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SHORT COMMUNICATION

J.-H. Kim
M. Ballauff

The volume transition in thermosensitive core–shell latex particles containing charged groups

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J.-H. Kim · M. Ballauff (✉)
Polymer-Institut, Universität Karlsruhe
Kaiserstrasse 12, D-76128 Karlsruhe
Germany
e-mail: matthias-ballauff@chemie.uni-karlsruhe.de

Abstract An investigation of the volume transition in thermosensitive core–shell particles by dynamic light scattering (DLS) is presented. The core of the particles consists of polystyrene (diameter 118 nm), whereas the thermosensitive shell is composed of a network of poly (*N*-isopropylacrylamide) containing 2 mol% acrylic acid counits. The hydrodynamic radius of these particles as determined by DLS decreases in a continuous manner when raising the temperature. It is shown that the volume transition in the core–shell microgels remains continuous for a wide range of ionic strengths and pH values. This behavior is opposite to that of macrogels of the same chemical composition, which undergo a discontinuous volume transition. The present investigation therefore demonstrates that affixing the network to solid colloidal particles profoundly alters the volume transition of thermosensitive networks. The reason is that shrinking can take place only along the radial direction of the particles. The solid core thus exerts a strong spatial constraint onto the network, which leads to the observed behavior.

Key words Latex · Volume transition · Microgels · Phase transition

Introduction

Networks composed of poly(*N*-isopropylacrylamide) (PNIPA) have attracted much interest because of the reversible volume transition which occurs in these systems. Gels composed of PNIPA and suitable comonomers may be shrunken by external stimuli; this has led to a number of interesting applications [1]. Tanaka and coworkers [2, 3] demonstrated that incorporation of charged comonomers, for example, acrylic acid (AA), increases the degree of swelling dramatically. In particular, depending on the content of charged counits the continuous volume transition may become a discontinuous process in which a highly swollen gel shrinks at a given temperature to a dense state [3].

The slow dynamics of this process in macroscopic gels has led to the synthesis of microgel particles in which the response to external stimuli will be much faster than in macroscopic systems [4]. Hence, gel beads with diameters in the submillimeter range could serve for the elucidation of the swelling kinetics of macroscopic systems. If, however, the size of the gel particle is decreased to that of the colloidal domain, the spatial constraint thus induced may profoundly alter the volume transition. This problem may be investigated for the case of nearly monodisperse colloidal microgel particles by dynamic light scattering (DLS) which gives the hydrodynamic radius, R_H, of the particles as a function of temperature. A study conducted by Hirose et al. [5] suggested that the volume transition becomes continuous for sub-micron-sized gel particles. The authors assigned this finding to possible spatial inhomogeneities within the gel beads. A more recent investigation of Kratz and Eimer [6] suggests that nearly monodisperse microgels of PNIPA chains with diameters of about 700 nm exhibit a swelling behavior as expected from the corresponding macroscopic gels: lowering the crosslink density seems to shift the continuous volume transition of the particles to a discontinuous process (cf. Fig. 5 of Ref. [6]). This finding is in full accord with similar observations on macrogels [7, 8].

If a thermosensitive network is affixed on the surface of colloidal particles the spatial constraint effected by this geometry is expected to exert a marked influence on the phase transition. Such core–shell microparticles have been prepared by a number of groups [9–13]. In a recent paper a study of the volume transition in a shell of about 30-nm thickness on a polystyrene (PS) particle using small-angle X-ray scattering (SAXS) was reported [14]. In the course of this study it could be shown that the spatial constraint exerted by the geometry of the particle changes the transition profoundly: most of the PNIPA chains are affixed to the surface of the core and the chains can only shrink along the radial directions (virtually no shrinking can occur along directions parallel to the surface). Hence, if the unconstrained gel shrinks by a factor of α, the network in the constrained shell may only shrink by a factor of approximately $\alpha^{1/3}$. It is evident that this type of spatial constraint has a profound influence on the volume transition which may be compared to external uniaxial forces [14].

