



Photodegradable Crosslinked Nanogels

Amanda Mc Kee,* Ali Sulehria,* Ryan Grant, and Dr. Lisa Kelly
Department of Chemistry and Biochemistry, University of Maryland, Baltimore County

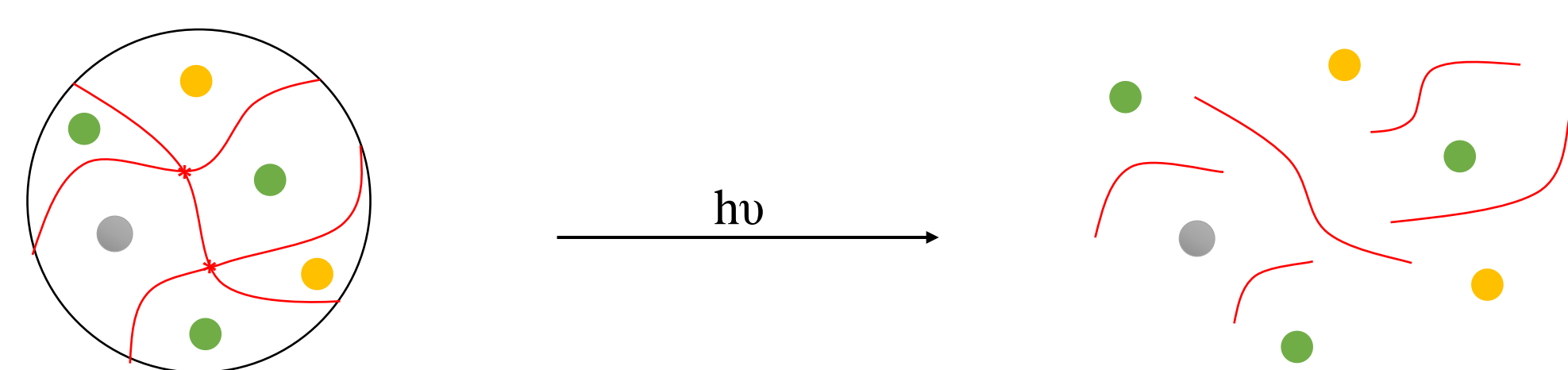


Abstract

The synthesis, characterization, and incorporation of a photocleavable crosslinker into nanogels is reported. 1,6-diisocyanohexane (**1**) was synthesized and confirmed using ^1H NMR and FTIR. PCDA (**2**) was synthesized using a Passerini reaction and the structure was confirmed using ^1H NMR and FTIR. Photocleavage using 365-nm light of 2-nitrobenzyl alcohol was monitored by UV-vis spectroscopy. Nanogels were synthesized from both non-photolabile and photolabile crosslinkers and had a diameter of 280.3 nm and 283.0 nm respectively. Photodegradation of the nanogels was observed using UV-vis spectroscopy and dynamic light scattering (DLS).

