

ABSTRACT

Thermo-responsive polymer networks have many different external parameters that affect the response speeds of the collapsing and swelling states. With a plasmonic heating technique that optically excites localized surface plasmon (LSP) modes on the surface of Au nanoparticles, the temperature of the polymer hydrogel layer can be precisely controlled with respect to the ambient bulk temperature. By testing different bulk temperatures, longer heating beam pulses, and a variety of temperature change increases, researchers realized response times as low as 1.5 ms for the collapsing state and single digit milliseconds for the swelling state of the polymer hydrogel. With the investigated complex and different response times of thermo-responsive polymer networks, advances can be made in biomedical and miniature actuator applications.

RESPONSIVE POLYMERS

There are key uses for responsive polymers today, including: drug delivery, switchable biocompatible coatings, and advanced biointerfaces in bioanalytical devices.¹ Responsive polymers essentially change key properties or parameters with specific stimuli. Thermo-responsive polymers, where changing the temperature stimulates changes in the polymer properties, are the most common in biomedical applications. All thermo-responsive polymers have a lower critical solution temperature (LCST). Above or below this temperature determines the state of the polymer. Lowering the temperature of the polymer to below the LCST causes the polymer to exhibit a hydrophilic state in which the structure expands or swells and contains high amounts of water molecules. Increasing the temperature to above the LCST causes the polymer to exhibit a hydrophobic state in which the structure collapses and expels water molecules from its proximity.¹ These two distinct states can be seen in **Figure 1**.

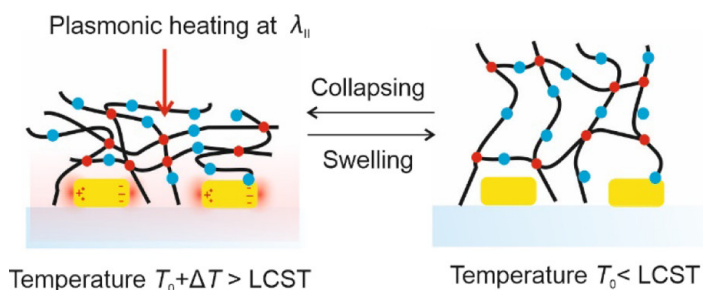


Figure 1. Polymer Network Collapsing and Swelling due to Temperature Stimuli¹

To use thermo-responsive polymers in real-world applications, they must be exploited as polymer brushes or polymer networks forming hydrogels or microgels after swelling with water. These hydrogels are attached to the surface or solid substrates as thin films. The key characteristic to study before providing advanced applications is the speed at which these LCST hydrogels respond to temperature stimuli. Recent experiments have realized single digit seconds time responses of LCST hydrogels as valves, switches, or even mechanical releases in various applications.

The response time of thermo-responsive polymer brushes or networks depends on a variety of factors: the speed of the individual chain response with respect to its solvation state, their collective conformation switching, and on the diffusion of water molecules in and out of the network structure.¹ It is common for polymer networks to be researched and studied by changing the bulk temperature of the aqueous solution.

PROBLEMS AND GOALS

Although heating and cooling the bulk temperature of the sample solution is the easiest technique, the change in temperature can be relatively slow, thus limiting the kinetic range of the responsive polymers. There are two main methods to create a more localized heating approach: thin resistive ITO microheaters or plasmonic heating. Microheaters change temperature electrically, while plasmonic heating changes temperature by optically exciting localized surface plasmon (LSP) modes on the surface of metallic nanostructures. While microheaters can be more efficient and require less setup and careful calibration, the

transition speeds are slow, not reaching millisecond results. Because the rapid differences in transitions of the swelling and collapsing kinetics are being studied in this experiment, plasmonic heating is the best possible method.

In plasmonic heating the optical excitation of the LSP modes create heat. These originate from collective oscillations of the electron density and the associated electromagnetic field.¹ It is these resonances that probe the close vicinity of the metallic nanostructure and dissipate heat by Ohmic losses in the metal.¹ Instead of heating the solution or electrically heating the sample, plasmonic heating uses metallic nanostructures to optically control the local temperature of the polymer networks.