The crosslink density of the PNIPA network reported in Ref. [14] was quite high and the volume transition was expected to proceed in a continuous fashion. It is thus interesting to modify the network using charged groups to see whether the volume transition in the shell will become discontinuous as in the case of macroscopic networks [2, 3]. In this communication we present the first results of the synthesis and the characterization of core–shell particles in which the thermosensitive network of the shell has been modified by incorporation of AA. As in our previous study [14] crosslinking has been achieved by use of *N*,*N′*-methylenebisacrylamide (BIS). Starting from narrowly distributed PS core particles the shell is produced by the method described recently [14].

The volume transition in these particles has been studied by DLS. Special attention is paid to the colloidal stability of the particles during the volume transition. Coagulation at elevated temperature occurring concomitantly with the phase transition in the shell of the particles would profoundly disturb the DLS measurements and impede the determination of the hydrodynamic radius of the particles.

Experimental

Materials

NIPA (Aldrich, analytical grade), BIS (Fluka), and sodium dodecyl sulfate (SDS; Fluka) were used as received. The initiator potassium peroxodisulfate (KPS; Fluka) was recrystallized from deionized water. Styrene (BASF) was destabilized by washing with aqueous NaOH and subsequently with deionized water. After careful drying with $CaCl_2$ the monomer was distilled in vacuo. AA (Fluka) was distilled in vacuo prior to use. Water was purified using reverse osmosis (MilliRO; Millipore) and ion exchange (MilliQ; Millipore). The deionized water had a conductivity less than 0.05 μS/cm.

Preparation of particles

Core particles

Emulsion polymerization was carried out using a 2-l flask equipped with a stirrer, a reflux condenser, and a thermometer. SDS (2.40 g) and NIPA (13.5 g) were dissolved in water (1000 g) with stirring and the solution was degassed by repeated evacuation. After addition of styrene (256 g) the mixture was heated to 80 °C under an atmosphere of nitrogen. KPS (0.6 g dissolved in 30 ml water) was added while the mixture was stirred at 400 rpm. After 8 h the latex was cooled to room temperature and filtered through glass wool to remove traces of coagulum. Dialysis of the latex against water for approximately 3 weeks served for purification.

In the course of this study one core latex was used, the diameter of which was 118 nm as determined by DLS.

Core–shell latex

In a second step 60 g of the core latex (solids content 23 wt%) was diluted with 500 g deionized water and 17 g NIPA 0.57 g AA (5 mol% with respect to NIPA) and 1.158 g BIS (5 mol% with respect to NIPA) were added. No additional surfactant was added in this step to avoid the formation of new particles. After the stirred mixture had been heated to 80 °C the reaction was started by addition of 0.36 g KPS (dissolved in 15 ml water) and the entire mixture was stirred for 5 h at this temperature. After cooling to room temperature the latex was purified by exhaustive serum replacement against purified water (membrane: cellulose nitrate with 0.05-μm pore width supplied by Schleicher & Schuell).

To investigate the influence of charges on the volume transition in these particles, one latex was prepared using the same core latex and the same molar ratio of NIPA to BIS but without AA units (latex CS).

Characterization

The weight fraction of the seed as well as of the core–shell system was determined gravimetrically. Here it was ensured that most of the monomeric compounds used in the second emulsion polymerization were incorporated into the resulting particles. The amount of AA incorporated into the network was determined by conductometric titration of the carboxyl groups. It was found that about 40% of the AA (2 mol%) added in the second emulsion polymerization was built into the shell.

The pH value of the latexes was determined using a pH meter supplied by WTW (Microprocessor pH meter 537). The electrical conductance was measured using a WTW LF535 conductometer. The sizes of the particles and their size distributions were determined by use of transmission electron microscopy (TEM, Hitachi 700). The size distributions of the latexes were determined using a Brookhaven disc centrifuge (BI-DCP). Hydrodynamic radii were determined using a Peters ALV 4000 DLS instrument.

