Unresolved Issues in the Preparation and Characterization of Thermoresponsive Microgels

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Summary: The preparation and properties of colloidal thermal responsive microgels based on poly(N-isopropylacrylamide) are described with an emphasis on the unresolved issues which will impair commercial implementation. The main difficulties are: 1) removal of sol, surfactants and other impurities; 2) obtaining colloidally stable particles less than 50 nm in diameter; 3) synthesis of concentrated, colloidally stable microgel dispersions; 4) accurate measurement of water content; and, 5) control of microgel particle morphology.

Introduction

Poly(N-isopropylacrylamide), PNIPAM, is the cornerstone of many current approaches to the development of controllable materials for a variety of potential applications. This popularity stems from the fact that PNIPAM is water soluble at room temperature but phase separates when heated above 32 °C.[1] Thus temperature change is the trigger causing dramatic changes in the properties of PNIPAM solutions.

Most of the published studies involve PNIPAM hydrogels manifest temperature sensitivity as a temperature-dependent degree of swelling. The temperature corresponding to the most rapid change in swelling is called the volume phase transition temperature. The transition temperature can be raised by copolymerizing with acrylamide, or lowered by employing more hydrophobic monomers. Macroscopic PNIPAM gels were first described in the scientific literature by Tanaka.[2] Monodispersed colloidal microgels (these days we would call them nanogels) were first prepared by Pelton and Chibante in 1978.[3] Both macro and microgels can display nearly a ninety percent decrease in volume upon heating, giving spectacular changes in most properties. The number of PNIPAM gel papers seems to be growing geometrically, if not exponentially and there have been a number of excellent reviews.[4-8] The objective of this paper is to review the properties of PNIPAM thermoresponsive microgels and to highlight the most important unresolved issues. These have been largely ignored by most researchers including ourselves. Many of these issues are also relevant to macrogel preparation and characterization.

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An Overview of Microgel Preparation and Characterization

N-isopropylacrylamide (NIPAM) is the major building block for temperature sensitive microgels. With a structure close to acrylamide, many of the properties of NIPAM are similar to those of acrylamide. In aqueous solution, it undergoes rapid free radical polymerization to give high molecular weight polymers at rates similar to that of acrylamide.[1-11] The first published account of PNIPAM-based microgels described a "surfactant-free emulsion polymerization" of aqueous NIPAM and methylene-bis-acrylamide (BA).[3] This recipe was essentially the same as that used to prepare monodisperse, surfactant-free polystyrene latex.[12] The polymerizations were conducted at 60 to 70 °C in order to generate free radicals by the decomposition of the persulfate initiator. However, elevated temperature was also required so that growing PNIPAM chains phase separated to form colloidal particles - some authors call this procedure "precipitation polymerization". The original procedure has been reproduced by many others.[13-19]

This simple polymerization procedure can produce remarkably uniform particles. Figure 1 shows a transmission electron micrograph of typical microgel particles. The TEM sample was prepared by placing a dilute drop of aqueous particles onto the sample grid and allowing it to dry. The surface tension forces pulled the swollen particles into a closely packed array of spheres which then dehydrated in vacuum to give disks. The original dimensions of the swollen microgels can be estimated from the center-to-center spacing of the ordered disks in Figure 1.

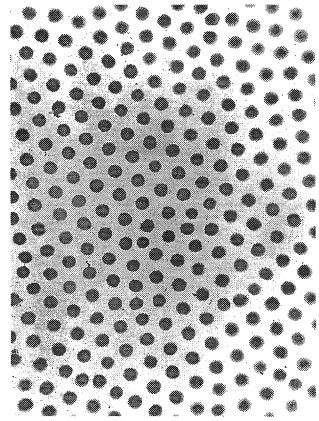

Figure 1. Transmission electron micrograph of PNIPAM microgels. Published with permission. [3]

