Photoinduced Phase Transitions in Poly(*N*-isopropylacrylamide) Microgels

Satish Nayak and L. Andrew Lyon*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received March 2, 2004. Revised Manuscript Received April 22, 2004

Photoresponsive microgels have been prepared by precipitation polymerization of the thermoresponsive polymer poly(*N*-isopropylacrylamide) followed by covalent conjugation of the temperature-jump dye malachite green. The photoresponsivity of these dye-labeled microgels was characterized by a pump−probe optical setup. A HeNe laser is used for exciting the dye molecules and a near-IR-diode laser is used to simultaneously measure the turbidity of the colloidal dispersion. Irradiation of malachite green increases the temperature of the sample through rapid nonradiative decay, thereby causing the polymer chains to aggregate. On deswelling, a decrease in the intensity of transmitted light is observed due to scattering. It is also observed that the photoresponsive behavior of the microgels is dependent on the concentration of the dye, intensity of the laser, and bath temperature.

Introduction

Photoresponsive polymers have found uses in many real world applications such as drug delivery,[1−3] photopatterning,[4] holographic sensors,[5] and mechanochromic materials.[6] A common material that has been used for devising photoresponsive gels is the thermoresponsive polymer poly(*N*-isopropylacrylamide) (pNIPAM), which belongs to a class of polymers that show an abrupt change in their solubility in response to a change in environmental conditions. For example, polymers have been designed to respond to changes in pH,[7,8] light intensity/wavelength,[9] temperature,[10] magnetic field,[11] and ionic strength.[12,13] pNIPAM has a lower critical solution temperature (LCST) of ∼31 °C in water. At this temperature the polymer goes from a hydrophilic random coil state to a desolvated globular state.[14] Gels composed of cross-linked pNIPAM show an abrupt change in volume when the polymer undergoes desolvation. In this manuscript, we will refer to the temperature at which the gel goes from a swollen state to a deswollen state as the volume phase transition temperature (VPTT).[15]

Photoresponsive gels have traditionally been made by one of several methods. The first method was pioneered by Irie and co-workers, wherein an azobenzene moiety was incorporated into the gel.[16] Under UV irradiation, the azobenzene group undergoes a trans to cis photoisomerization, which changes the free energy of mixing in the gels and hence the VPTT. Another interesting example of photoresponsive gels belonging to the abovementioned class was reported by Ikeda et al.,[6] where a liquid crystalline gel containing an azobenzene moiety was constructed. In the presence of UV light the gel folds in one direction and in the presence of visible light, the reverse cis-to-trans isomerization takes place and the gel unfolds. Kamenjicki et al. have made polymerized colloidal crystal arrays that have azobenzene moieties in them.[17] Following irradiation with either UV or visible light the photonic crystal diffraction is shifted. Irie et al. have also made photoresponsive gels by copolymerizing triphenylmethane leuco dyes in the gels, which photodissociate in the presence of UV light resulting in a charged species.[18,19] The gel then undergoes osmotic swelling due to formation of these charged species. Gels that are responsive to light via photothermal processes have also been reported previously. Tanaka and co-workers synthesized monolithic gels of pNIPAM containing the trisodium salt of chlorophyl-

* To whom correspondence should be addressed: lyon@chemistry.gatech.edu.

