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Temperature-Induced Formation and Contraction of Micelle-Like Aggregates in Aqueous Solutions of Thermoresponsive Short-Chain Copolymers

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A combination of turbidity, light scattering, and steady shear viscosity experiments has revealed that aqueous solutions of an amphiphilic diblock copolymer or a negatively charged triblock copolymer, both containing poly(N-isopropylacrylamide), can undergo a temperature-induced transition from loose intermicellar clusters to collapsed core–shell nanostructures. Turbidity, light scattering, and viscosity results of these short-chain copolymers disclose transition peaks at intermediate temperatures. At high temperatures, the compact core–shell particles from the diblock copolymer aggregate, whereas no renewed interpolymer association is observed for the triblock copolymer or for the solution of the diblock copolymer with added sodium dodecyl sulfate because the electrostatic repulsive interactions suppress the tendency of forming interpolymer clusters. The temperature-induced building up of intermicellar structures and the formation of large aggregates at high temperature in the solution of the diblock copolymer is significantly reduced under the influence of high shear rates.

Introduction

The temperature-induced self-aggregation of amphiphilic polymers in aqueous media and the observation of a coil-to-globule transition are phenomena of interest not only because of their fundamental importance as related to polymer nanostructures but also because of various biological applications such as protein folding. Poly(N-isopropylacrylamide) (PNIPAAM) belongs to this family of polymers and is a thermoresponsive water-soluble polymer that exhibits a lower critical solution temperature (LCST) at approximately 32 °C.[1] When the temperature is lower than LCST, PNIPAAM is hydrophilic and can exist as individual chains with a random coil conformation in water, while at higher temperatures, the PNIPAAM chain backbone becomes hydrophobic and collapses into individual single-chain globules or multichain aggregates, depending on the solution condition.[2,3] Studies on very dilute aqueous solutions of high molecular weight (the weight average molar masses are typically larger than 3×10^6 g/mol) PNIPAAM[2,4–6] and copolymers grafted with short polyethylene oxide chains[7–9] (PNIPAAM-g-PEO) have revealed a coil-to-globule transition upon heating the solutions. When a lower molecular weight sample (usually in the range 3×10^5 to 3×10^6 g/mol) is utilized, a higher polymer concentration is usually required to obtain reliable results. However, this concentration effect often leads to an intricate interplay between coil-to-globule crossover and interchain aggregation at elevated temperatures. It has been reported[7] from studies on aqueous PNIPAAM-g-PEO that elevated temperature gives rise to interchain aggregation prior to the partial collapse of the intrachain structure. To suppress the tendency of multichain associations of PNIPAAM at elevated temperatures, an ionic surfactant (e.g., sodium dodecyl sulfate) has been added[10–12] because binding of the surfactant to the polymer endows it with a polyelectrolyte character and thereby the inclination of forming intermolecular aggregates is reduced.

In the present work, a quite different problem is addressed, namely, to examine whether it is possible for thermoresponsive short-chain copolymers, containing NIPAAM segments and hydrophilic units, under the influence of temperature to self-assemble into supramolecular assemblies that can collapse over a narrow temperature interval upon a temperature raise. A central issue in this study is the unusual temperature-induced transition zones in aqueous solutions of a diblock and a triblock copolymer, and how the association structures are affected by charges on the polymer and shear flow. Although it is known[13] that aqueous amphiphilic block copolymers exposed to external stimuli, such as temperature and pH, can form micelle-like structures, the special transition phenomena reported here have not been addressed previously.

For this purpose, we have synthesized a methoxy-poly-(ethylene glycol)-*block*-poly(N-isopropylacrylamide) (MPEG$_{53}$-b-P(NIPAAM)$_{113}$ diblock copolymer, which contains 53 hydrophilic PEG units and PNIPAAM segments, together with an analogous charged methoxy-poly(ethylene glycol)-*block*-poly(N-isopropylacrylamide)-*block*-poly(4-styrenesulfonic acid sodium) triblock copolymer (MPEG$_{53}$-b-P(NIPAAM)$_{54}$-b-P(SSS)$_4$). These copolymers have narrow molecular weight distributions, and the chemical structures and characteristic data of them are displayed in Figure 1.