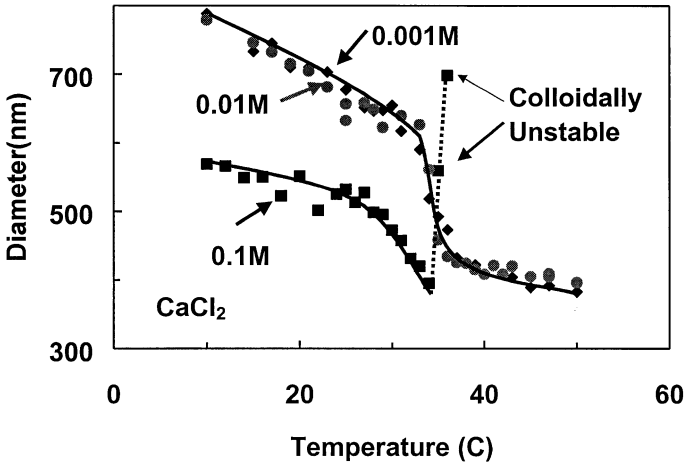

Figure 2. The diameter of PNIPAM microgel spheres as a function of temperature and $CaCl_2$ concentration. The particles display a volume phase transition at ~ 35 °C which is close to the lower critical solution temperature of linear PNIPAM. Adapted from Pelton et al. [29]

Temperature sensitive microgel swelling is most easily demonstrated by dynamic light scattering (DLS). Figure 2 shows that particle diameters can change by more than a factor of two over a narrow temperature range. The microgels whose behaviors are shown in Figures 1 and 2 are generally considered to be homogenous in composition.

Much work has also been reported on the preparation of core-shell gel particles. Core-shell gels consist of a water-insoluble latex particle coated with a gel layer. The composite particles have properties characteristic of both the core and the shell. The core dominates light scattering (turbidity) behavior, whereas colloid stability is determined by the hydrogel shell. The first reported preparation of PNIPAM-coated core-shell particles was by Pelton[20] who described both the one-shot surfactant free preparation of polystyrene/PNIPAM gels and the grafting of PNIPAM onto existing latex particles. Unlike the homogenous microgel preparations, these polymerizations are conducted below the LCST so that PNIPAM does not phase separate. Similar polystyrene-co-PNIPAM surfactant free latexes are obtained when starting with either NIPAM monomer or with PNIPAM. This reflects the fact that NIPAM polymerizes much more quickly than does styrene in aqueous media. Thus, most of the NIPAM is

converted to PNIPAM at extremely low styrene conversions.

Makino et al.[21] refined Pelton's procedure with a two-stage approach. The first stage was a one-shot surfactant free polymerization with styrene and NIPAM. In the second stage, the surface gel layer was expanded by adding more NIPAM monomer and a nonionic water-soluble free radical initiator.

Zhu and Napper employed a two-stage procedure for the preparation of polystyrene-PNIPAM core-shell particles.[22] In the first stage, styrene was added slowly to an aqueous PNIPAM solution, presumably at room temperature, in the presence of a redoxinitiator. The objective of this stage was to produce a soluble NIPAM-co-styrene copolymer; however, the polymer from this stage was not isolated. In the second stage, the remainder of the styrene was added quickly to yield latex.

Duracher and coworkers[23] investigated the preparation and properties of cationic polystyrene-PNIPAM core shell particles. Positively charged groups were introduced by both cationic initiator and aminoethylmethacrylate. The cationic monomer gave smaller particles; however, a variety of particle morphologies was obtained, depending upon the polymerization conditions.

Publications describing new microgel synthesis schemes are published nearly every month. The above summary is meant to be neither a comprehensive nor an up-to-date account of these activities. However, in spite of scores of publications, there remain a number of unresolved issues regarding the preparation and characterization of microgels. These are now considered.

Unresolved Issues

1. Microgel Cleaning

Microgel polymerizations can yield a significant fraction of sol (i.e. linear or slightly branched polymer). Centrifugation, followed by decantation and redispersion in clean water is currently the only effective cleaning procedure. However, this is a tedious procedure requiring extended ultracentrifugation, because microgel densities are close to that of water. Membrane processes and ion-exchange beds, commonly used to generate clean polystyrene latex[24], are not effective with PNIPAM microgels – membranes do not remove high molecular weight sol components and nonionic sol components will not be captured in an ion-exchange resin bed.

Surfactant contamination is related to the cleaning issue. Most microgel preparations involve surfactants such as sodium dodecyl sulfate (SDS) to facilitate the formation of uniform particles. Furthermore, most ionic surfactants change the swelling/temperature response of PNIPAM gels. For example, Figure 3 shows that the presence of SDS increases microgel swelling and attenuates the temperature sensitivity. Thus, removing surfactant is important. There have been at least two published SDS binding isotherms,[25,27] one of which is shown in Figure 4. It is generally assumed that surfactant binding is reversible which, in turn, means that it is possible to remove bound surfactant by washing. The complete reversibility of SDS binding has not been proved for SDS or other surfactants. In other words, the extent to which surfactant can be removed from microgels has not been proved. In summary, microgel cleaning is tedious in a research laboratory and an unsolved problem for commercial scale production.

