Macromol. Symp. ***142***, *217–225 (1999)*

The Volume Transition in Thermosensitive Core-shell Latex Particles Investigated by Small-angle X-ray Scattering and Dynamic Light Scattering

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Summary: We present a survey over recent studies of the volume transition in colloidal core-shell particles composed of a solid poly(styrene) core and a shell of a thermosensitive crosslinked polymer chains. The thermosensitive shell is built up from poly(N-isopropylacrylamide) chains (PNIPA) crosslinked by N,N'-methylenbisacrylamide (BIS). In addition, particles containing acrylic acid (AA) as comonomer have been synthesized and investigated. The volume transition of these particles have been studied by dynamic light scattering (DLS) and by small-angle X-ray scattering (SAXS). In all cases analyzed so far the volume transition was found to be continuous. This finding shows that the core-shell microgels behave in a distinctively different manner than ordinary thermosensitive gels: The crosslinked chains in the shell are bound to a solid boundary independent of temperature. The spatial constraint by this boundary decreases the maximum degree of swelling but also prevents a full collapse of the network above the volume transition.

Introduction

Gels composed of cross-linked poly(N-isopropylacrylamide) (PNIPA) chains may undergo a volume transition as a function of temperature in which the network shrinks in a continuous or discontinuous fashion1). Hence, gels composed of PNIPA and suitable comonomers may be shrunken by external stimuli which has lead to a number of interesting applications2). Tanaka and coworkers demonstrated that incorporation of charged comonomers as e.g. acrylic acid increases the degree of swelling dramatically1,3). In particular, depending on the content of charged co-units the continuous volume transition may become a discontinuous process in which a highly swollen gel shrinks at a given temperature to a dense state.

The slow dynamics of this process in macroscopic gels has lead to the synthesis of microgel particles in which the response to external stimuli will be much faster than in macroscopic systems1). Hence, gel beads with diameters in the sub-millimeter range could serve for the elucidation of the swelling kinetics of macroscopic systems4. Recent experiments conducted

CCC 1022-1360/99/$ 17.50+.50/0

by Kratz and Eimer[5) on PNIPA-microgels having colloidal dimensions suggest that these systems behave in a similar way as macroscopic gels[6, 7)].

If a thermosensitive network is affixed on the surface of colloidal particles, however, 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[8-12)]. In a recent paper the volume transition in a shell of ca. 30nm thickness on a poly(styrene) (PS) particle has been studied by small-angle X-ray scattering (SAXS)[13)]. Here it could be demonstrated that fixing the chains to a solid particle leads indeed to a profound change of the volume transitions. Rheological studies by Senff et al.[14)] furthermore showed that suspensions of these particles present ideal model systems for the investigation of the flow behavior of sterically stabilized particles.

In this paper a survey over recent studies on these thermosensitive core-shell particles will be given. Special emphasis is laid on the alterations effected on the volume transition by the presence of charged groups in the thermosensitive network of the shell.

Uncharged networks

Recently, we have presented the synthesis and the characterization of latex particles having a PS-core of ca. 80nm diameter onto which a shell of crosslinked PNIPA-chains has been affixed[13)]. The volume transition in these particles has been studied by dynamic light scattering and by SAXS. Here it could be shown that SAXS is uniquely suited to investigate the swelling and deswelling of the shell upon change of temperature. Figure 1 displays schematically the structure of such particles and their analysis by SAXS[13)]. Here are three terms which contribute to the observed scattering intensity $I(q)$ ($q=(4\pi/\lambda)\sin(\theta/2)$; θ: scattering angle; λ: wave length)[13)]:

$$I(q) = I_{CS}(q) + I_{network}(q) + I_{PS}(q) \qquad (1)$$

Here $I_{CS}(q)$ is the part of $I(q)$ due to the core-shell structure of the particles, i.e., the scattering intensity caused by a composite particles having a homogeneous core and a shell. The core and the shell are characterized by a different electron density which is shown schematically in fig. 1. The shell consists of a polymeric network which exhibits static inhomogeneities and thermal fluctuations taken into account by $I_{network}(q)$ (see the discussion of $I_{network}(q)$ in ref.[16, 17)]). Finally, $I_{PS}(q)$ denotes the scattering intensity which is caused by the density fluctuations of the solid PS-core of the particles.