The idea is that, under the influence of temperature, micelle-like aggregates are formed with a core of PNIPAAM chains and stabilized by a corona of MPEG chains. This investigation demonstrates a novel temperature-induced clustering-collapse transition of these copolymers. The delicate interplay between
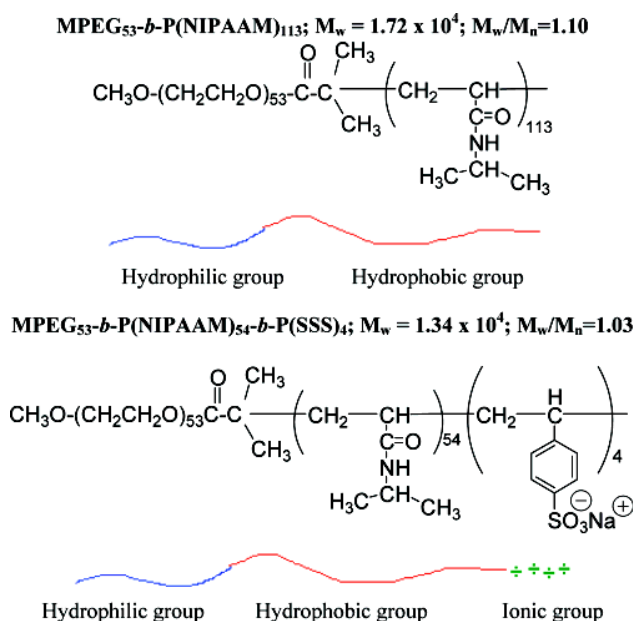
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MPEG₅₃-*b*-P(NIPAAM)₁₁₃; M_w = 1.72 x 10⁴; M_w/M_n=1.10

MPEG₅₃-*b*-P(NIPAAM)₅₄-*b*-P(SSS)₄; M_w = 1.34 x 10⁴; M_w/M_n=1.03

Figure 1. Chemical structures and characteristic data of the uncharged amphiphilic diblock copolymer and the negatively charged triblock copolymer.

associative and electrostatic interactions affects the transition features, which are examined with the aid of different experimental methods. The self-assembly of copolymer chains is a hydrophobically driven process, and in this study, we utilize turbidity that is a powerful method to record temperature-induced changes in the intensity of the hydrophobic interactions. At quiescent conditions, intensity light scattering (ILS) is employed to probe the sizes of molecules and aggregates during the temperature-induced transition. In addition, steady shear viscosity measurements were conducted because the intensity of the interpolymer aggregation can often be modulated by the magnitude of the shear flow. To further illustrate the impact of electrostatic interactions on the transition behavior, an aqueous mixture of the uncharged diblock copolymer and the anionic surfactant sodium dodecyl sulfate (SDS) was studied. The aim of this work is to elucidate the intricate interplay between interchain association and disaggregation generated by electrostatic repulsive forces in solutions of thermoresponsive amphiphilic copolymers.

Experimental Section

The MPEG macroinitiator was synthesized according to a procedure reported in the literature.[14] The diblock and triblock copolymers were synthesized by means of atomic transfer radical polymerization (ATRP)[15,16] by using a water/DMF 40:60 (v/v) mixture as the solvent at 25 °C with MPEG-MI/CuCl/Me₆TREN (for diblock copolymer) or MPEG-MI/CuCl/CuCl₂/Me₆TREN (for triblock copolymer) as the initiator/catalyst systems. To remove impurities such as unreacted monomer, low molecular components, organic solvent (DMF), and trace amounts of Cu ions, dilute aqueous solutions of the copolymers were dialyzed against distilled water for several days using a dialysis membrane of regenerated cellulose with a molecular weight cutoff of 3500. The white solid products were isolated by lyophilization.