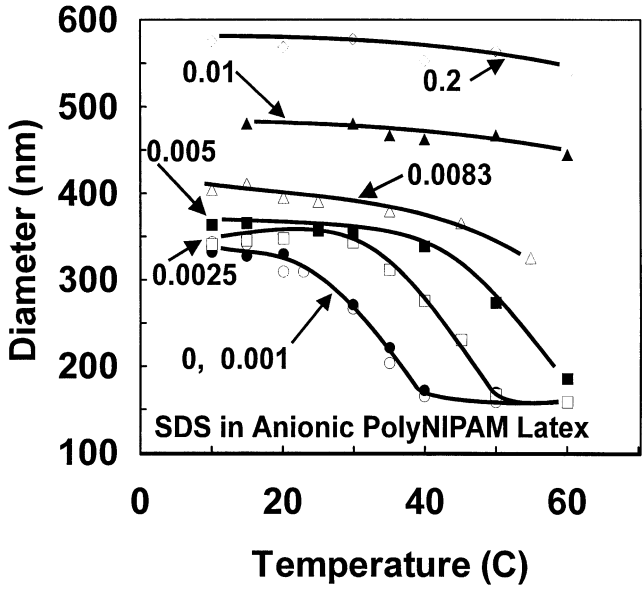

Figure 3. Diameter of PNIPAM microgel spheres as functions of temperature and the molar concentration of SDS. From Tam et al.; used with permission. [26]

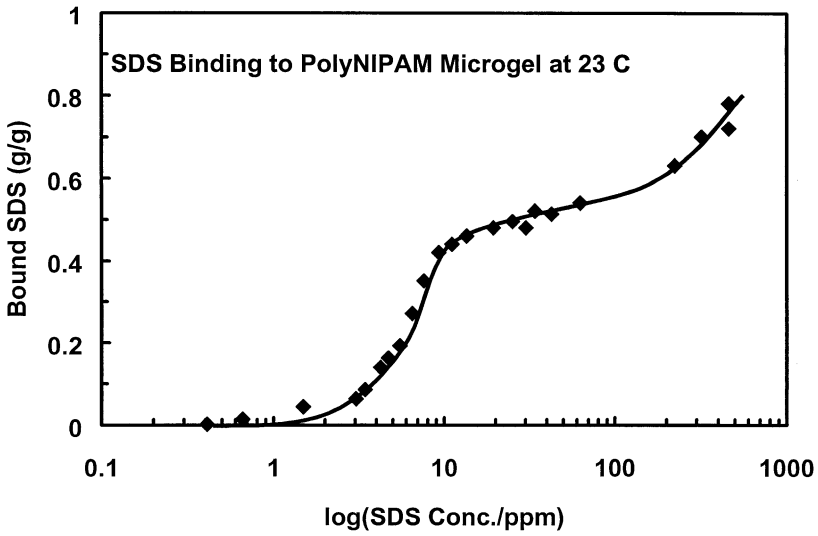

Figure 4. The amount of SDS bound on PNIPAM microgel as a function of the equilibrium SDS concentration. Adapted from Mears et al. [27]

2. Very small particles

It is difficult to prepare small microgels by surfactant-free methods because there is simply not enough available charge to stabilize high concentrations of small particles. The surface charge density of a PNIPAM microgel latex was found to be 3.8 μeq/g [28] which is about two orders of magnitude lower than that of a corresponding surfactant free polystyrene latex.[12] Surfactant will give smaller particles; however, colloidally stable, clean, 10~20 nm microgels have yet to be prepared. Indeed, such small species would not normally be called microgels.

3. High volume fraction synthesis

Commercial latex dispersions typically contain 30 to 60 wt% polymer whereas most microgel recipes produce less than 5 wt%. This is a significant limitation for anything other than the very highest value added applications. In my opinion, this limitation can be eliminated by using high surfactant concentrations; however, the cleaning issue remains a problem.