Results and discussion

Two systems are compared:

1. A core–shell latex containing AA units termed CSAA.
2. A core–shell latex without AA but otherwise of the same composition (latex CS).

Both systems have similar spatial dimensions (see later). Their comparison may therefore serve for a quantitative investigation of the influence of charges on the volume transition.

The present study aims at a quantitative investigation of the alterations effected on the volume transition by confining the network in a thin shell of colloidal dimensions. The core particles must therefore have a narrow size distribution which could be shown by disc centrifugation as well as by TEM. The narrow size distribution is a highly important condition for a meaningful analysis of the volume transition in these particles using DLS. In addition to this, broader distributions would certainly be accompanied by a concomitant chemical polydispersity which is expected to smear out the transition.

The seeded emulsion polymerization employed here led to narrowly distributed particles which are therefore suitable for a quantitative analysis of the hydrodynamic radius. This fact is demonstrated by the transmission electron micrograph of the CSAA core–shell system in Fig. 1. From this micrograph the polydispersity can be determined to be 3%. The same analysis of the uncharged CS system also led to a polydispersity of 3%.

Another important prerequisite for the present analysis using DLS is the colloidal stability of the particles even above the volume transition. A previous investigation [14] had demonstrated that PNIPA core–shell particles have an enhanced stability against flocculation even above the temperature of the volume transition. This has been partially traced back to the restricted shrinking of the shell: even above the volume transition the chains in the network are retained in a fluidlike state despite the fact that the network has been shrunken considerably [14]. Thus, the steric stabilization of the particles is still operative to a certain extent. As shown in the course of the present investigation, residual charges on the surface of the core particles introduced by the initiator KPS enhance the stability of the particles above the volume transition (see later).

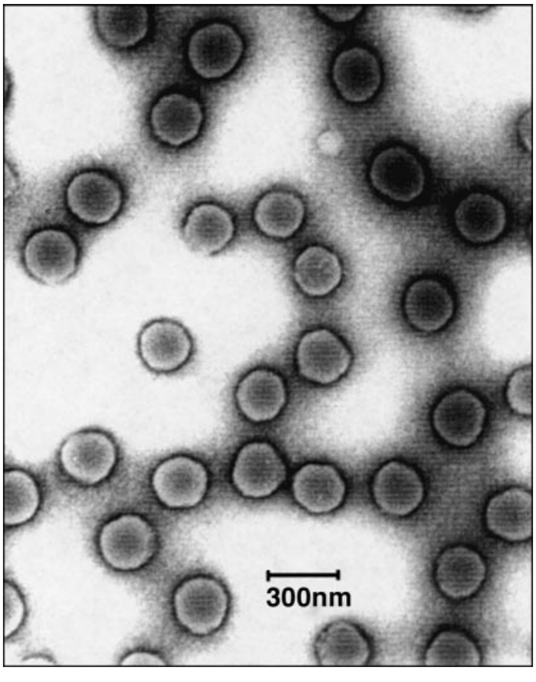

Fig. 1 Transmission electron micrograph of the core–shell particles containing 2 mol% acrylic acid (*AA*) units

The stability of the particles against flocculation is shown in Fig. 2: the comparison of the R_H of an uncharged and a core–shell latex bearing AA counits as a function of temperature shows that both systems remain stable above the volume transition. In both latexes the weight fraction of the network in the particles was the same in order that a meaningful comparison is possible. The data displayed in Fig. 2 were obtained in pure water at high dilution and refer to practically fully dissociated AA units (see later).

The data shown in Fig. 2 immediately reveal the following facts:

1. The transition seen in R_H is fully reversible: within experimental uncertainty (about 3%) the same hydrodynamic diameter is obtained in the heating as well as in the cooling run.