The chemical compositions and the chemical structures of the synthesized copolymers were all ascertained by ¹H NMR with a Bruker AVANCE DPX 300 NMR spectrometer, operating at 300.13 MHz at 25 °C by employing heavy water (D₂O)

as the solvent. The weight-average molecular weights (M_w) and polydispersities (M_w/M_n) of the copolymers were determined in very dilute aqueous solutions with the aid of asymmetric flow field-flow fractionation (AFFFF) methods,[17] and the molecular weights and polydispersity indexes from the measurements on very dilute solutions of the copolymers are given in Figure 1. Both copolymer samples have low molecular weight and narrow molecular weight distributions.

The turbidity measurements were conducted on an NK60-CPA cloud point analyzer from Phase Technology, Richmond, B.C., Canada. A detailed description of the equipment and determination of turbidities have been given elsewhere.[18] This apparatus utilizes a scanning diffusive technique to characterize phase changes of the sample with high sensitivity and accuracy. The light beam from an AlGaAs light source, operating at 654 nm, was focused on the measuring sample that was applied onto a specially designed glass plate that is coated with a thin metallic layer of very high reflectivity (mirror). Directly above the sample, an optical system with a light-scattering detector continuously monitors the scattered intensity signal (S) of the sample as it is subjected to prescribed temperature alterations. The relation between the signal and the turbidity (τ) is given by the following empirical relationship τ (cm⁻¹) = 9.0 × 10⁻⁹$S^{3.751}$.[18] In these experiments, the heating rate was set to 0.2 °C/min.

The intensity light scattering (ILS) experiments were conducted with the aid of an ALV/CGS-8F multi-detector version compact goniometer system, with 8 fiber-optical detection units, from ALV-GmbH., Langen, Germany. The beam from a Uniphase cylindrical 22 mW HeNe-laser, operating at a wavelength of 632.8 nm with vertically polarized light, was focused on the sample cell (10-mm NMR tubes, Wilmad Glass Co., of highest quality) through a temperature-controlled cylindrical quartz container (with 2 plane−parallel windows), vat (the temperature constancy being controlled to within ±0.01 °C with a heating/cooling circulator), which is filled with a refractive index matching liquid (*cis*-decalin). The polymer solutions were filtered in an atmosphere of filtered air through a 0.2 μm filter (Millipore) directly into precleaned NMR tubes. Because of the experimental circumstances, the ILS experiments were not performed with a temperature gradient (0.2 °C/min) as for the turbidity and steady shear viscosity measurements. Instead, the samples were measured at several fixed temperatures. The samples were allowed to equilibrate for 30 min at each temperature before the ILS experiments were carried out.

From ILS measurements, the radius of gyration ($\langle R_g \rangle$) of scattering objects in a dilute solution or dispersion can be determined from the angular dependence of the excess scattering intensity, $I(q)$, by using the Guinier equation[19]

$$I(q) = I(0) \cdot \exp\left(-\frac{R_g^2 q^2}{3} \right) \quad (1)$$

where q is wave vector of magnitude $q = (4\pi n/\lambda) \sin(\theta/2)$, λ is the wavelength of the incident light in a vacuum, θ is the scattering angle, and n is the refractive index of the medium. $I(0)$ is the scattered intensity at $q \rightarrow 0$. In this study, the values of R_g were determined with the aid of eq 1 in the dilute concentration regime and in the domain $qR_g < 1$. In the ILS experiments, the scattered light was collected at 16 angles in the range 17°−144.5°.

Steady shear viscosity measurements were conducted in a Paar-Physica MCR 300 rheometer using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 75 mm.

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This rheometer operates effectively with this geometry even on dilute polymer solutions, and the viscosity of water can easily be measured over an extended shear rate domain. The solutions were introduced onto the plate, and to prevent evaporation of the solvent, the free surface of the sample was always covered with a thin layer of low-viscosity silicone oil that virtually did not affect the solution viscosity. The apparatus is equipped with a temperature unit (Peltier plate) that provides for a fast and accurate alteration of the temperature over the considered temperature domain.