(1) Sershen, S. R.; Westcott, S. L.; Halas, N. J.; West, J. L. *J. Biomed. Mater. Res.* **2000**, *51*, 293−298.
(2) Sershen, S. R.; Westcott, S. L.; West, J. L.; Halas, N. J. *Appl. Phys. B* **2001**, *73*, 379−381.
(3) Sershen, S. R.; Westcott, S. L.; Halas, N. J.; West, J. L. *Appl. Phys. Lett.* **2002**, *80*, 4609−4611.
(4) Hoffmann, J.; Plotner, M.; Kuckling, D.; Fischer, W. J. *Sens. Actuators, A* **1999**, *77*, 139−144.
(5) Marshall, A. J.; Blyth, J.; Davidson, C. A. B.; Lowe, C. R. *Anal. Chem.* **2003**, *75*, 4423−4431.
(6) Ikeda, T.; Nakano, M.; Yu, Y. L.; Tsutsumi, O.; Kanazawa, A. *Adv. Mater.* **2003**, *15*, 201.
(7) Moselhy, J.; Wu, X. Y.; Nicholov, R.; Kodaria, K. *J. Biomater. Sci., Polym. Ed.* **2000**, *11*, 123−147.
(8) Jones, C. D.; Lyon, L. A. *Macromolecules* **2000**, *33*, 8301−8306.
(9) Suzuki, A.; Tanaka, T. *Nature* **1990**, *346*, 345−347.
(10) Tanaka, T.; Fillmore, D. J.; Sun, S.-T.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636−1639.
(11) Zrinyi, M. *Colloid Polym. Sci.* **2000**, *278*, 98−103.
(12) Duracher, D.; Sauzedde, F.; Elaissari, A.; Pichot, C.; Nabzar, L. *Colloid Polym. Sci.* **1998**, *276*, 920−929.
(13) Snowden, M. J.; Chowdhry, B. Z.; Vincent, B.; Morris, G. E. *J. Chem. Soc.-Faraday Trans.* **1996**, *92*, 5013−5016.
(14) Wu, C.; Wang, X. *Phys. Rev. Lett.* **1998**, *80*, 4092−4094.
(15) Shibayama, M.; Tanaka, T. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1993; Vol. 109, pp 1−62.
(16) Kungwatchakun, D.; Irie, M. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 243−246.
(17) Kamenjicki, M.; Lednev, I. K.; Mikhonin, A.; Kesavamoorthy, R.; Asher, S. A. *Adv. Funct. Mater.* **2003**, *13*, 774−780.
(18) Irie, M.; Kungwatchakun, D. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 829−832.
(19) Irie, M.; Kunwatchakun, D. *Macromolecules* **1986**, *19*, 2476−2480.

10.1021/cm049650i CCC: $27.50
Published on Web 05/26/2004

lin.[9,20] This dye acts as a photon antenna and locally heats the gel in the presence of light of an appropriate wavelength. This increase in temperature causes the thermosensitive pNIPAM gel to collapse locally in the region being irradiated. Unfortunately, these studies did not study the photothermal effects or the optical properties of chlorophyllin in detail. The investigators did, however, compare their experimental results to a basic theoretical description of the system with good agreement. Wen et al. have used an IR-absorbing dye in a poly(methyl methacrylate) (PMMA) matrix to heat the polymer.[21] Halas and co-workers have made pNIPAM gels that release drugs or macromolecules in the presence of IR radiation.[1−3] The photoresponsive moiety used in that work is a nanoparticle having a dielectric core surrounded by a gold nanoshell. These designer nanoparticles absorb IR radiation and then give off heat via nonradiative relaxation, thus deswelling the polymer and subsequently releasing the entrapped material. Finally, our group has made photonic crystals doped with gold nanoparticles. These crystals can be patterned photothermally using a frequency doubled Nd:YAG laser, which heats the gold nanoparticles and subsequently melts or anneals the colloidal crystals in a spatially confined manner.[22]

In this work we use colloidally stable hydrogel nanoparticles, or microgels, as our polymeric material.[8,23−25] These microgels are composed of lightly cross-linked pNIPAM copolymerized with an amine-containing comonomer, which is then used to attach a malachite green derivative to the network. In all previously cited examples of photoresponsive gels, the responsive material was in the physical form of a monolithic gel. Microgels made from "smart materials" have potential applications in several fields[26] including drug delivery,[27−30] biosensing,[31−33] chemical separations,[34,35] catalysis,[36−38] and optics.[22,39−41] The temperature-jump dye used in the work described below is malachite green, which belongs to the class of triphenylmethane dyes. The photophysics of this dye have been well studied.[42−44] Because of the rapid nonradiative decay and large extinction coefficient of the dye, it has been used as a photon-to-heat converter for many studies.[45−49] In this study we label the microgels with this dye and study their deswelling behavior as a function of light intensity to ascertain the utility of such a system in the design of photoresponsive materials.