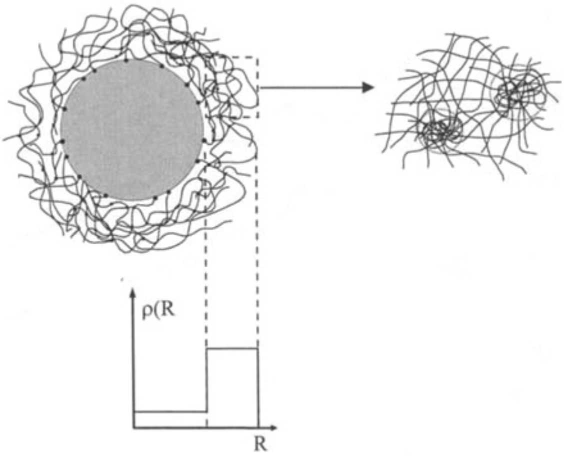


Fig. 1 Analysis of core-shell microgels by SAXS. The term $I_{CS}(q)$ (see eq.(1)) which is dominant at low q-values refers to a core-shell particle with the excess electron density ρ(R). The network exhibits static and dynamic inhomogeneities which lead to $I_{network}(q)$. Finally, the poly(styrene) cores of the particles are not entirely homogeneous but the density of the solid poly(styrene) fluctuates weakly around a mean value. This gives the third term $I_{PS}(q)$ which gives a small but non-negligible contribution to I(q). All three contributions to I(q) derive from statistically independent fluctuations of the electron density in the system and no cross term appears in eq.(1).

The analysis of these terms$^{13)}$ show that $I_{PS}(q)$ can easily be determined from the SAXS-intensity of the core particles. Furthermore, $I_{CS}(q)$ decreases approximately with q^{-4} whereas $I_{network}(q)$ diminishes with q^{-2}. Experimental data corroborate this prediction: Figure 2 displays I(q) obtained at 25°C (squares) and at 50°C (triangles). For the sake of clarity the latter curve has been multiplied by 100.

The decomposition of I(q) may be done as follows: First $I_{PS}(q)$ obtained from the core-latex (see above) is subtracted from the measured intensity I(q). In a second step $I_{CS}(q)$ is determined from I(q) taking into account only the data in the q-range smaller than 0.2nm^{-1}. The lines in fig. 2 show the respective fits achieved by the fit routine described recently$^{18,13)}$. The excess electron densities $\rho(R)-\rho_m$ resulting from this fit are displayed in the inset of fig. 2 where ρ_m is the electron density of water. The profiles $\Delta\rho(R) = \rho(R) - \rho_m$ shown in the inset of fig. 2 indicate the swelling of the PNIPA-shell when going from poor solvent conditions (50°C; dashed lines) to good solvent conditions (25°C; solid lines). Furthermore, it can be shown that virtually all NIPA used in the synthesis is built into the thermosensitive shell.

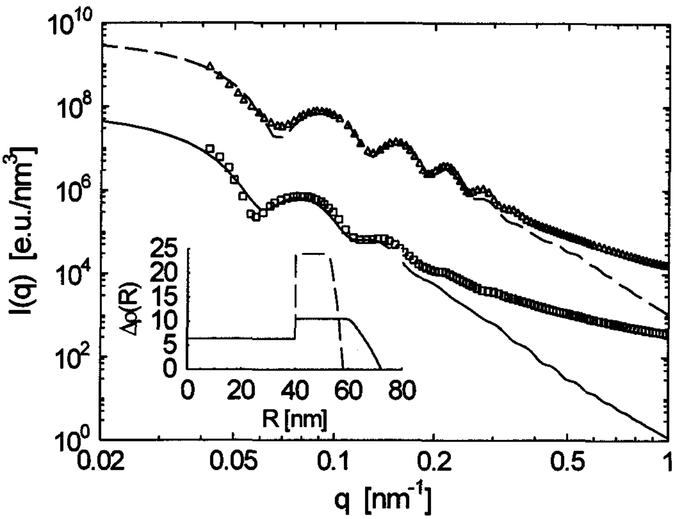


Fig. 2 Measured SAXS-intensities I(q) of the core-shell particles below the volume transition (25°C; squares) and above the volume transition (50°C; triangles). For the sake of clarity the data measured at 50°C have been multiplied by 100. The lines display the fit of $I_{CS}(q)$ (cf. eq.(1)) to the data at low q-values ($q<0.2\text{nm}^{-1}$; 25°C: solid line; 50°C: dashed line). The radial excess electron density $\Delta\rho(R)$ deriving from this fit is shown in the inset. The marked deviation between I(q) and I_{CS} (q) seen at high q-values is due to $I_{network}(q)$, i.e., the contribution of the network in the shell of the particles.[13)]