Results and Discussion

The micellization process in solutions of block copolymers depends essentially on two parameters: the critical micelle concentration (CMC) and the critical micelle temperature (CMT).[13] If neither of these states is reached, self-assembly will not occur, and the polymer is molecularly dispersed in the solution and will behave as a unimers. When micelles are formed, they will be in thermodynamic equilibrium with unimers. The polymer concentration (1 wt %) considered in this investigation is well above the CMC, and the physical properties of the system are governed by the micelles. When an amphiphilic copolymer is dissolved in a selective solvent for one of the blocks, the soluble block (MPEG) is oriented toward the continuous solvent medium and becomes the corona of the micelle, whereas the hydrophobic part is shielded from the solvent in the core of the structure. When the copolymer concentration is sufficiently high and the temperature rises above CMT, this may lead to aggregation of individual micelles into larger complexes, which may be called loose micellar clusters.[20,21] In the case of aqueous solutions of $MPEG_{53}$-b-$PNIPAAM_{113}$, the PNIPAAM block is expected to become more hydrophobic (more sticky) with increasing temperature; since the micelles consist of a rather large core with a much shorter corona (a type of "crew-cut micelles"[22]), the steric hindrance is modest, and temperature-induced intermicellization is foreseeable. In aqueous solutions of the anionic triblock copolymer ($MPEG_{53}$-b-$P(NIPAAM)_{54}$-b-$P(SSS)_4$) or in solutions of the diblock copolymer in the presence of SDS, a different scenario emerges. In this case, the repulsive electrostatic interactions may reduce the ability of the polymer to form association complexes.

Temperature dependences of the turbidity for 1 wt % solutions of the uncharged diblock copolymer, charged triblock copolymer, and $MPEG_{53}$-b-$PNIPAAM_{113}$ in the presence of 1 mmolal SDS are depicted in Figure 2. The turbidity results for all three systems disclose narrow transition peaks at intermediate temperatures. The cloud point (the temperature at which the first deviation of the scattered intensity from the baseline takes place is assigned as the cloud point for the considered system) for the diblock copolymer is higher[23] (37 °C) than for a corresponding solution of the homopolymer PNIPAAM (31 °C), which is attributed to the hydrophilic corona. Upon addition of SDS to a solution of the diblock copolymer, the cloud point is shifted toward a somewhat higher temperature, while for the triblock copolymer a significantly higher value (43 °C) of the cloud point is found.[24] This trend is probably related to the electrostatic interactions that reduce the intensity of the attractive hydrophobic interactions. A more comprehensive study of the effect of surfactant concentration on the physical properties of the diblock copolymer/SDS mixtures is in progress. The synergism between amphiphilic polymers and surfactants has been well-established in recent years.[25] We notice that the value of the turbidity at the peak maximum is much higher for the diblock copolymer solution than for the other systems. The lower
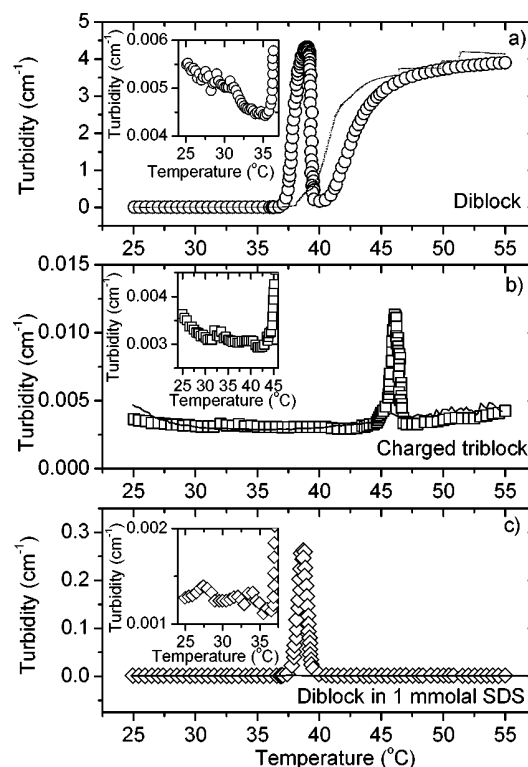

Figure 2. Temperature dependences of the turbidity during a heating rate of 0.2 °C/min of 1 wt % solutions of $MPEG_{53}$-b-$PNIPAAM_{113}$, $MPEG_{53}$-b-$P(NIPAAM)_{54}$-b-$P(SSS)_4$, and the diblock copolymer in the presence of 1 mmolal SDS. The solid curves indicate down ramps at a cooling rate of 0.2 °C/min. The insets show magnifications of the pre-transition regions.

values of the turbidity for the triblock copolymer are ascribed to the electrostatic interactions. In the solution of the diblock copolymer, the solution becomes milky at the maximum, whereas for the charged triblock copolymer, no cloudiness can be detected by the naked eye over the considered temperature domain.