Experimental Section

Materials. *N*-isopropylacrylamide (NIPAM, Aldrich) was purified by recrystallization from hexane (J. T. Baker) prior to use. *N*,*N*′-methylenebis(acrylamide) (BIS), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), and malachite green oxalate were purchased from Aldrich and used as received. *N*-(3-Aminopropyl)methacrylamide hydrochloride (APMA) was purchased from Polysciences. Malachite green isothiocyanate (MALG) was purchased from Molecular Probes (Eugene, OR). Water was purified with a Barnstead E-Pure system to a resistance of 18 MΩ and then filtered through a 0.2-μm filter to remove particulate matter.

Microgel Synthesis. A detailed procedure for preparation of microgels by free radical precipitation polymerization is described elsewhere.[8,23] The total monomer concentration in the pregel solution was kept constant at 70 mM, out of which 1 mol % was BIS and 1 mol % was APMA, with the remaining 98 mol % being NIPAM. All the monomers and 70 mg of SDS were dissolved in 250 mL of water, and the resulting solution was filtered through a 0.2-μm membrane filter (Pall Gelman Metricel) to remove particulate matter. The reaction mixture was heated in a three-neck round-bottom flask equipped with a condenser and inlet for nitrogen. The mixture was heated to 70 °C under a gentle stream of nitrogen for 1 h, after which 60 mg of APS dissolved in 1 mL of water was added to initiate the reaction. The reaction mixture was kept at 70 °C for 4 h to complete the reaction. After synthesis, the microgel solution was filtered using fine-porosity filter paper (Fisher Scientific) to remove aggregated material, if any. The particles were then purified by dialysis (Spectra/Por 7 dialysis membrane, MWCO 10 000) against daily changes of water for at least three weeks.

Conjugation of Malachite Green. The dialyzed microgel solution was lyophilized and rehydrated in 250 mL of pH 9.8 bicarbonate buffer. Five 20-mL portions of the microgel solution were removed. To each portion, varying amounts of malachite green isothiocyanate were added as shown in Table 1. The samples were left to react overnight at 4 °C and then dialyzed at 4 °C in the dark with daily changes of water for three weeks to remove unreacted dye. After dialysis, each sample was lyophilized separately and then rehydrated in deionized water to give a 50 mg/mL solution of the particles. Note that the amount of amine that is used for calculating the reaction stoichiometries is the amount that was present in the pregel solution. In Table 1, the actual amount of MALG that is conjugated to the particles is calculated from the Beer's Law plot in Figure 3.

UV−Vis Characterization. The absorption spectra of the dye and the dye-conjugated microgels were obtained using a Shimadzu UV 1601 spectrophotometer.