2. Figure 2 also demonstrates that the incorporation of a small number of charged units (2 mol%) suffices to increase the degree of swelling enormously. While R_H of the uncharged particles increases gradually to about 120 nm at 10 °C, the charged system is characterized by a R_H of about 200 nm despite the fact that the degree of crosslinking is the same. It is interesting to note that the

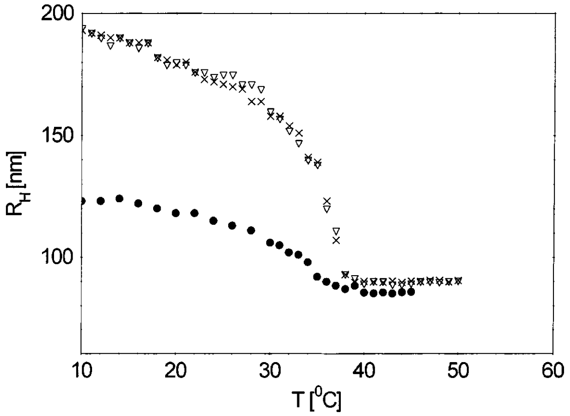

Fig. 2 Hydrodynamic radius, R_H, as a function of temperature for thermosensitive core–shell networks without charges (latex *CS*; *circles*) and with 2 mol% AA counits (latex *CSAA*; *triangles* and *crosses*). All measurements were made in pure water. *Crosses* denote the data obtained on cooling, whereas *triangles* display R_H obtained from heating runs

network in the shrunken state has approximately the same size as was found for the uncharged particles; R_H of the charged and uncharged particles virtually coincide above 40 °C.

3. A further important point seen in Fig. 2 commands attention. Despite the charges in the network the volume transition as detected from R_H is continuous. The transition takes place in a temperature range of about 5 °C and not within less than 1 °C as expected for a discontinuous transition (cf., e.g. Fig. 5 of Ref. [6]). It is obvious that the continuous variation of R_H is not due to coagulation since the particles do not flocculate at any temperature.

In this context it is important to note that PNIPA/AA macrogels studied by Hirotsu et al. [15] with similar ratios of PNIPA to AA units undergo a discontinuous volume transition (cf. Figs. 1, 2 of Ref. [15]). Even at a much lower content of AA units the macrogels exhibit a marked discontinuity of the volume as a function of temperature; hence, it becomes obvious that the transition in the micronetworks is markedly different compared to macronetworks of the same chemical structure. Adding AA counits to the PNIPA macronetworks leads to a discontinuous volume transition, whereas the uncharged network exhibits a continuous transition. In the present core–shell micronetworks, however, the transition is always continuous even upon adding AA counits.

It must be noted in this context that the present analysis by DLS does not allow the possible influence of spatial inhomogeneities of the network in the shell to be excluded. A strongly inhomogeneous distribution of crosslinks or of the AA units would lead to the same findings. Our previous study of uncharged core–shell networks by SAXS [14], however, did not detect any marked inhomogeneity of the network of the uncharged shell; therefore, we do not expect that the systems prepared here will be strongly influenced by inhomogeneities. Further studies of this problem by SAXS are under way.

The volume transition can be investigated further by studying the dependence of the transition on the ionic strength in the system. Data for R_H obtained at different ionic strengths are shown in Fig. 3. The different ionic strengths were achieved by diluting the core–shell latex with KCl solutions of the respective concentration. In some cases this procedure was checked by adjusting the ionic strength by dialysis against a KCl solution of given ionic strength. This procedure led to the same results.

Figure 3 demonstrates the decisive influence of the ionic strength: raising the ionic strength leads to a decrease in the maximum degree of swelling and impedes the colloid stability of the particles. In 0.1 M KCl solution measurements could only made below the volume transition since coagulation takes place around 29 °C. If the residual electrostatic stabilization is totally screened, the colloidal stability of the particles above the volume transition is strongly impeded.