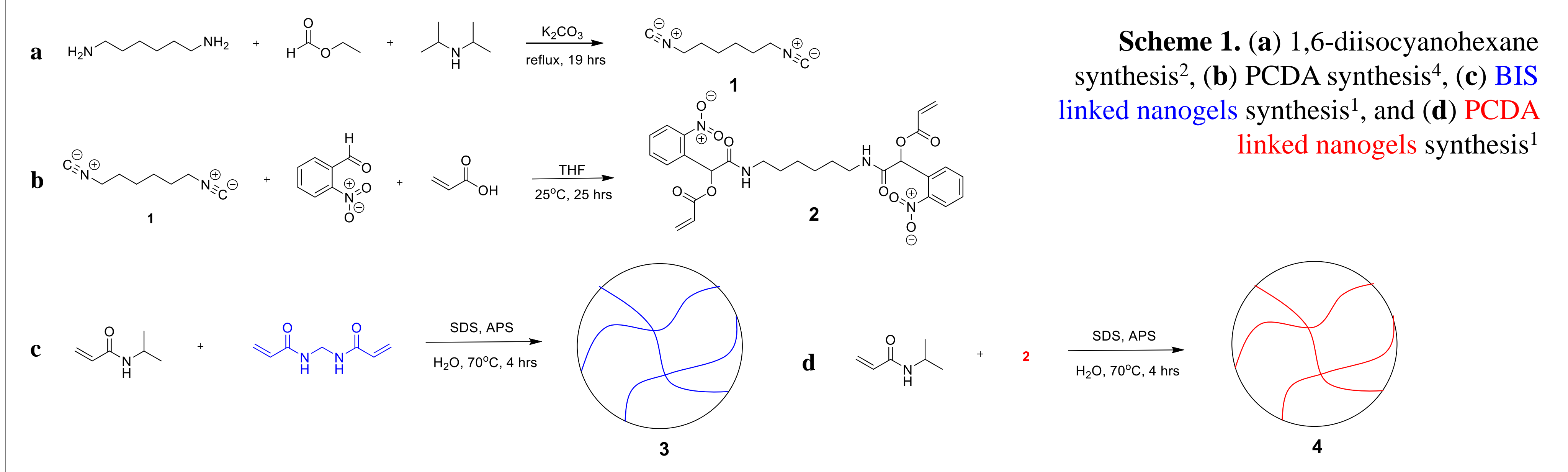
Significance

- Nanogels are crosslinked polymers that absorb other molecules.
- A photolabile crosslinker allows for the nanogel to be broken down with exposure to UV light.
- Photosensitive crosslinkers generally require long, complex syntheses.
 - One-pot Passerini reaction is a simpler and more efficient synthesis.
- The dual responsiveness of the PCDA nanogels makes them a powerful tool for a variety of applications, especially those where controlled or targeted release is essential, like drug delivery and water treatment.
- Lower critical solution temperature (LCST) is the temperature the nanogels collapse and expel water.