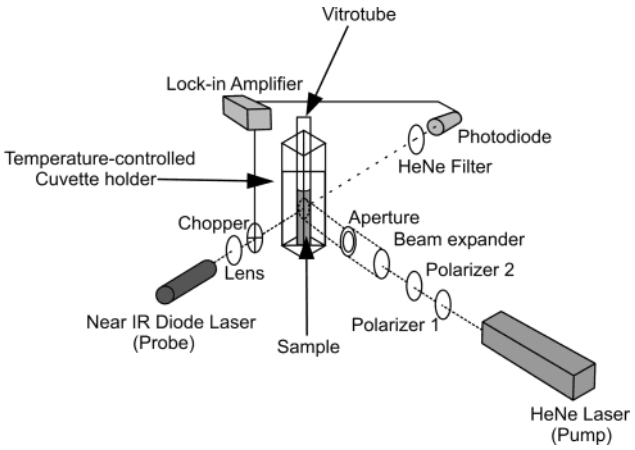
(20) Suzuki, A.; Ishii, T.; Maruyama, Y. *J. Appl. Phys.* **1996**, *80*, 131−136.
(21) Wen, X.; Tolbert, W. A.; Dlott, D. D. *J. Chem. Phys.* **1993**, *99*, 4140−4151.
(22) Jones, C. D.; Lyon, L. A. *J. Am. Chem. Soc.* **2003**, *125*, 460−465.
(23) Jones, C. D.; Lyon, L. A. *Macromolecules* **2003**, *36*, 1988−1993.
(24) Gan, D.; Lyon, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 7511−7517.
(25) Gan, D.; Lyon, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 8203−8209.
(26) Pelton, R. *Adv. Colloid Interface Sci.* **2000**, *85*, 1−33.
(27) Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* **1997**, *388*, 860−862.
(28) Hoffman, A. In *Controlled Drug Delivery: Challenges and Strategies*; Park, K., Ed.; American Chemical Society: Washington, DC, 1997; pp 485−498.
(29) Kurisawa, M.; Terano, M.; Yui, N. *Macromol. Rapid Commun.* **1995**, *16*, 663−666.
(30) Brondsted, H.; Kopecek, J. *Pharm. Res.* **1992**, *9*, 1540−1545.
(31) Miyata, T.; Jikihara, A.; Nakamae, K.; Uragami, T.; Hoffman, A. S.; Kinomura, K.; Okumura, M. *Adv. Biomater. Biomed. Eng. Drug Delivery Syst. [Iketani Conf. Biomed. Polym.]* **1996**, 237−238.
(32) Miyata, T.; Asami, N.; Uragami, T. *Macromolecules* **1999**, *32*, 2082−2084.
(33) Holtz, J. H.; Asher, S. A. *Nature* **1997**, *389*, 829−832.
(34) Umeno, D.; Kawasaki, M.; Maeda, M. *Bioconj. Chem.* **1998**, *9*, 719−724.
(35) Kawaguchi, H.; Fujimoto, K. *Bioseparation* **1998**, *7*, 253−258.
(36) Bergbreiter, D. E.; Case, B. L.; Liu, Y.-S.; Caraway, J. W. *Macromolecules* **1998**, *31*, 6053−6062.
(37) Bergbreiter, D. E.; Liu, Y.-S.; Osburn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250−4251.
(38) Nagayama, H.; Maeda, Y.; Shimasaki, C.; Kitano, H. *Macromol. Chem. Phys.* **1995**, *196*, 611−620.
(39) Jones, C. D.; Serpe, M. J.; Schroeder, L.; Lyon, L. A. *J. Am. Chem. Soc.* **2003**, *125*, 5292−5293.
(40) Debord, J. D.; Lyon, L. A. *J. Phys. Chem. B* **2000**, *104*, 6327−6331.
(41) Debord, J. D.; Eustis, S.; Debord, S. B.; Lofye, M. T.; Lyon, L. A. *Adv. Mater.* **2002**, *14*, 658−661.
(42) Ishikawa, M.; Ye, J. Y.; Maruyama, Y.; Nakatsuka, H. *J. Phys. Chem. A* **1999**, *103*, 4319−4331.
(43) Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381−433.
(44) Sundstrom, V.; Gillbro, T. *J. Chem. Phys.* **1984**, *81*, 3463−3474.
(45) Miyata, R.; Terazima, M. *Anal. Sci.* **2001**, *17*, S231−S233.
(46) Lian, T. Q.; Locke, B.; Kholodenko, Y.; Hochstrasser, R. M. *J. Phys. Chem.* **1994**, *98*, 11648−11656.
(47) Indig, G. L.; Jay, D. G.; Grabowski, J. J. *Biophys. J.* **1992**, *61*, 631−638.
(48) Jay, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 5454−5458.
(49) Robl, T.; Seilmeier, A. *Chem. Phys. Lett.* **1988**, *147*, 544−550.

Table 1. Particle Conjugation with Malachite Green Isothiocyanate

sample	reaction stoichiometry[a] [MALG]/[NH_2]	malachite green isothiocyanate conjugated per gram of the polymer[b] (μmol/g)
MAL1	0.01	4.8
MAL2	0.05	7.2
MAL3	0.10	9.6
MAL4	0.50	12.0
MAL5	1.00	26.4

[a] Reaction stoichiometries are calculated by taking the amount of APMA in the pregel solution. [b] Amount of malachite green isothiocyanate conjugated to per gram of polymer is calculated from the Beer's plot shown in Figure 3.