All of the solutions only exhibit a modest alteration of the turbidity at low temperatures, and at this stage, we envisage self-organization of the short polymer chains to form intramicellar structures with PNIPAAM segments as the core and MPEG segments as the shell to stabilize the structure. Actually, a close inspection of the initial part of the turbidity curves before the transition peaks discloses (see the insets) that the turbidity decreases slightly, which may indicate shrinking of the polymeric micelles before intermicellization occurs. This trend seems to be strongest for the diblock copolymer. This type of behavior has been reported[3,9,18] previously for thermosensitive polymers.

The sharp rise of the turbidity observed in all panels of Figure 2 is attributed to the temperature-induced formation of intermicellar structures as a result of enhanced hydrophobicity of the PNIPAAM blocks. After passing the maximum of the turbidity peak at intermediate temperatures, the hydrophobic segments in the core pack together to avoid water contact when the temperature is raised, and this leads to a compaction of the loose micellar complexes for all systems. At still higher temperatures, the turbidity for the solution of the diblock copolymer (Figure 2a) exhibits a renewed strong upturn and this indicates that the compressed entities form intermicellar aggregates because of enhanced stickiness of the contracted moieties. It is interesting to note that for the solution of the diblock copolymer with SDS, no upturn of the turbidity at high temperatures is registered, and only a weak growth of the
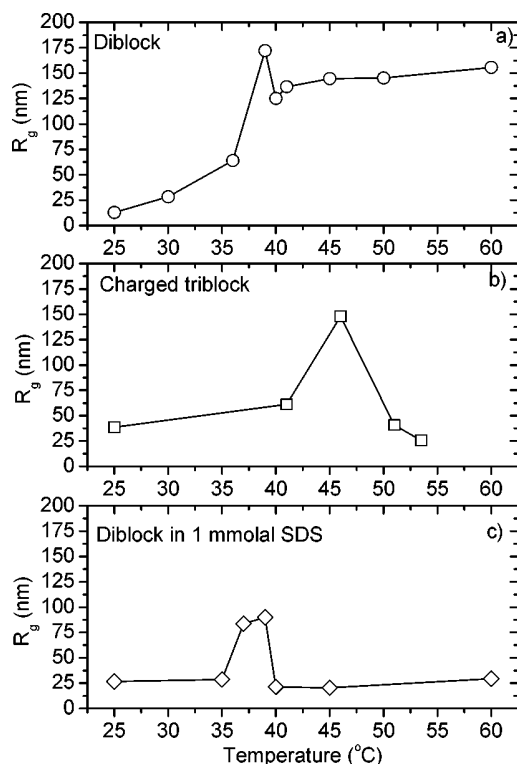
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Figure 3. Effect of temperature on the apparent radius of gyration for 1 wt % solutions of the polymer systems indicated. The measurements are carried out at fixed temperatures. See text for details.

Figure 4. Effects of temperature and shear rate on the relative viscosity for 1 wt % solutions of the polymer systems indicated and at a heating rate of 0.2 °C/min. The solid curves represent down ramps at a cooling rate of 0.2 °C/min. The insets show the shear rate dependence of the relative viscosity at the temperatures indicated.

turbidity is found for the solution of the triblock copolymer. The conjecture is that the compressed structures are decorated with charges, which prevent them from forming intermolecular association complexes. In the case of the diblock copolymer with added SDS, the surfactant can be adsorbed onto the amphiphilic polymer and this endows the polymer with a polyelectrolyte character. The interplay between interchain association and compaction has recently been reported[9,26] for aqueous solutions of PNIPAAM with grafted chains of poly-(ethylene oxide) on the PNIPAAM chain backbone.