PCDA Linked Nanogels

Reactions



^1H NMR of PCDA

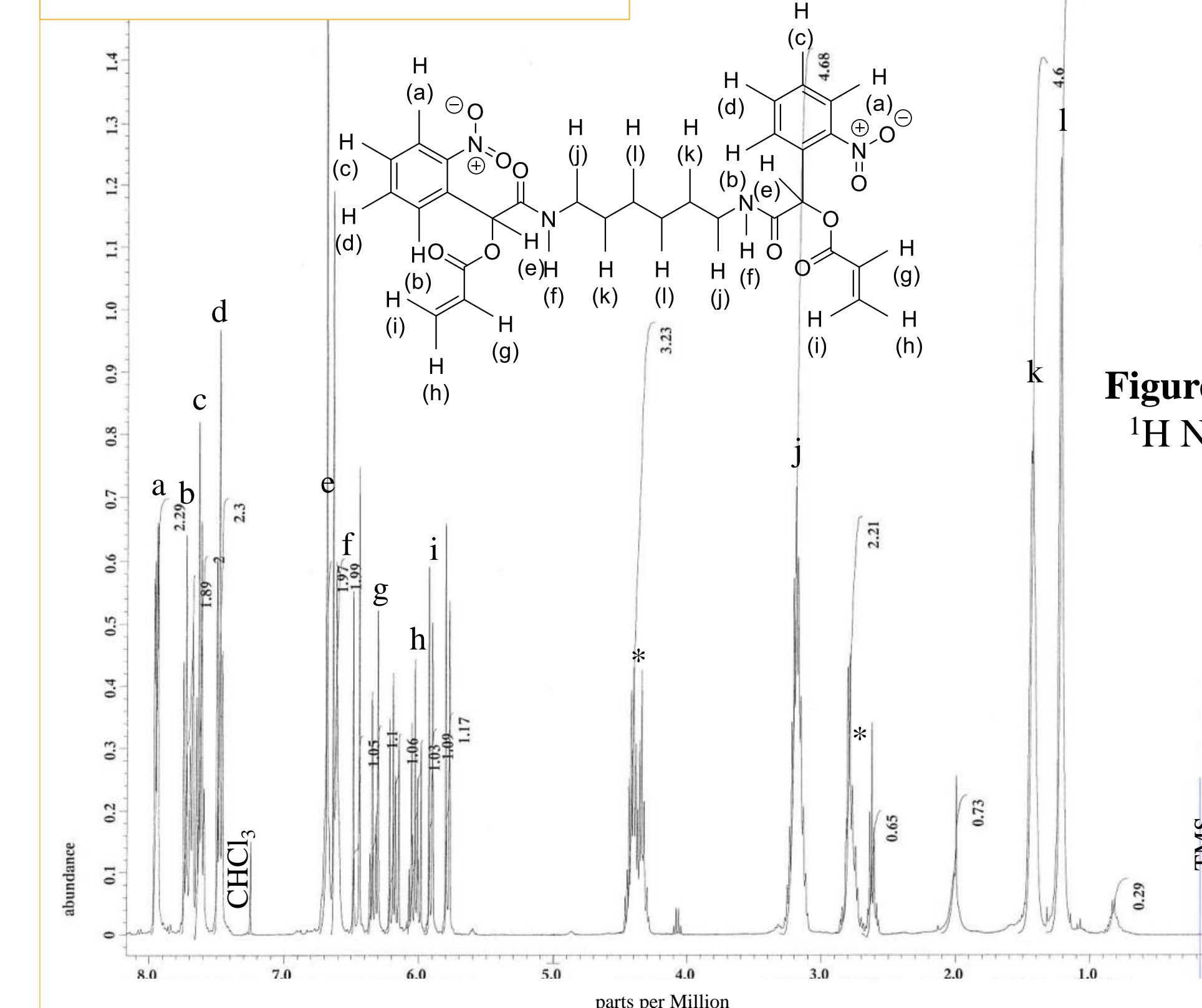


Figure 5. 400 MHz, ^1H NMR of PCDA (**2**) in CDCl_3 .