Scheme 1. Pump−Probe Instrumental Setup



Pump−Probe Instrument. To measure the turbidity of the sample as a function of pump laser power, a pump−probe instrument was built. The schematic of the setup is shown in Scheme 1. The excitation arm of this instrument consists of a helium neon laser (HeNe; λ = 632.8 nm; Spectra Physics) pump laser, which is nearly resonant with the S0−S1 transition of malachite green (λ_{max} = 620 nm), making it appropriate for excitation of the dye. The laser is passed through two polarizers. The second polarizer is fixed to pass p-polarized radiation, while the first can be rotated to control the total transmitted laser intensity. The beam is then expanded and impinged on the sample through an aperture. The sample is housed in a temperature-controlled cuvette holder (Quantum Northwest). To interrogate the sample turbidity, a near-IR diode laser (Thor Labs, λ = 820 nm) is oriented 90° relative to the pump arm. This beam is focused on the sample through an aperture and a chopper (Stanford Research Systems) and the transmitted light intensity is measured at a silicon photodiode. A HeNe interference filter is placed in front of the detector to eliminate stray or scattered pump laser light. The chopper (1 kHz) and detector are interfaced with a lock-in amplifier (SRS530, Stanford Research Systems) and the transmitted intensity was detected at the chopper frequency to eliminate contributions from stray light. Note that the apertures were chosen such that the pump illumination area was ∼4-fold larger than the probe area and the beams were aligned to be concentric at the sample. This should provide pseudo-steady-state conditions during the measurement.

Sample Preparation. For the pump−probe experiments, the sample was contained in a rectangular glass capillary tube, or vitrotube (0.2 × 4.0 mm, Vitrocom). To directly compare data from different samples, the same volume of sample was held in each vitrotube, which was achieved by allowing the sample to rise by capillary action to the same height in the vitrotubes. The tubes containing the sample were then attached to a glass coverslip (Fisher Scientific) that had been cut to fit diagonally in a standard 1-cm plastic cuvette. The cuvette was placed in the cuvette holder in such a fashion that the sample was at a 45° angle to the pump and probe beams, see Scheme 1.

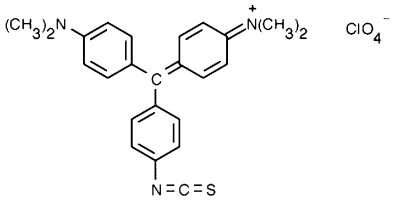


Figure 1. Structure of malachite green isothiocyanate.

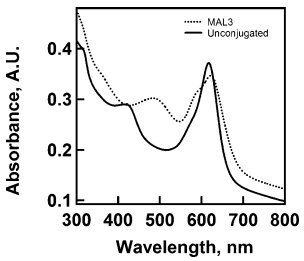


Figure 2. Absorption spectra of MAL3 and an unconjugated sample with the same concentration of particles and dye as in MAL3.

Photon Correlation Spectroscopy. Particle sizes were determined via photon correlation spectroscopy (PCS, Protein Solutions Inc.) equipped with an integrated Peltier temperature control device (±0.1 °C), as previously reported.[8,23] The hydrodynamic radii of the particles were calculated from the diffusion coefficient using the Stoke−Einstein equation. The sample was allowed to equilibrate at the proper temperature for 10 min before data collection. Scattered light from the fiber-coupled diode laser (798 nm) was collected at 90° with a fiber-coupled avalanche photodiode detector connected to a 248-channel autocorrelator board. The data were analyzed with Protein Solutions' Dynamics Software Version 5.25.44.

Results and Discussion

Thermoresponsive pNIPAM hydrogel particles having primary amines were synthesized as described in the Experimental Section. These particles are found to have a hydrodynamic radius of ∼700 nm, with a polydispersity of ±14%, as determined by PCS in water at 25 °C and ∼270 nm with a polydispersity of ±6% at 41 °C, where the polydispersity represents ± 1 SD about the intensity-weighted average particle size. An isothiocyanate derivative of malachite green was used to react with the amines in the microgel to form an isothiourea bond. Figure 1 shows the structure of malachite green isothiocyanate. The particles were conjugated with malachite green to varying degree, as shown in Table 1.

