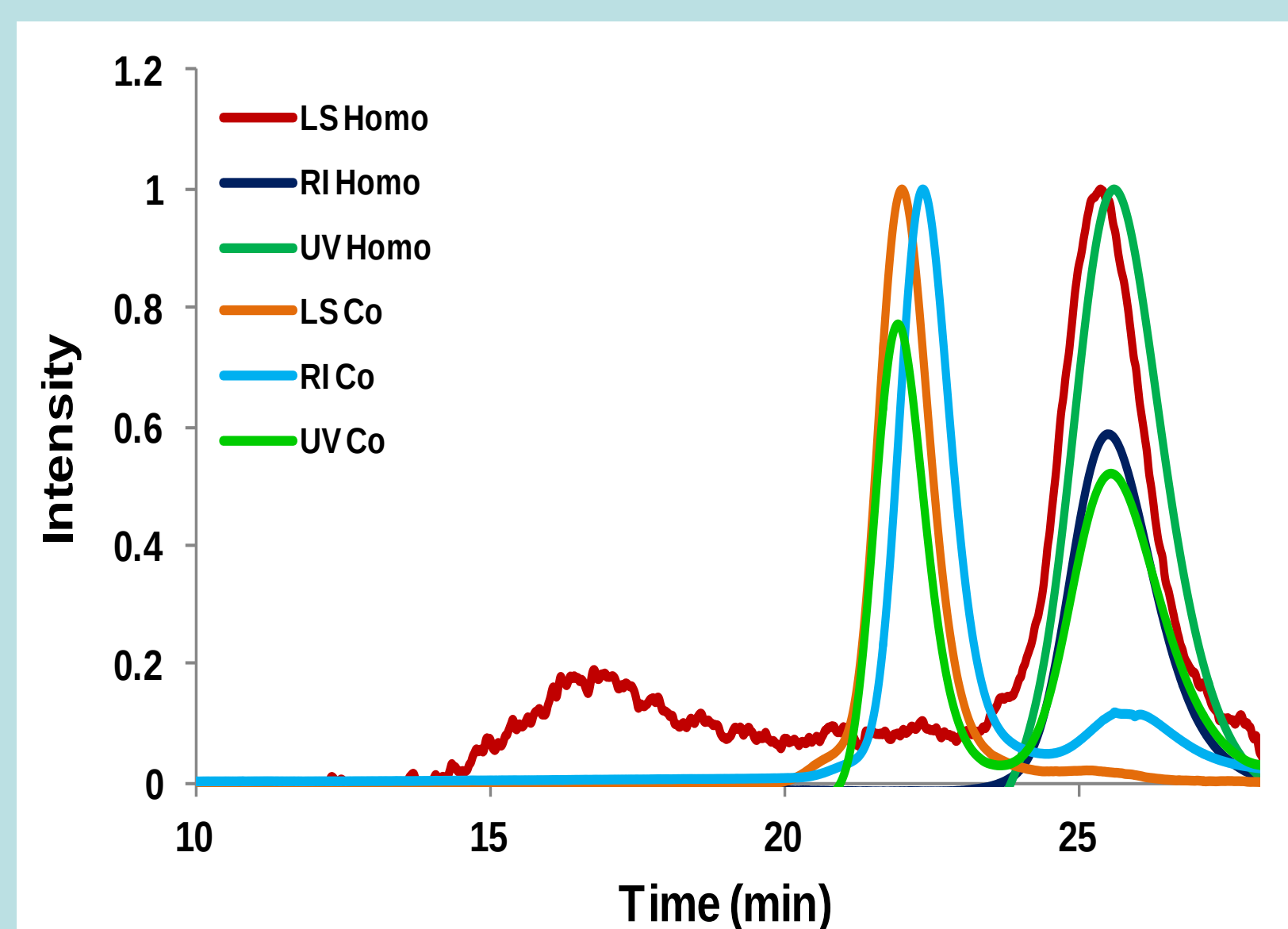
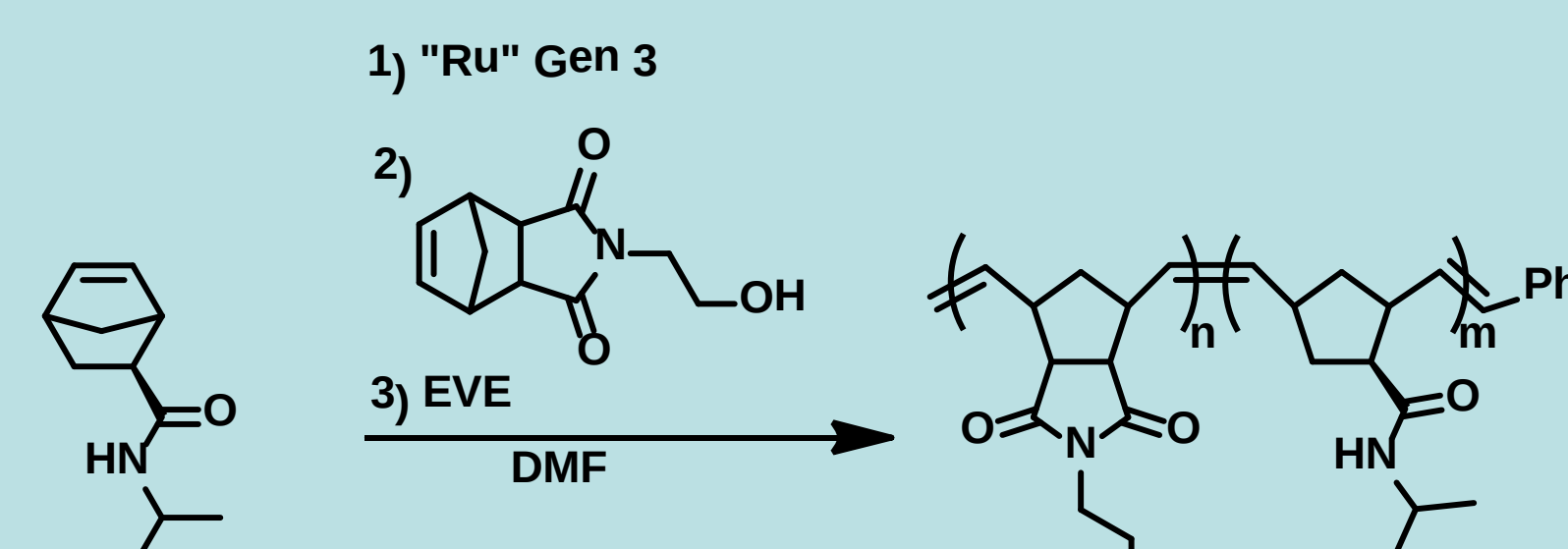
Polymerization - Homopolymer Unsymmetric