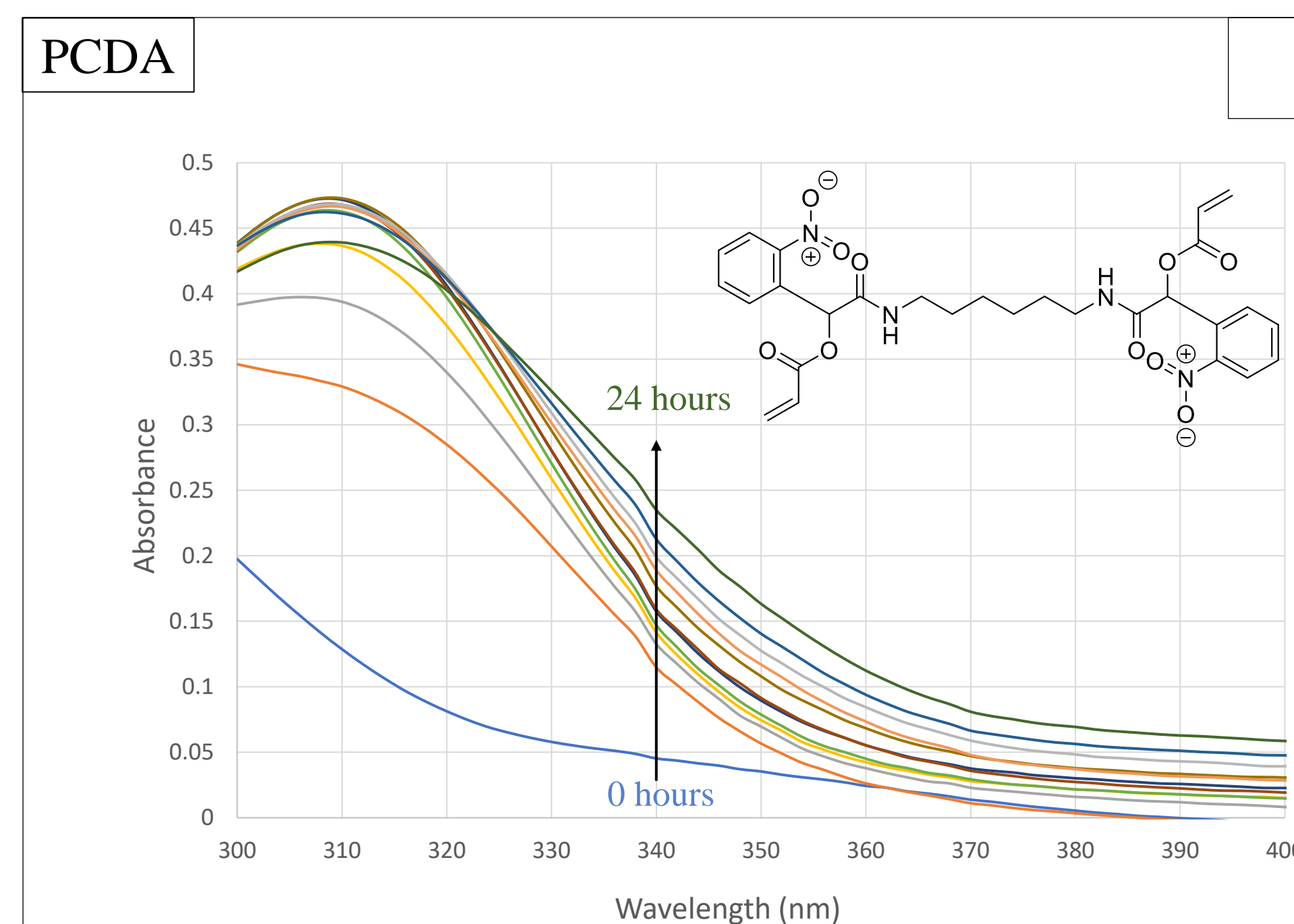


Figure 1. 1.1×10^{-4} M PCDA in THF was irradiated at 356-nm from 0 hours to 24 hours and monitored by UV-vis.⁵