Figure 2 shows the absorption spectra of sample MAL3 and an unconjugated sample, which is simply a mixture of particles and free dye. The unconjugated sample was prepared to contain the same concentration of particles and malachite green as in sample MAL3. The free dye used to make the unconjugated sample is an oxalate salt of malachite green, which has spectral properties similar to those of malachite green isothiocyanate. The rationale for using malachite green oxalate was to avoid any reaction between the amine and the malachite green during the measurement. As can be seen from the spectra, the peak associated with the S0 to S1 transition for the conjugated sample is slightly red shifted as compared to the free dye plus microgel spectrum, while there is large red shift for the S0 to S2 peak. Similar shifts have been observed previously by Indig et al.,[47] where they conjugated malachite green to bovine serum albumin (BSA). Also it can be seen that the S0 to S1 peak has an exaggerated shoulder on the blue side of the band. In free dye solutions this shoulder has been assigned to the presence of more than one stable ground-state dye conformation.[43] The shoulder may be exaggerated when conjugated to the particles because of the

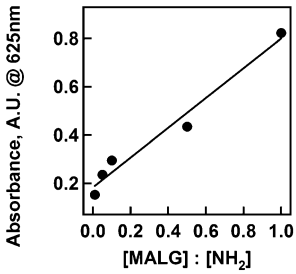


Figure 3. Absorbance of malachite-green-modified particles at 625 nm as a function of reaction stoichiometry.

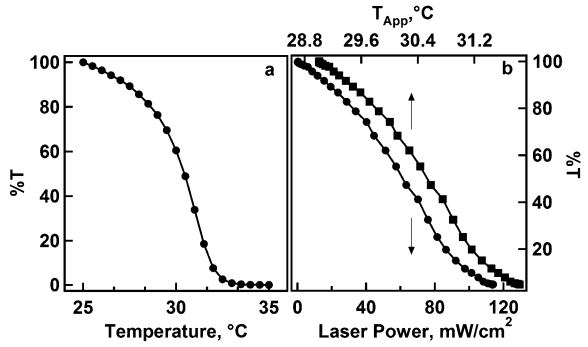


Figure 4. (a) Percent transmitted light as a function of temperature for MAL3. (b) Percent transmitted light as a function of laser power for MAL3 at 29 °C (circles) and percent transmitted light as a function of apparent temperature (T_{App}) (squares). See text for explanation.

presence of different dye environments that cause shifts in the conformational equilibria of the dye. To test the efficiency of malachite green conjugation, the electronic spectra of the particles were measured as a function of dye loading. These data are shown in Figure 3, which is a plot of the absorbance at 625 nm for samples conjugated with different ratios of MALG to APMA. The nonzero absorbance at zero concentration indicates that the reaction may become less efficient at higher dye concentrations. This may be due to instability of isothiocyanates in water, hence at high dye concentration not all the dye molecules are able to incorporate in the microgels covalently. Nonetheless, the linear trend that is observed suggests that by simply controlling the particle to dye stoichiometry in the range studied here, one can control the amount of dye loaded on the particle.

As described in the Experimental Section, a two-polarizer configuration is used in the pump−probe instrument to control the pump laser power (please refer to the Supporting Information for the plot of laser power intensity as a function of polarizer angle). Using this method to control laser intensity, we interrogated the photothermally induced deswelling of malachite-green-modified pNIPAM microgels. As stated above, the HeNe acts to excite the dyes, which then relax nonradiatively, causing local heating of the surroundings. If this laser-induced increase in temperature causes the VPTT of the particles to be traversed, one should observe particle deswelling. Particle deswelling can be observed as a change in solution transmittance, as the entropically favored expulsion of water from the network and the associated polymer phase separation is accompanied by an increase in particle scattering and hence an increase in solution turbidity.