Monomer undergoes complete polymerization in 2 minutes as seen by the disappearance of monomer olefin ^1H NMR signal (6.12 ppm).



NIPN-EAN Block-copolymer



Homo
 $M_n = 1835$
PDI = 1.048
M:I = 20
DP = 10

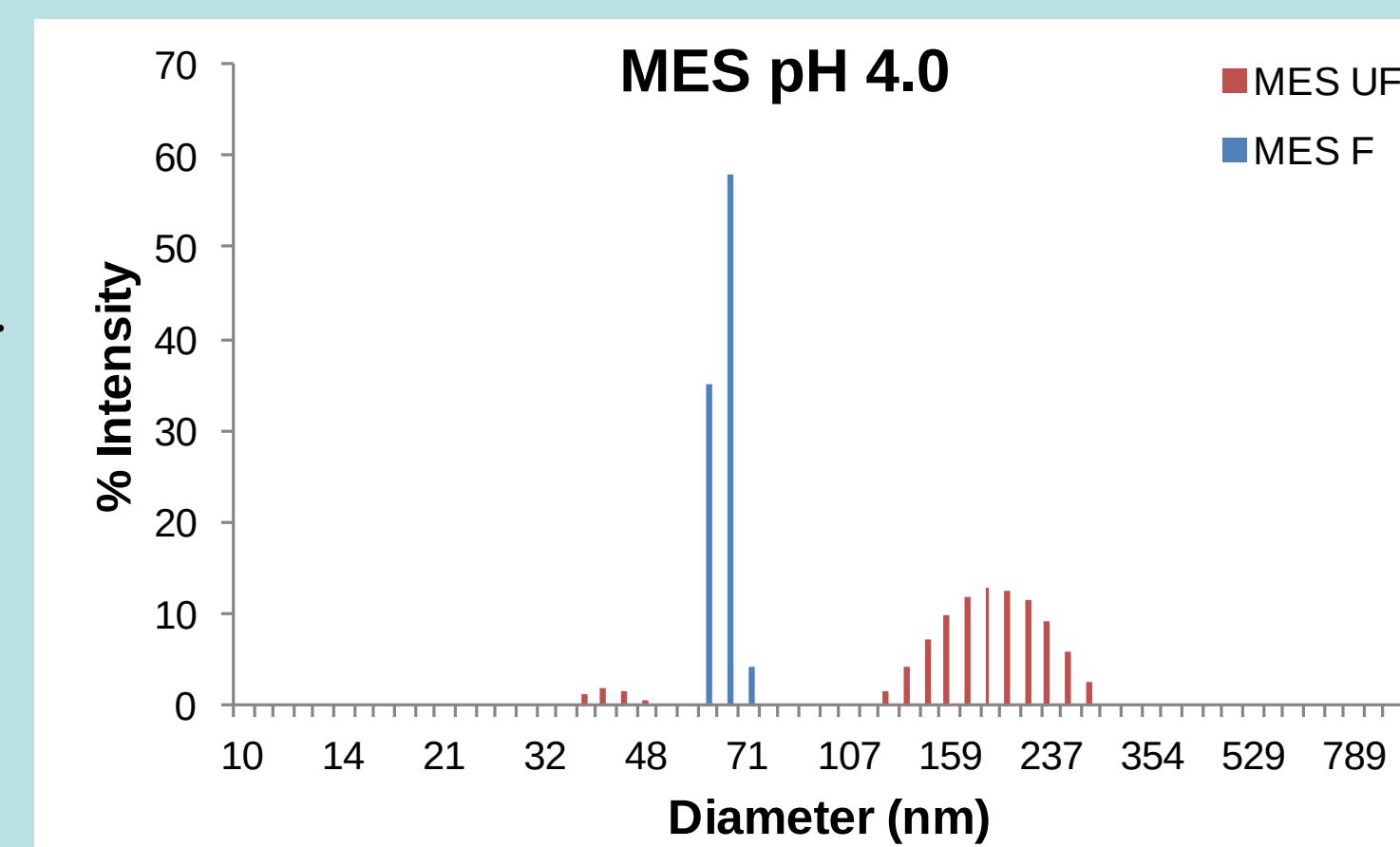
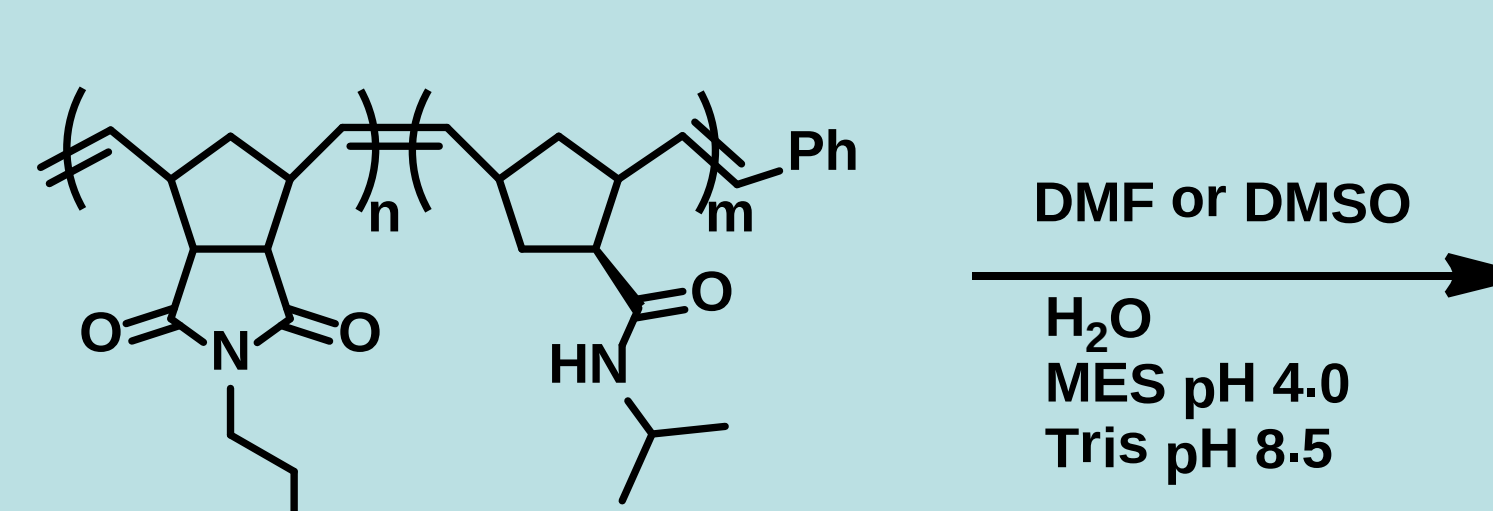
Copolymer
 $M_n = 13730$
PDI = 1.002
M:I = 40
DP = 57