UV-vis

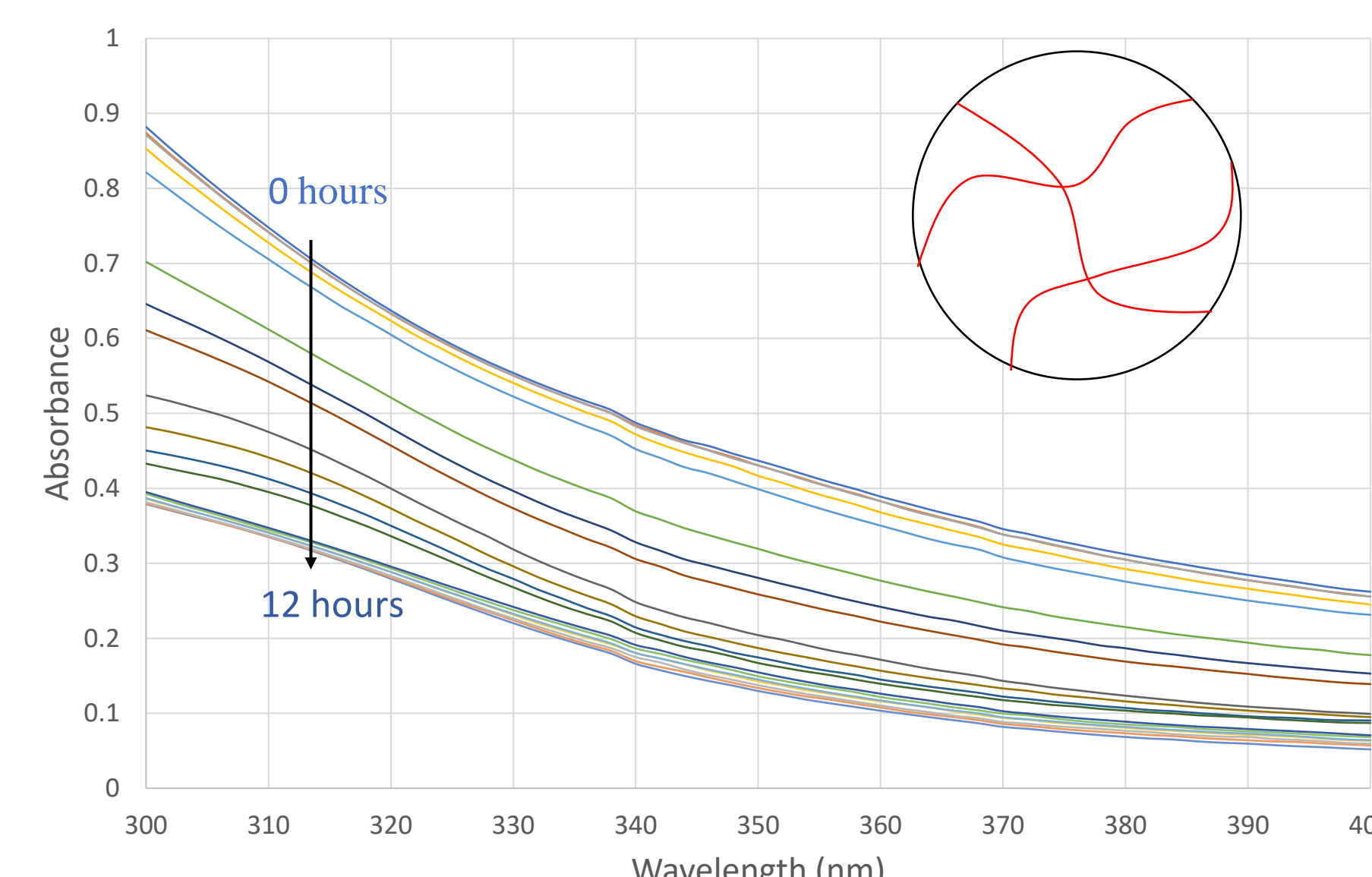


Figure 2. PCDA linked nanogels in H_2O was irradiated at 365-nm from 0 