From the profile shown in the inset in fig. 2 the average volume fraction ϕ of PNIPA can be estimated to be 0.5 at 50°C whereas a value of 0.23 follows from the SAXS-analysis at 25°C. At 25°C the shell has an extension of ca. 32nm which shrinks to 18nm above the transition. This corresponds to a shrinking of the volume of the shell by a factor of 2.2 which is small compared to PNIPA macrogels having a similar degree of crosslinking[6, 7)]. It must be noted that the gel does not collapse but remains swollen to a certain extend even far above the volume transition.

This point can be discussed further when analyzing the excess scattering intensity visible at higher q-values in fig. 2. Here the difference between the measured intensity I(q) corrected for $I_{PS}(q)$ and $I_{CS}(q)$ can be assigned to $I_{network}(q)$ and analyzed accordingly[13)]. The main contribution to the latter term is deriving from the thermal fluctuations of the network[16)] which may be described by a Lorentzian[17)]:

$$I_{network}(q) \approx I_{fluct}(q) = \frac{I_{fluct}(0)}{1+\xi^2 q^2} \qquad (2)$$

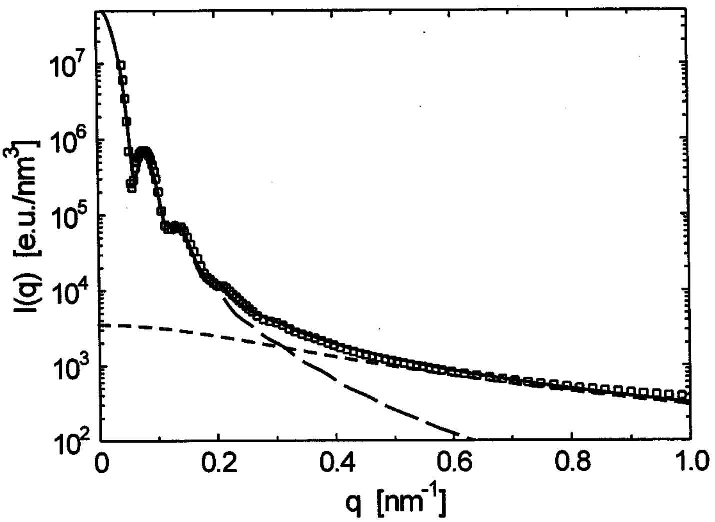
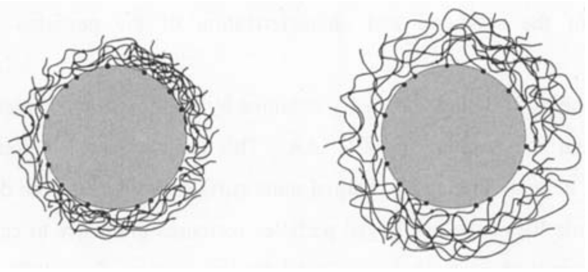


Fig. 3 Comparison of $I_{CS}(q)$ (long-dashed line) and $I_{fluct}(q)$ (short dashed line) with the scattering intensity $I(q)-I_{PS}(q)$ measured at 25°C (squares). The solid line gives $I_{CS}(q)+ I_{fluct}(q)$ (cf. eq.(1) and (2))[13].

where ξ denotes the correlation length of the thermal fluctuations. As demonstrated by figure 3, the measured scattering intensity $I(q) - I_{PS}(q)$ (cf. eq.(1)) can be described quantitatively by the superposition of $I_{CS}(q)$ dominating at small q and of $I_{fluct}(q)$ dominating at high q-values.



	poor solvent conditions 50 °C	good solvent conditions 25 °C
d_{shell}	18nm	32nm
$\phi_{network}$	0.50	0.25
ξ	2.1nm	3.2nm

Fig. 4 Analysis of the volume transition in uncharged thermosensitive core-shell particles[13].

Fig. 4 displays the main results of the SAXS-analysis of the uncharged core-shell particles: Due to the fixation of the chains of the network on the core particles the volume transition is strongly restricted, i.e., the transition does not lead to a fully collapsed state but only to a markedly higher volume fraction indicated in fig. 4. The chains can only shrink along the direction of the surface normal but no marked contraction can result parallel to the surface. If the unconstrained gel shrinks by a factor of 10, the corresponding shrinking of the microgel layer is expected to be of the order $(10)^{1/3} \approx 2.15$ which is of the order observed in the present system (cf. fig. 4).