Figure 4a shows the change in turbidity of sample MAL3 as a function of bath temperature and Figure 4b shows the change in relative transmittance *%T* as a function of laser power (circles) for MAL3 at a bath temperature of 29 °C.

$$\%T = \left(\frac{V_{\text{Final}}}{V_{\text{Initial}}}\right) \times 100 \qquad (1)$$

The change in solution turbidity is calculated using eq 1, where

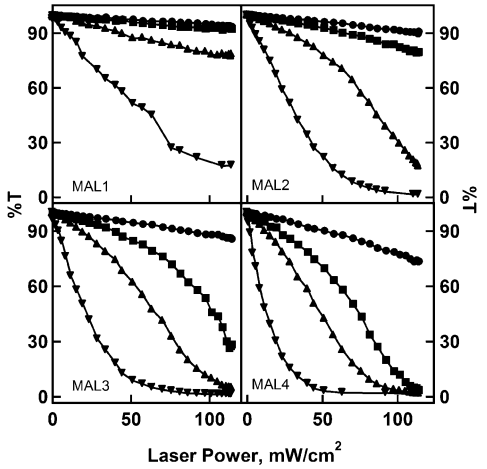


Figure 5. Percent transmitted light as a function of laser power intensity for samples MAL1, MAL2, MAL3, and MAL4 at 25 °C (circles), 27 °C (squares), 29 °C (triangles), and 31 °C (inverted triangles).

%T is the relative percent transmitted light for each measurement, V_{Initial} is the detector voltage before HeNe illumination, and V_{Final} is detector voltage reached following equilibration of the system under HeNe illumination. It typically takes about 300 to 500 s for the transmitted intensity to reach a stable value during irradiation. In Figure 4b

$$T_{\text{App}} = 29.0 + \Delta T \qquad (2)$$

where 29 °C is the temperature of the bath and ΔT is the increase in temperature brought about by the laser at each laser power value. ΔT is calculated by determining the *%T* value at 31 °C from Figure 4a and then determining the corresponding laser power value from the photothermal curve at 29 °C. Application of this single point calibration to the entire photothermal deswelling curve gives the data in Figure 4b, where the *%T* values for MAL3 are plotted as a function of T_{App} (squares). As expected, both curves in Figure 4b have the same shape, suggesting a linear increase in the photothermal effect with laser power. A table showing the effective increase in temperature as function of laser power is provided in the Supporting Information.

Figure 5 shows the change in transmittance as a function of the pump laser power for samples MAL1, MAL2, MAL3, and MAL4 at different bath temperatures (25, 27, 29, and 31 °C, respectively). In all the cases in Figure 5 the *%T* decreases with the increase in laser power intensity. In these experiments there are two sources of heat. One source is the temperature-controlled cuvette holder, which we will refer to as the "bath". This temperature is held constant for each measurement performed as a function of laser power. The second source of heat is the radiation absorbed and released by the malachite green. By increasing the laser power one is increasing the number of dye molecules being excited and hence a higher laser power increases the photothermal heating, which in turn results in more microgel deswelling. In Figure 5 for all the samples it is observed that higher bath temperatures result in faster decreases in transmittance with laser power. In other words, for the same photon flux more deswelling is observed for the samples that are at higher bath temperatures. This is expected because as the bath temperature gets closer to the VPTT of the particles, a smaller photothermal effect is required to deswell the particles. It is also observed that as the concentration of the conjugated dye is increased in the sample it becomes easier to deswell the particles at a given bath temperature and at a given laser intensity. Again this can be explained that as the conjugation of the dye to the particles is increased, the number of molecular heaters in the sample increases and hence at a given temperature fewer photons are needed to cause deswelling of the particles. For example, in the case of MAL1 it is observed that

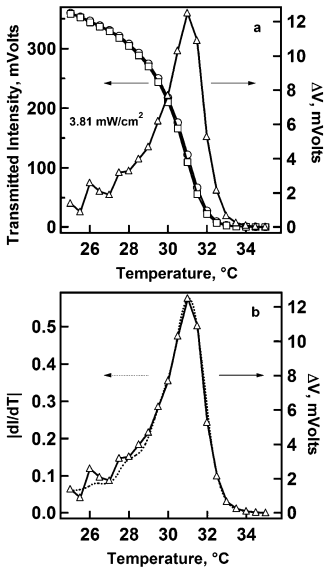


Figure 6. (a) Transmitted intensity as a function of temperature: thermal curve (open circles) and photothermal curve (open squares) and the difference of the thermal and photothermal curve as a function of temperature (open triangles). (b) First derivative of the thermal curve as a function of temperature (dotted line) and difference of the thermal and photothermal curve as a function of temperature (open triangles).

only at a bath temperature of 31 °C is significant deswelling observed during irradiation at the highest laser power, whereas for MAL2, MAL3, and MAL4 almost complete deswelling is observed for a bath temperature of 31 °C at that laser power. Together, these data show the expected trends: higher bath temperatures and higher dye loadings decrease the laser power required for particle deswelling.