hours to 12 hours and monitored by UV-vis.

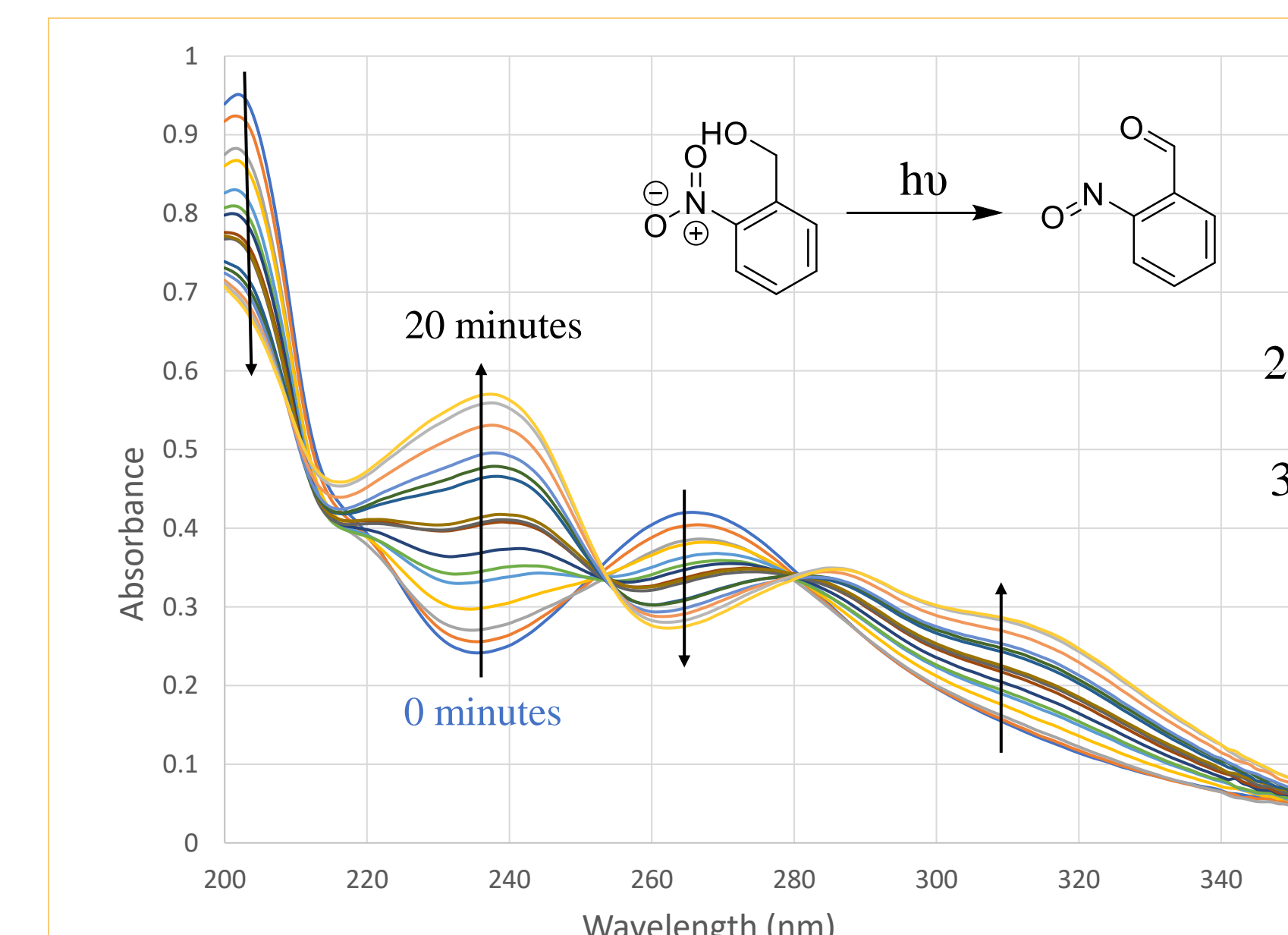
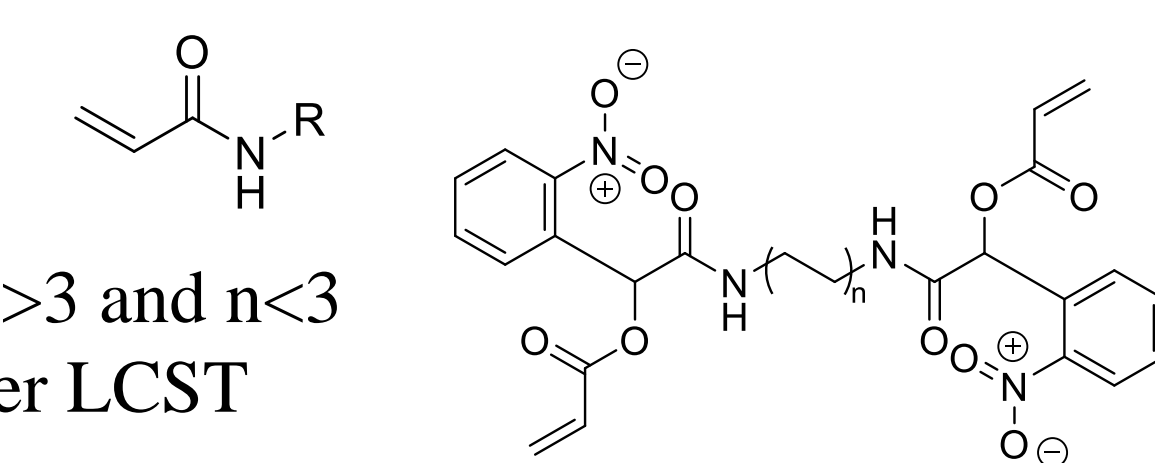