Polymer Solubility

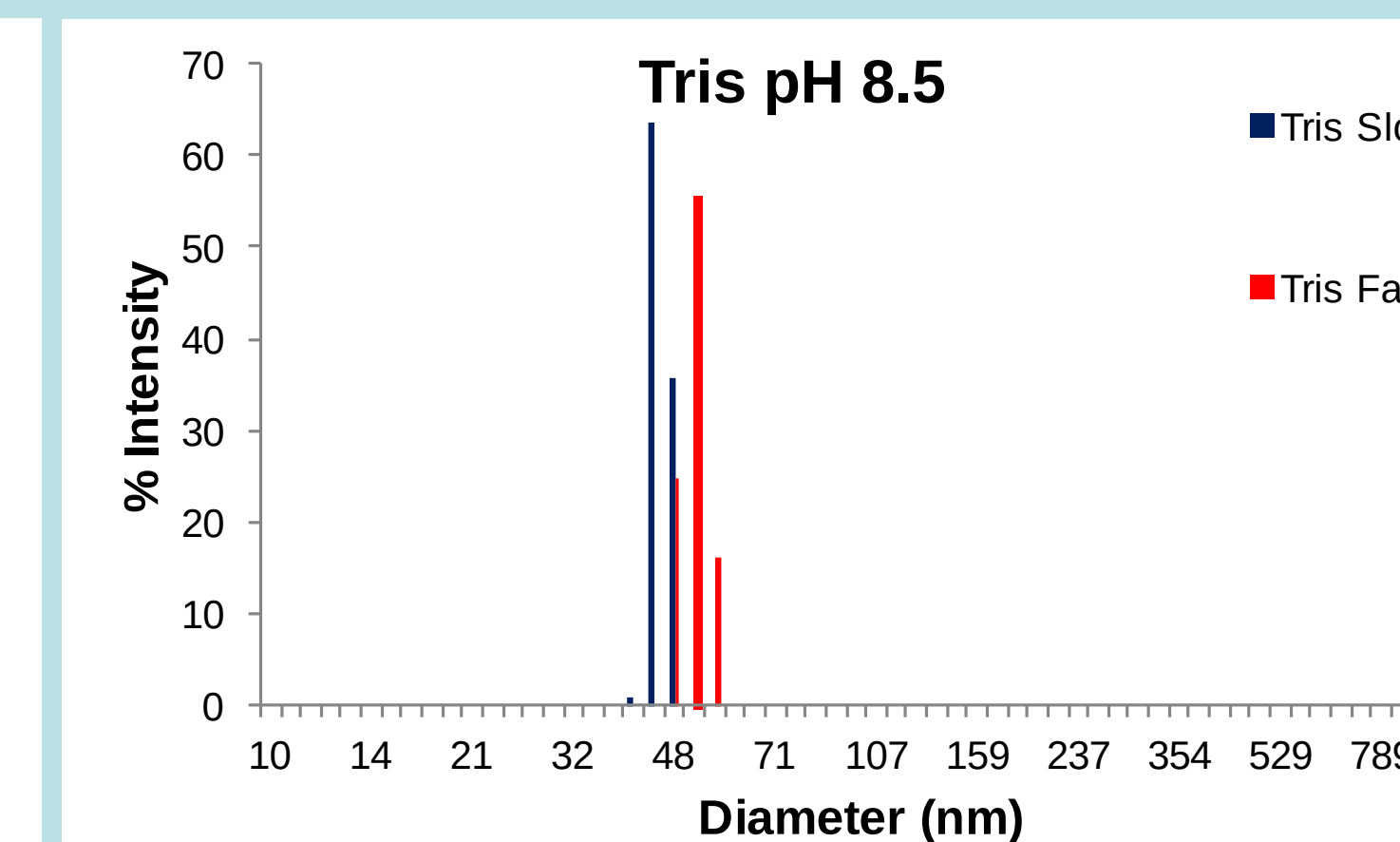
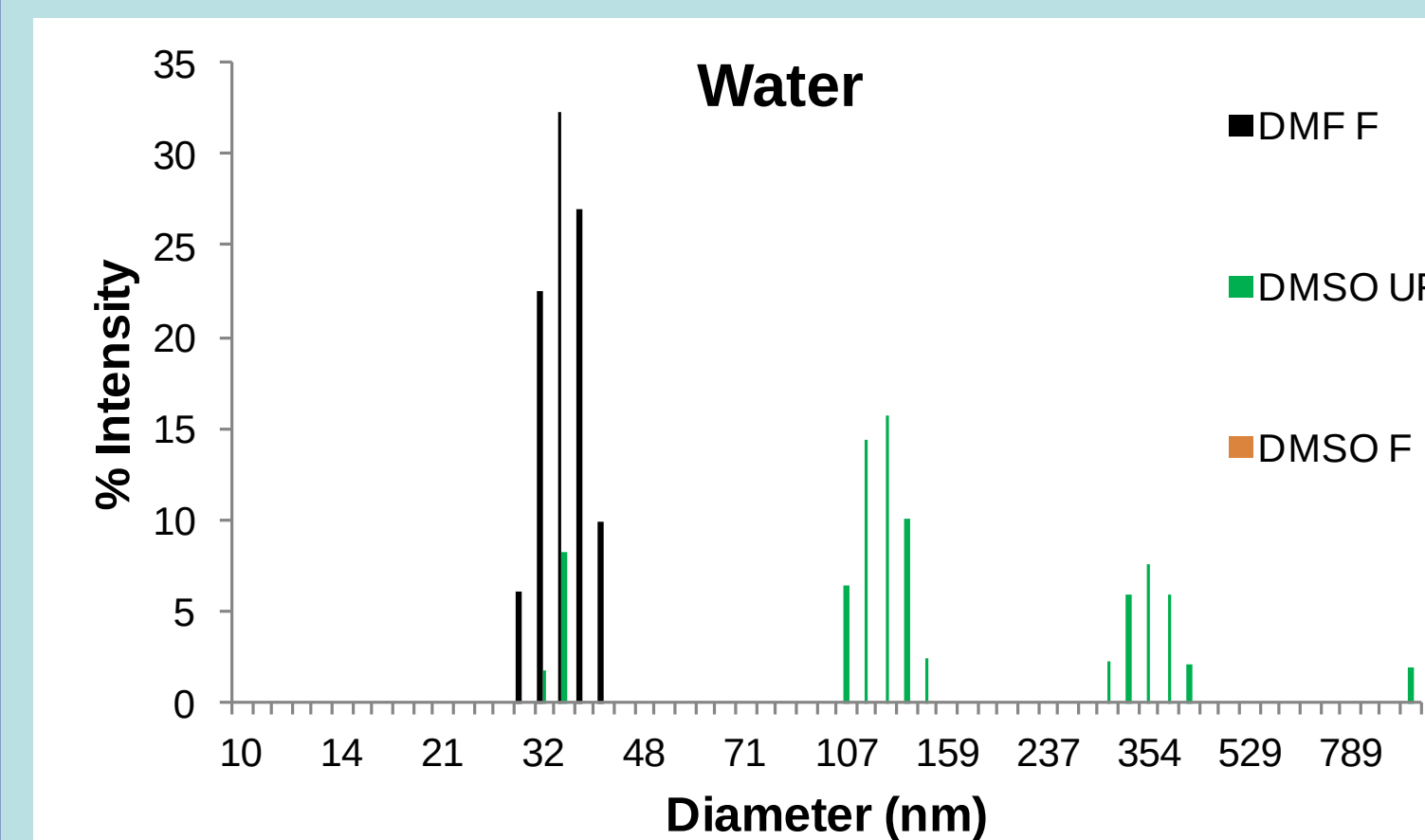
Water n
DCM n
MeOH mostly
THF slightly
DMF y
DMSO y

Polymer backbone may be limiting the solubility of the polymers in aqueous media.

Dialysis



Dialysis of the copolymer results in micellar particles with a diameter ranging from 32 nm to 71 nm (filtered samples). Heating the MES F sample does not result in a significant change in the diameter of the particles



Summary and Acknowledgments

Norbornene analogues of NIPAM were synthesized and used to make homo and block copolymers. These polymers are not soluble in water however dialysis from DMSO into water gives micellar aggregates. The thermo-responsive properties of these systems are still being explored

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Gianneschi Group