To determine the photothermal efficiency of the dye as a function of particle conformation or solvent content, we performed an experiment involving subtle photoinduced temperature jumps as a function of bath temperature. This was investigated to determine whether particle deswelling impacts the relative contributions of radiative and nonradiative pathways in malachite green, and hence the photothermal efficiency. Others have shown that the photoemission quantum yield of malachite green is dependent in some cases on the rigidity of its environment,[50,51] which may be expected to change as the microgel deswells. For this experiment MAL3 was chosen and the transmitted intensity was determined as a function of temperature without using the pump laser, which is denoted by the thermal curve in Figure 6a. At each bath temperature, after the transmitted intensity had stabilized, the sample was irradiated with pump laser intensity of 3.81 mW/cm^2 and the decrease in transmitted intensity was measured. This intensity decrease is plotted as the photothermal curve in Figure 6a. The difference between the thermal and photothermal curve as a function of temperature is also plotted in Figure 6a, where

$$\Delta V = V_{\text{photothermal}} - V_{\text{thermal}} \quad (3)$$

$V_{\text{photothermal}}$ is the detector voltage during illumination, and V_{thermal} is the detector voltage in the absence of HeNe illumination. Here ΔV is taken as a measure of photothermal efficiency, where the photothermal efficiency is the ability of the dye molecules to bring about aggregation of the polymer chains at a fixed laser flux. From Figure 6a it is found that the maximum ΔV is obtained at 31 °C, which is the VPTT of the hydrogel particles. Above 31 °C, the change in turbidity brought about by irradiation decreases. This is expected, as the shape of the thermal turbidity curve is asymmetric, with the instantaneous slope of the curve decreasing at temperatures greater than the VPTT. The impact of the thermal turbidity curve shape on the shape of the photothermal efficiency curve is illustrated in Figure 6b, where we compare the photothermal efficiency curve to the first derivative of the thermal curve. The two curves are nearly indistinguishable in shape. Thus, it can be inferred that the shape of the photothermal efficiency curve is a direct result of the asymmetric shape of the thermal curve and that the photothermal efficiency is independent of particle deswelling. Apparently, the increase in polymer density accompanied by particle deswelling does not strongly modulate the rotation of the phenyl rings on the dye.

Conclusions

We have demonstrated that photoresponsive microgels can be made by conjugating malachite green to pNIPAM microgels. Upon excitation with a HeNe laser the dye molecules undergo a nonradiative decay causing an increase in the temperature of the sample, which in turn causes the microgels to undergo partial or complete deswelling depending on several parameters. The deswelling of the microgels can be manipulated by the amount of dye conjugated to the particles, the bath temperature, and the power of the pump laser. As expected, it is observed that as the bath temperature approaches the VPTT, it becomes easier to deswell the particles photothermally. Interestingly, the increased density of the microgel following deswelling does not directly impact the conformational flexibility of the dye, as evidenced in a deswelling-independent photothermal yield. This simple particle construct suggests a synthetically trivial route to a wide range of photomodulated colloidal materials based on synthetic polymers.

Acknowledgment. Financial support from the NSF Division of Materials Research (DMR-0203707) is gratefully acknowledged.

Supporting Information Available: Graph of variation in laser power intensity as a function of rotation of the polarizers, graph of percent transmitted light as a function of laser power intensity, and table of temperature increase as a function of laser power (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

CM049650I

(50) Baptista, M. S.; Indig, G. L. *J. Phys. Chem. B* **1998**, *102*, 4678−4688.

(51) Abedin, K. M.; Ye, J. Y.; Inouye, H.; Hattori, T.; Sumi, H.; Nakatsuka, H. *J. Chem. Phys.* **1995**, *103*, 6414−6425.