Figure 6. 7.0×10^{-5} M 2-nitrobenzyl alcohol in H_2O was irradiated at 365-nm from 0 minutes to 20 minutes and monitored by UV-vis.³

Future Direction

- Improve purity of PCDA (**2**)
- Vary chain length of PCDA, $n > 3$ and $n < 3$
- Synthesize nanogels with lower LCST
 - Variation of acrylamide monomer
- Design of degradable capsule



Methods

- Synthesis and characterization of PCDA (**2**) (Scheme 1b.)
- 1,6-diisocyanohexane (**1**) (Scheme 1a.)
- Passerini reaction
- Irradiation monitored by UV-vis (Figure 1.)
- ^1H NMR (Figure 5.)
- FTIR
- Synthesis and characterization of cross linked nanogels
 - BIS linked (**3**) (Scheme 1c.)
 - Dynamic light scattering (DLS) (Figure 3.)
 - PCDA linked (**4**) (Scheme 1d.)
 - Irradiation monitored by UV-vis (Figure 2.)
 - DLS (Figure 4.)
- Photolysis of 2-nitrobenzyl alcohol (Figure 6.)

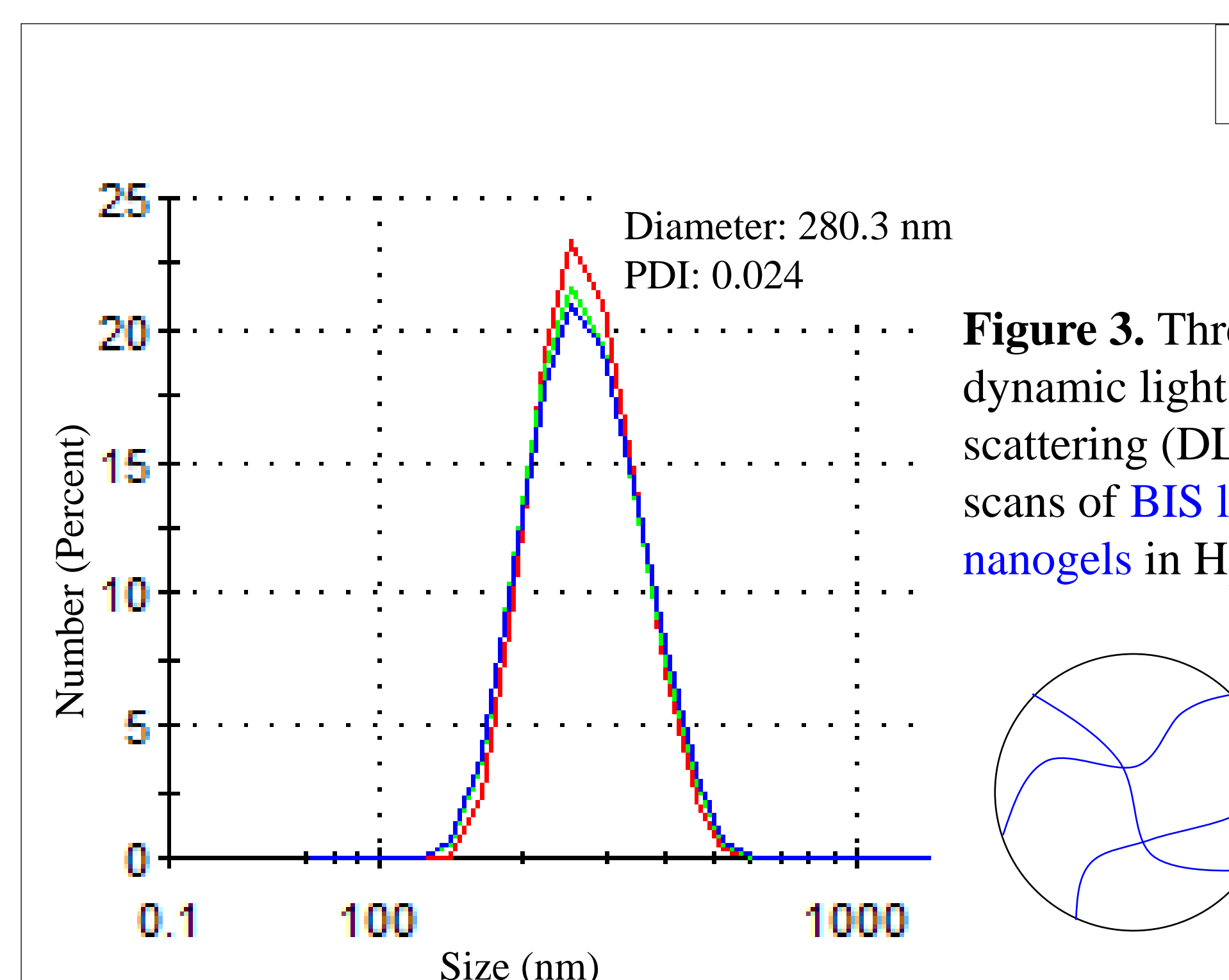


Figure 3. Three dynamic light scattering (DLS) scans of BIS linked nanogels in H_2O .