It is also interesting to note that screening off the charges inside the network leads to a degree of swelling of approximately the same magnitude as observed for the uncharged systems. Also, far above the transition the degree of swelling becomes virtually independent of ionic strength. Again all data show clearly that the transition remains continuous within the wide range of ionic strengths.

The influence of the charges in the network can be tuned by the pH value of the solution [6, 16]. The pH was adjusted by adding small amounts of NaOH to

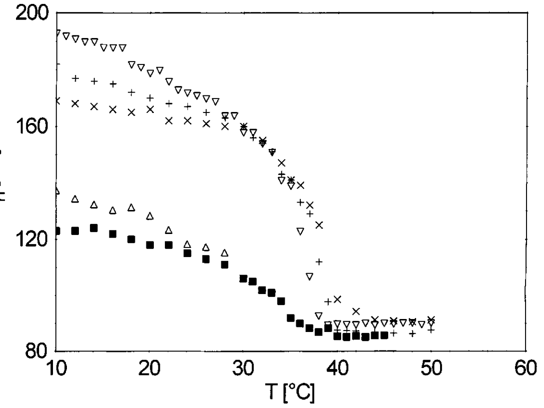

Fig. 3 Hydrodynamic radius, R_H, as a function of temperature for thermosensitive core–shell networks at different ionic strength. Uncharged CS particles (■), CSAA without added salt (▽), CSAA with 10^{-5} M KCl (+), 10^{-3} M KCl (×), 0.1 M KCl (Δ). At the highest ionic strength (0.1 M) the data at higher temperature could not be measured because of coagulation

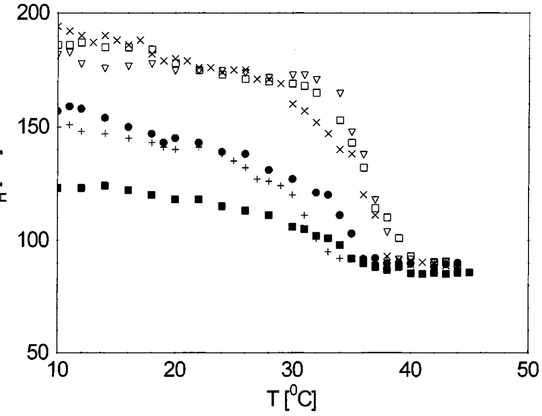

Fig. 4 Hydrodynamic radius, R_H, as a function of temperature for thermosensitive core–shell networks at different pH. Uncharged CS particles (■), charged particle CSAA at pH 2 (+), pH 4 (●), pH 7 (×), pH 9 (□), pH 12 (▽)

dilute systems in order to avoid a concomitant change in ionic strength (Fig. 4). At low pH (2–4) the degree of swelling decreases but remains above the respective value of the uncharged system. At sufficiently high pH (7–12), however, the degree of swelling is markedly increased and is nearly independent of the pH. This is in accord with the fact that poly(AA) is practically fully dissociated above pH 7 [17]. If all AA units are dissociated the maximum degree of swelling is achieved as expected.

There is also a shift in the transition temperature to higher values with increasing pH. This is expected from general considerations [3] because the electrostatic repulsion operative in charged networks leads to a stabilization of the swollen state. For all pH values, however, it again becomes obvious that the variation of R_H remains continuous despite the fact that the maximum degree of swelling varies strongly at different pH.

Conclusion

The investigation of the volume transition of charged microscopic networks has been presented. The number of charges in the network is large enough to cause a discontinuous transition in macroscopic systems [15]. The results discussed here show, however, that the volume transition in a thin shell of colloidal particles proceeds in a continuous fashion. We ascribe this finding to the spatial constraint exerted by the surface of the core particles onto which the chains of the network are affixed. This constraint together with the finite size of the shell prevent the formation of a macroscopic phase and lead to the observed shift from a discontinuous to a continuous volume transition.

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