Previous plasmonic heating studies have realized time responses from seconds to less than a millisecond depending on the thickness of the polymer layer and how the polymer chain segments are connected. Plasmonic heating exhibits promising results for studying differences in response kinetics for swelling and collapsing polymer networks hydrogels.

wavelengths can be excited by changing the polarization of the incident beam perpendicular \perp or parallel \parallel to their long axis. The shorter wavelength λ^\perp is used to probe the refractive index change, and the longer wavelength λ^\parallel is used to couple the heating beam. **Figure 3** shows the pNIPAAm hydrogel and Au nanoparticle layers, distinct LSPs at \perp or \parallel wavelengths, heating beam for plasmonic heating of the sample, and the chemical structure.

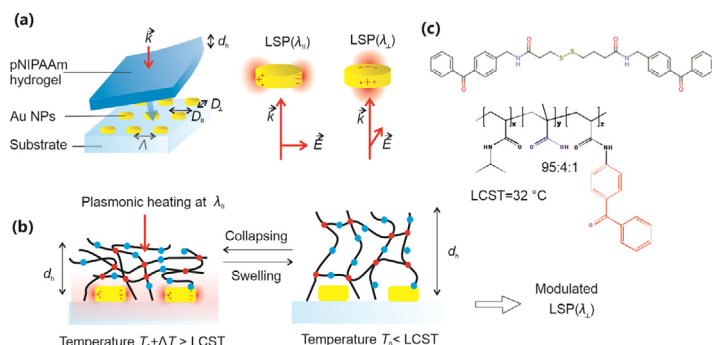


Figure 3. Schematics of the (a) substrate with arrays of elliptical Au nanoparticles that exhibit distinct LSPR wavelengths and that carry thermo-responsive poly(N-isopropylacrylamide)-based (pNIPAAm) hydrogel layers on the top. (b) pNIPAAm polymer network swelling and collapsing by using the temperature stimulus and (c) chemical structure of the benzophenone disulfide linker and used pNIPAAm-based terpolymer.¹

METHOD

Researchers from Institutes and Universities in Austria, Czech Republic, and Germany have developed a rapid plasmonic heating method for swelling and collapsing kinetics of poly(N-isopropylacrylamide)-based (pNIPAAm) networks using Au nanoparticle arrays (**Figure 2**). The design is based on pNIPAAm hydrogels with Au nanoparticles that exhibit distinct localized surface plasmon resonance (LSPR) wavelengths. The LSPs at different

Figure 2 shows the complete setup of this experiment, highlighting laser sources, the main substrate with nanoparticle and hydrogel layers, as well as measuring

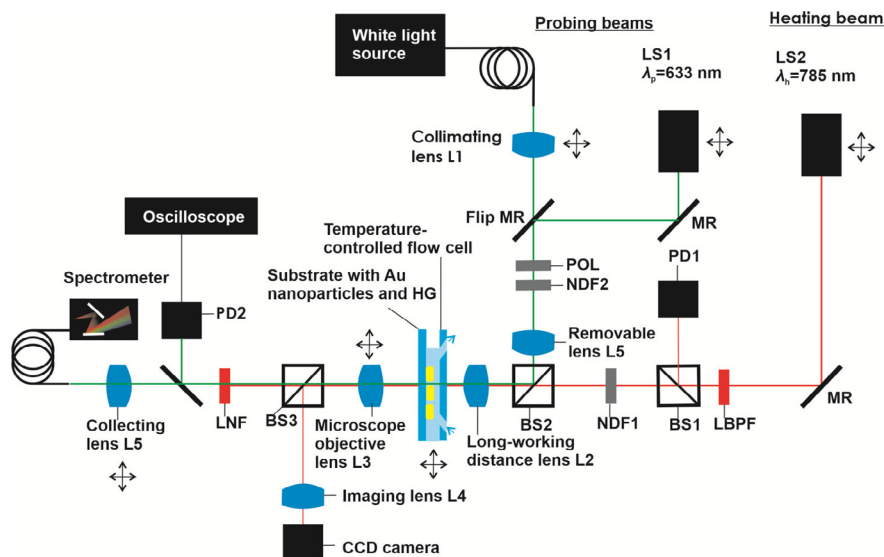


Figure 2. Optical setup employed for the combined wide-field optical microscopy observation of the surface carrying arrays of Au nanoparticles with a thermo-responsive hydrogel (HG) overlayer and for the beam alignment, transmission wavelength spectroscopy-based recording of LSPR spectra, and for the optical heating and monitoring of rapid LSPR kinetics.¹

hardware. This plasmonic heating method allows researchers to explore differences in the swelling and collapsing kinetics of the pNIPAAm networks. These transitions are studied as functions of strength of the local temperature increase, heating pulse duration, and ambient temperature offset with respect to the LCST of the polymer. One of the main variables in response speeds of the polymer networks is the ambient bulk temperature T_0 . The substrate with Au nanoparticles and the pNIPAAm-based hydrogel is clamped to a transparent flow cell that is temperature controlled by a Peltier device. Changing this temperature affects how the polymer hydrogel responds around the LCST.