DLS

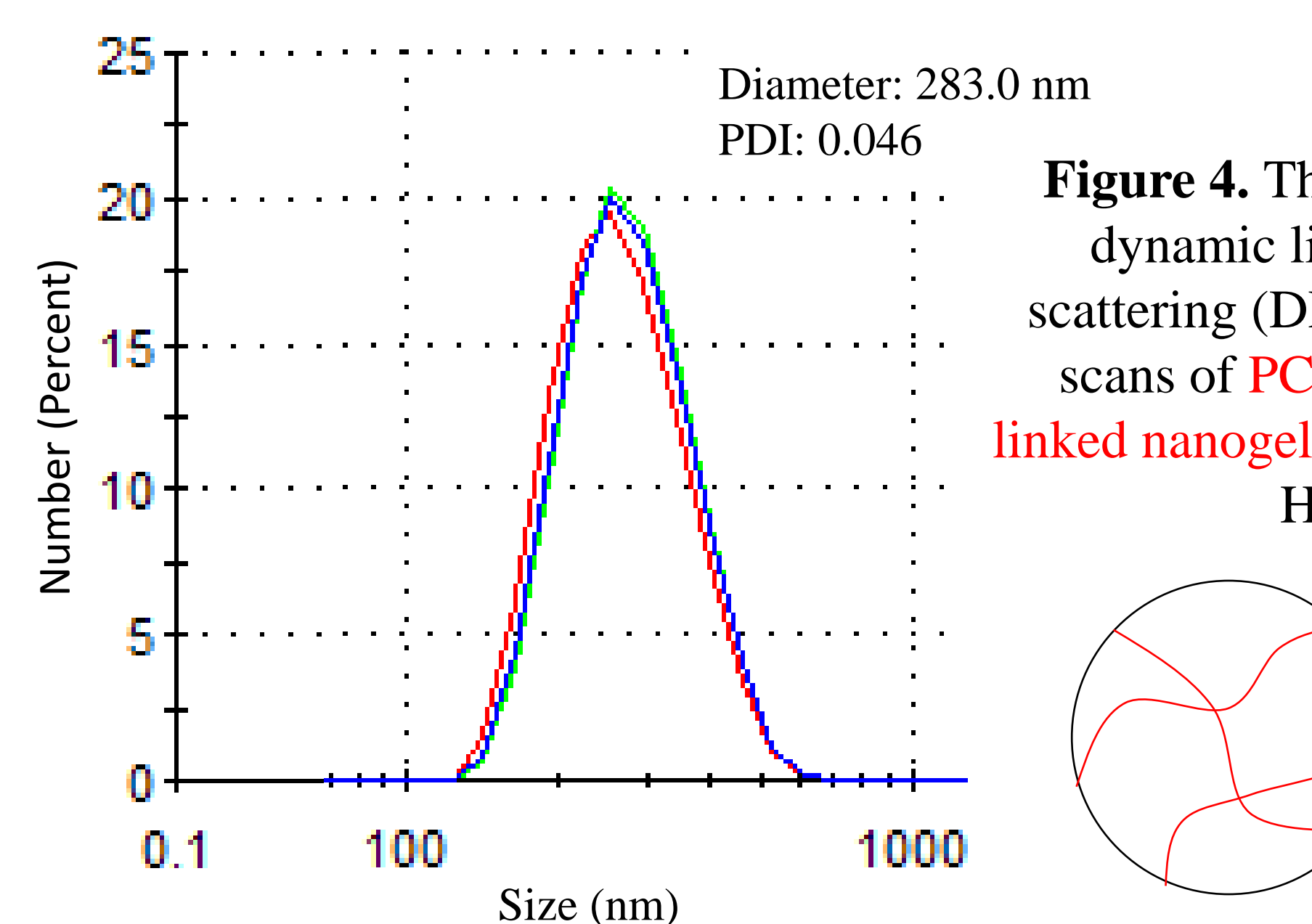


Figure 4. Three dynamic light scattering (DLS) scans of PCDA linked nanogels in H_2O .

References

- Manning, Steven J. Synthesis, characterization, and incorporation of benzopyrene monoimides into stimuli-responsive polyacrylamide nanogels. Ph.D. Dissertation, University of Maryland, Baltimore County, Baltimore County, MD, 2013.
- Sehlinger, Ansgar et al. "Diversely substituted polyamides-macromolecular design using the Ugi four-component reaction." *Macromolecules*, 2014, 47, 2774-2783. dx.doi.org/10.1021/ma500504w.
- Gaplovskiy, Martin et al. "Photochemical reaction mechanisms of 2-nitrobenzyl compounds: 2-nitrobenzyl alcohols form 2-nitrobenzyl aldehydes by dual proton transfer." *Photochem. Photobiol. Sci.*, 2005, 4, 33-42. doi:10.1016/j.pbi.2005.05.013.
- Deveci, Gozde and Kahveci, Muhammet U. "One-pot one-step synthesis of a photo-cleavable cross-linker via Passerini reaction for fabrication of responsive polymeric particles." *Polymer Bulletin*, 2019, 76, 1471-1487. https://doi.org/10.1007/s00289-018-2449-0.
- Blackburn, William H. and Lyon, L. Andrew. "Size-controlled synthesis of monodisperse core/shell nanogels." *Colloid Polym. Sci.*, 2008, 286, 563-569. DOI 10.1007/s00396-007-1805-7.

Acknowledgements

- Brittany Hopgood Berdecia
- Owen Sparr
- Olivia Edwards
- Dr. Steven Manning
- Dr. Muhammet Kahveci (Istanbul Technical University)
- Dr. Swapnil Ambade
- Shreyasi Sengupta
- Josh Valencia

National Science Foundation (NSF) – Grant No. 2050728