Charged networks

The crosslink density of the PNIPA-network in the thermosensitive core-shell particles discussed so far was quite high and the volume transition was expected to proceed in a continuous fashion[1, 3)]. It is thus interesting to modify the network by charged groups to see whether the volume transition in the shell will become discontinuous as is the case for macroscopic networks[1, 3)]. Here we present first results obtained by dynamic light scattering (DLS) from core-shell particles in which the thermosensitive network of the shell has been modified by incorporation of acrylic acid (AA). As in the previous study[13)] crosslinking has been achieved by use of N,N'-methylenebisacrylamide (BIS; 5Mol% with regard to NIPA). Starting from narrowly distributed PS-core particles the shell is produced by the method described recently[13)]. For comparison one core-shell system has been prepared without AA-units. Details of the synthesis and characterization of the particles will be reported elsewhere[15)].

Fig. 5 displays the hydrodynamic radii R_H obtained by DLS of an uncharged system and of a core-shell system containing 5Mol% AA. This comparison demonstrates that the incorporation of a small amount of charged units suffices to increase the degree of swelling enormously. While R_H of the uncharged particles increases gradually to ca. 120nm at 10°C, the charged system is characterized by a hydrodynamic radius of ca. 200nm despite the fact that the degree of crosslinking is the same. It is also interesting to note that the network in the shrunken state has approximately the same size as has been found for the uncharged particles; R_H of the charged and uncharged particles virtually coincide above 40°C.

The data shown in fig. 5 furthermore show clearly that the transition seen in R_H is fully reversible; within experimental uncertainty (3%) the same hydrodynamic radius is obtained in the heating as well as in the cooling run. As in the case of uncharged particles the colloidal

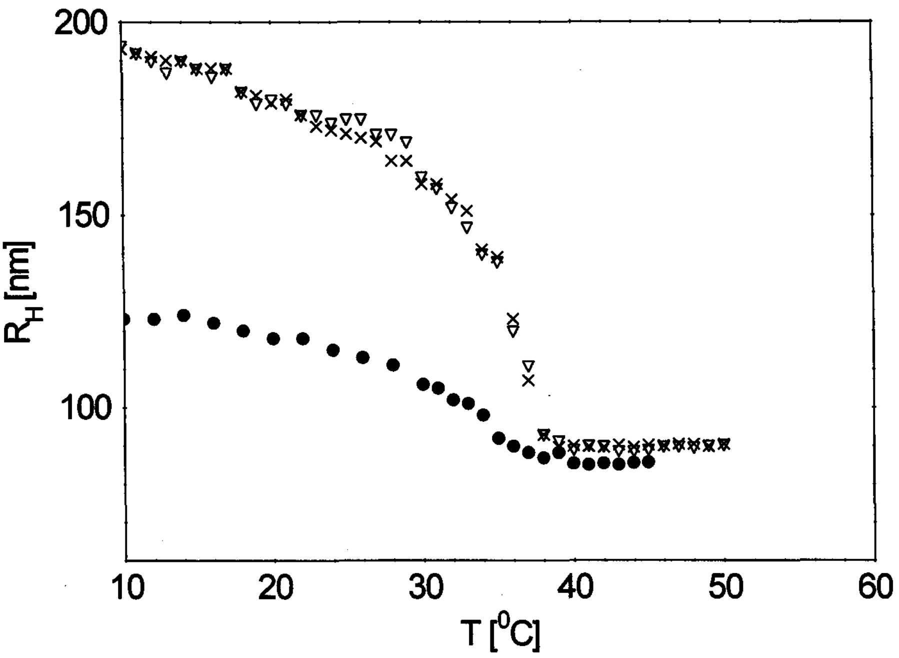


Fig. 5 Hydrodynamic radius R_H as function of temperature for thermosensitive core-shell networks without charges (filled circles) and with 5mol% acrylic acid co-units (triangles and crosses). All measurements have been done in pure water. Crosses denote the data obtained on cooling whereas triangles display R_H obtained from heating runs[15].

stability of the system may be traced back to the restricted shrinking of the network during the volume transition. The chains in the network are retained in a fluid-like state despite the fact that the network has been shrunken considerably. Hence, the steric stabilization of the particles will still be operative above the volume transition. In addition to this, residual charges on the surface of the core particles introduced by the initiator will enhance the stability of the particles above the volume transition.