There are two main lasers in the optical system: a HeNe laser emitting the probing wavelength of 633 nm and a wavelength stabilized diode laser emitting the heating wavelength of 785 nm. The probing laser measures the refractive index of the hydrogel layer to calculate the thickness and state of the pNIPAAm-hydrogel. A lower refractive index correlates to a swollen state, and a higher refractive index represents a collapsed state. In **Figure 2**, the setup shows a polarizer that can change the polarization of the beam, \perp or \parallel , to heat or to probe the substrate.

The plasmonic heating optical system was calibrated by gradually increasing the power of the laser from 0 to 5.9 mW. By doing so, shifts in the resonant wavelength λ^\perp caused by changes in the bulk ambient temperature can be distinguished from those locally induced by the heating beam. For the maximum used power of $I_h = 7$ mW, a temperature increase as high as $\Delta T = 15$ K was calculated.

RESULTS

All LSPR shifts measured due to temperature change are primarily attributed to the swelling and collapsing of the pNIPAAm-based hydrogel. Other effects (thermal expansion of the substrate, modulating the period of the gold nanoparticle arrays, and temperature variations of the refractive index of the glass substrate and water) are less significant and provide optical changes at least one order of magnitude weaker.¹

With calibration and setup complete, researchers moved to recording LSPR kinetics for the collapse and swelling states of the pNIPAAm-based polymer networks. Three different measurements were taken: varying local temperature increase, ΔT , (plasmonic) from below to above LCST, increasing the bulk temperature, T_0 , while applying constant ΔT , and changing the pulse duration for the plasmonic heating laser beam. **Figure 4** shows the results of these three measurement scenarios.

By varying the local temperature increase with steps of 3, 6, 9, 12, and 15 K through the plasmonic laser power, while keeping T_0 at 25°C (below the LCST), the signal