4. Accurate measurement of water content

Temperature dependent swelling with water is perhaps the most interesting feature of

PNIPAM gels. In the case of macroscopic gels, it is relatively easy to measure water contents; one simply weighs a piece of gel before and after drying. Most microgel swelling is reported as average particle diameters or volumes measured by dynamic light scattering.[29] However, DLS measurements alone do not give absolute water contents. More information is required to relate particle volume to polymer or water content of the microgel. Some have avoided this problem by reporting swelling volume or diameter ratios calculated by comparing particle size to a reference particle size. However, if the average mass of polymer per gel particle is known, then the diameters are easily converted to absolute measures of swelling. A few approaches have been applied to the measurement of absolute water content in microgels. McPhee et al.[28] centrifuged PNIPAM microgels to give an ordered, packed bed of particles, which was iridescent, indicating ordered packing. The water content of the bed was calculated from the bed mass before and after drying.

Wu's group was the first to employ intensity light scattering to measure the water content of uniform microgels[30,31] based on the weight average molecular weight and particle radius of gyration. This is the most direct method; however, it does require careful determination of the microgel optical properties.

Another approach is to measure the particle size at a temperature above the VPTT and assume a water content based on macrogel data, such as that given by Dong and Hoffman.[32] For example, consider a microgel with a particle diameter at 45 °C of 100 nm and a corresponding diameter of 200 nm at 20 °C. If we assume that the mass concentration of water in the particles at 45 °C is 25%, then the corresponding concentration of water in the particles at 20 °C is 0.8912. Note that this calculation is based upon the assumptions that: the density of PNIPAM is 1269 kg/m3, the PNIPAM density is independent of temperature over this range; and, that there is no excess volume of mixing. If the actual water content is 30% instead of 25% at 45 °C (i.e. an error of 20%), the corresponding water content of the particles at 20 °C is 0.8996. Thus, a large (20%) error in the estimate of the water content at 45 °C corresponds to only a 0.94 % error in the estimated water content at 20 °C. It seems therefore that this is a robust method for estimation of microgel water content in swollen gels.

5. Microgel particle morphology

Most of the reported microgel preparations are batch copolymerizations of NIPAM and N-methylenebisacrylamide (BA) crosslinker. Figure 5 shows the consumption of NIPAM and BA crosslinker as functions of time and temperature[10]. BA is consumed more quickly than NIPAM, indicating that the particles are unlikely to have a uniform composition. Indeed, it seems reasonable to speculate that there exists a zone of relatively high crosslink density in each particle. Since polyBA is more hydrophilic than PNIPAM at elevated temperature, one might further speculate that at least part of the high crosslink density zone is situated on the particle/water interface.

For applications requiring very well controlled gel morphologies, it might be better to completely decouple the growth of PNIPAM linear chains from the crosslinking reactions. For example, Hiratani et al. described gel crosslinking with reversible disulfide bonds.[33]

PNIPAM microgel polymerizations are usually initiated with ionic initiators such as potassium persulfate which lead to the incorporation of electrically charged groups in the gel network. Although many experimental and theoretical studies have addressed the electrokinetic properties of PNIPAM microgel dispersions, it has not been possible to measure the topographical distribution of electrical charges in PNIPAM gels. There is no reason to presume that the charges are only located near the particle surfaces.

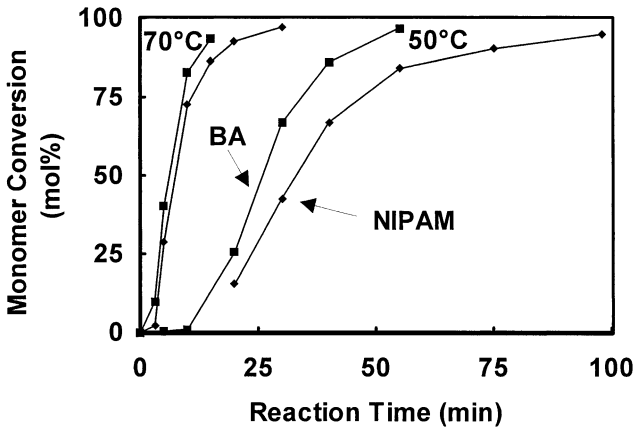

Figure 5. Monomer consumption versus time during PNIPAM microgel preparation. Adapted from Wu et al. [10] The crosslinking monomer, BA, polymerized at a faster rate than did NIPAM.

Concluding Remarks

The many current research efforts focused on PNIPAM microgels are likely to lead to promising applications. For example, Zhibing Hu has described the assembly of microgels into macrogels with nonlinear optical properties.[34] Highlighted in this paper are engineering difficulties which will have to be overcome before microgels can be prepared on a commercial scale.

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