A further important point seen in fig. 5 commands attention: Despite the charges in the network the volume transition as detected by R_H is continuous. The transition is taking place in a temperature range of ca. 5^{0}C and not within less than one degree as expected for a discontinuous transition (cf. e.g. fig. 5 of ref.[5]). From the complete reversibility of the data it is obvious that the continuous variation of R_H is not due to coagulation. Also, the size distribution of the particles is rather narrow (standard deviation: 3%) so that no smearing out of the transition by polydispersity of sizes and structure may take place.

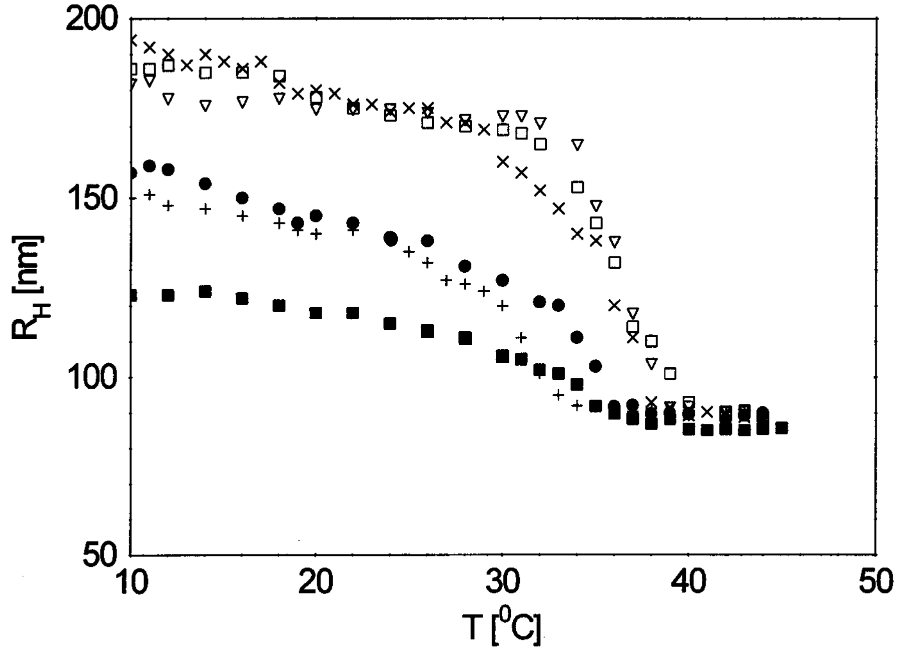


Fig. 6 Hydrodynamic radius R_H as a function of temperature for thermosensitive core-shell networks containing 5Mol% acrylic acid co-units at different pH. ■: uncharged core-shell particles CS;: +: charged particle at pH= 2; ●: pH = 4; x: pH = 7; □: pH=9;∇: pH = 12.

In must be kept in mind that the number of charges in the network is large enough to cause a discontinuous transition in macroscopic system[1,3)]. The results displayed in fig. 5 clearly demonstrate, however, that the volume transition in a thin shell of colloidal particles proceeds in a continuous fashion.

The influence of the charges in the network can be tuned by the pH-value of the solution[15)]. Figure 6 displays the hydrodynamic radius of the charged core-shell networks measured at different pH. The pH has been adjusted by adding small amounts of NaOH to dilute systems in order to avoid a concomitant change of ionic strength. Lowering the pH below the pK_s (5.6) of poly(acrylic acid) the degree of swelling decreases but remains above the respective value of the uncharged system. Above the pK_s of PAA the degree of swelling is markedly increased and nearly independent of the pH. Here all charges are ionized leading to the maximum degree of swelling. Again it becomes obvious that the variation of R_H remains continuous for all pH-values despite the fact that the degree of swelling varies strongly at different pH.

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. Together with the results$^{13)}$ obtained from uncharged networks it is obvious that core-shell micronetworks present an interesting class of gels in which the chains are subjected to geometric constraint. These constraints exerted by the solid surface of the core particles lead to a continuous volume transition even when in case of charged networks which undergo a discontinuous transition in macrogels.

Acknowledgment: Financial support by the Bundesministerium für Forschung und Technologie, and by the Deutsche Forschungsgemeinschaft, and by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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