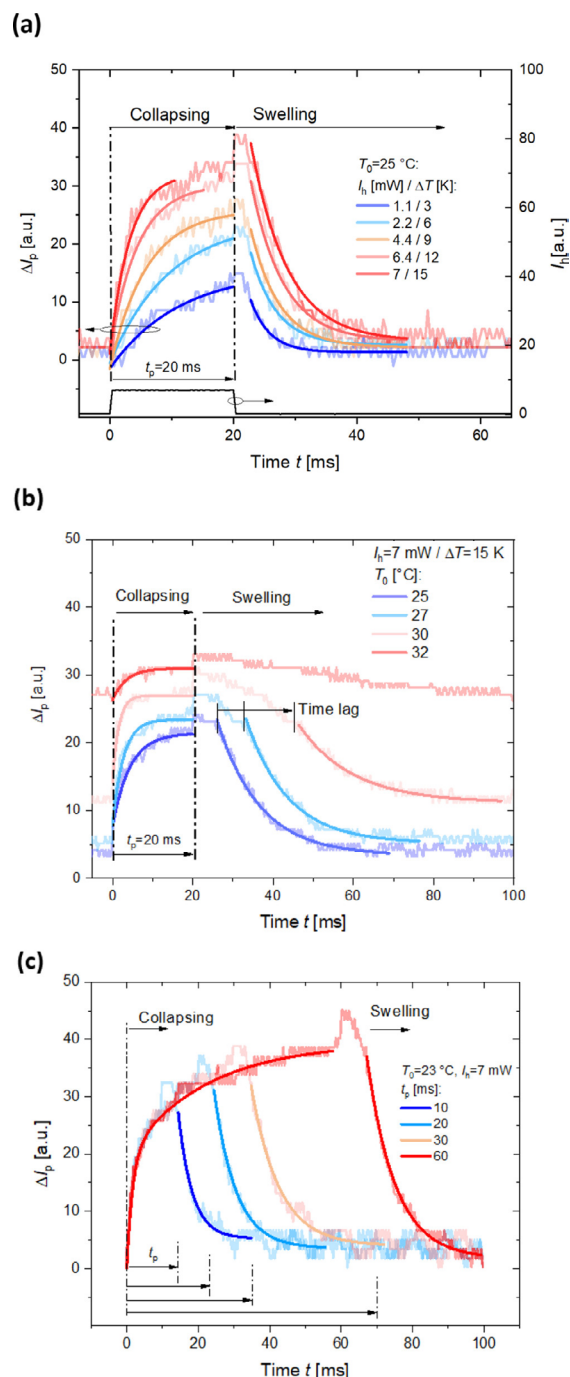


Figure 4. Recorded LSPR kinetics for the pNIPAAm-based polymer network collapse and swelling when (a) varying local temperature increase ΔT from below to above LCST, (b) increasing the bulk temperature T_0 to LCST and applying constant ΔT , and (c) for changing the time duration of the plasmonic heating pulse t_p . The measured data (presented as curve with light color) are fitted with exponential functions (shown as a curve with corresponding dark colors).¹

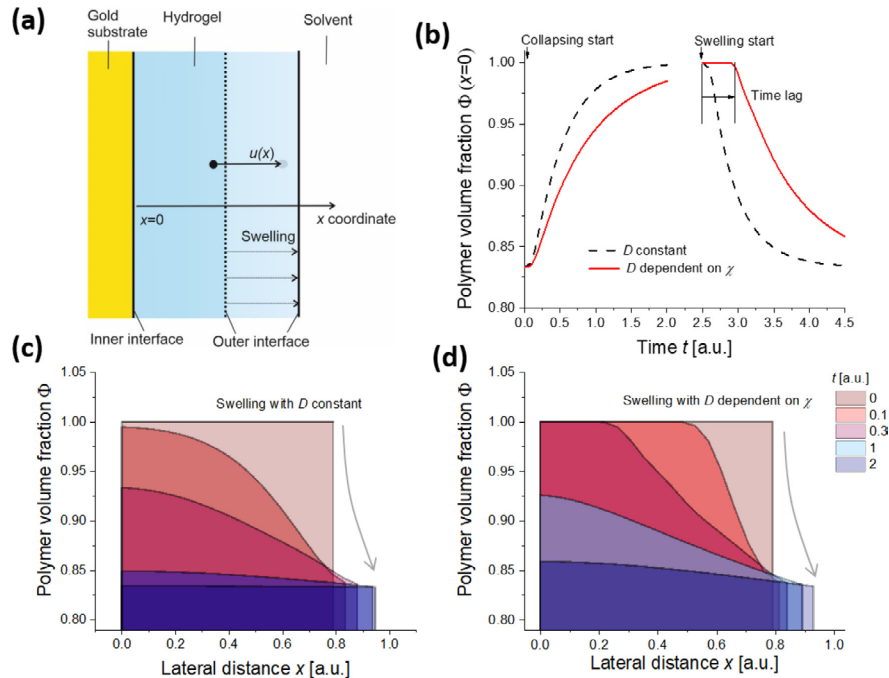


Figure 5. (a) Assumed geometry and definition of the displacement distance describing the swelling and collapsing process of an attached hydrogel layer. (b) Simulated time dependence of the polymer volume fraction Φ upon the collapsing and swelling process at the inner interface ($x = 0$). The spatial distribution of the polymer volume fraction upon the swelling process for the model with (c) constant D and (d) when taking into account its dependence on the Flory–Huggins parameter χ .¹

intensity kinetics slows down for higher heating strength. The collapsing speed increases for increasing heating strength with time constants of 9.6 and 3.3 ms fitted with an exponential curve. However, the swelling speed does not change significantly with ΔT , and a time constant of $4.8 \text{ ms} \pm 1 \text{ ms}$ was realized with the exponential function. This data is seen in **Figure 4a**.

During the second experiment of changing the bulk temperature with steps of $T_o = 25, 27, 30,$ and 32°C , the hydrogel's collapsing state is faster at 1.5 ms. The swelling state, after turning the heating beam off, is more complex with two stages. The estimated time constant for the swelling and the transition during the swelling state is 25 ms for 30°C bulk temperature. **Figure 4b** shows these results.

The last experiment was changing the pulse duration with a set bulk temperature of below the LCST at $T_o = 23^\circ\text{C}$ and the local temperature increase set to $\Delta T = 15 \text{ K}$, the heating pulse duration was increased from $t_p = 10$ to 60 ms. From this data in **Figure 4c**, shorter pulse lengths from 10 to 20 ms correlated to faster collapsing kinetics with a time constant of 6 ms. At longer pulse durations, deviation occurs and the collapsing kinetics can be fitted as two overlaid exponential processes with time constants of 1.6 and 23.0 ms.¹

The volumetric changes, due to collapsing and swelling, can be described with a time-dependent displacement distance $u(x, t)$ for the investigated geometry of a thin layer allowed to swell only in the perpendicular direction to its surface.¹ The assumed geometry and definition of the displacement distance is shown in **Figure 5**. The simulations shown in **Figure 5b,c** are related to the experimental data shown in **Figure 4a-c** as the polymer volume fraction, Φ , changes are proportional to the refractive index changes measured by LSPR at the inner interface of the hydrogel film ($x = 0$).¹ The simulated data show similar behavior to the experimental data with regards to the swelling and collapsing kinetics and the exponential behavior.

Although at times the swelling and collapsing kinetics were shown to be complex, the overall response speeds can be controlled by the external parameters. For the investigated micrometer-thick pNIPAAm hydrogel layer with attached Au nanoparticle array, the swelling and collapsing state time responses varied significantly for all external variables changed. The collapsing speed took up to over 20 ms, but with specific bulk temperatures and local temperature increases it reached as low as 1.5 ms. The swelling state response was less affected by the magnitude of driving temperature range and resulted in a time constant of close to 5 ms.

This experiment shows that the response speeds of the swelling and collapsing states of pNIPAAm-based hydrogels is complex with many variables to consider. With these quick response speeds of as low as 1.5 ms, the polymer hydrogels can be considered for a multitude of future applications. This research provides a guideline for novel miniature actuator designs and micromachines using temperature induced volume transitions in thermo-responsive hydrogel materials.¹

WAVELENGTH'S ROLE

While the main focus was on plasmonic heating of the polymer network, the effect of the ambient bulk temperature on the sample was critical to the speed and timing of the thermo-response. To control this temperature, researchers used Wavelength Electronics' LFI-3751 temperature controller to operate a Peltier device attached to the flow cell and substrate with the nanoparticle and polymer hydrogel layer. The high performance and high precision LFI-3751 temperature controller ensured constant and stable temperature of the polymer networks as ambient bulk temperature was found to be a critical variable in response speed of the collapsing or swelling state of the thermo-responsive polymer network. By controlling this temperature and carefully increasing or decreasing above or below the LCST, researchers found the effects on ambient bulk temperature paired with plasmonic heating on thermo-responsive polymer networks.

The LFI-3751 temperature controller enables linear stability of as low as 0.001°C with a drive current of up to ±5 A to either thermoelectric coolers or resistive heaters. Autotune PID allows for a sophisticated algorithm to optimize the PID control parameters of the load. By using the LFI-3751 temperature controller, researchers were able to maintain the desired temperature of the sample for accurate and repeatable results with rapid actuation of thermo-responsive polymer networks.

REFERENCES

1. Auer, S. K., Fossati, S., Morozov, Y., Mor, D. C., Jonas, U., Dostalek, J., Rapid Actuation of Thermo-Responsive Polymer networks: Investigation of the Transition Kinetics, *J. Phys. Chem. B* **126**, 16, 3170-3179 (2022). <https://doi.org/10.1021/acs.jpcc.2c01160>

USEFUL LINKS

- LFI Temperature Controller [Product Page](#)

PERMISSIONS

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A caption was added to Figure 1, but no other changes were made to the images or the captions. They are presented here in their original form.

PRODUCTS USED

LFI-3751 Temperature Controller

KEYWORDS

Thermo-responsive polymer, swelling, collapsing, transition kinetics, lower critical solution temperature, LCST, plasmonic heating, localized surface plasmon, LSP, localized surface plasmon resonance, LSPR, LFI-3751, temperature controller, pNIPAAm

REVISION HISTORY

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A	June 2022	Initial Release