The solid curves in Figure 2 illustrate the turbidity feature upon subsequent cooling (0.2 °C/min) of the solution. It is obvious for all solutions that the return is not reversible, but hysteresis effects are observed and this suggests that the structural reorganization of the complexes is a slow process, especially the swelling step of the clusters at intermediate temperatures.

Figure 3 shows effects of temperature on the apparent radius of gyration R_g, calculated with aid of eq 1, for 1 wt % solutions of the diblock copolymer, triblock copolymer, and the diblock copolymer with 1 mmolal SDS. Because of experimental difficulties, it was not possible to conduct the light scattering experiments under the influence of a constant temperature gradient (0.2 °C/min) as in the turbidity and shear viscosity experiments. Instead, the samples were measured at several fixed temperatures, and they were allowed to equilibrate for 30 min at each temperature before commencement of measurement. In the solution of MPEG$_{53}$-b-PNIPAAM$_{113}$, the signature of the transition behavior at intermediate temperatures is a weak maximum of R_g over a narrow domain, followed at higher temperatures by a moderate raise of R_g. In the course of the temperature-induced crossover, the process is governed by a perpetual competition between the growth of the intermicellar clusters and the interchain contraction of the species. For the
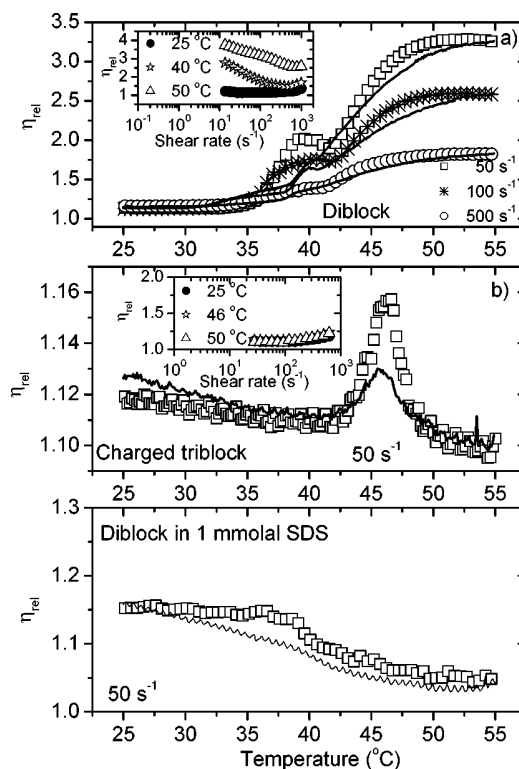
solution of the diblock copolymer, it is evident that fairly large aggregation complexes are formed and the growth of the species is modulated by compression of the structures at high temperatures. In the mixture of the diblock copolymer and SDS, the size of the aggregates is much smaller at high temperatures, and a pronounced maximum of R_g is observed. The marked drop of R_g at elevated temperatures suggests that contraction of the species plays a leading role in the process, and the growth of loose interchain clusters seems to be hampered. The reason for this special behavior is attributed to the ionic surfactant, which through adsorption to the polymer may generate charges on the surfaces of the compressed interchain moieties and thereby the species are stabilized. The results for the charged triblock copolymer are similar and can be rationalized in the same framework, where the PSSS segments provide the polymer with charges. In spite of that, the charge density and distribution of charges are different for the two polymers; it is interesting to note that the effects of temperature on the turbidity and R_g are similar for the two systems.

It is known that shear flows tend to bring particles close to each other more rapidly than Brownian motion does, hence altering aggregation kinetics by speeding up the process.[27] Shear-induced interchain association is known as "orthokinetic" aggregation and frequently operates in solutions containing sticky particles at low shear rates (low Peclet number), whereas at high shear rate, the clusters are expected to break up under the action of large shear stresses. In this process, the aggregation rate levels off or even decreases.

Effects of temperature and shear rates on the relative viscosity η_{rel} ($\eta_{rel} \equiv \eta/\eta_{water}$, with η_{water} the solvent viscosity at a given temperature) for 1 wt % solutions of the polymer systems indicated under the influence of a heating rate of 0.2 °C/min
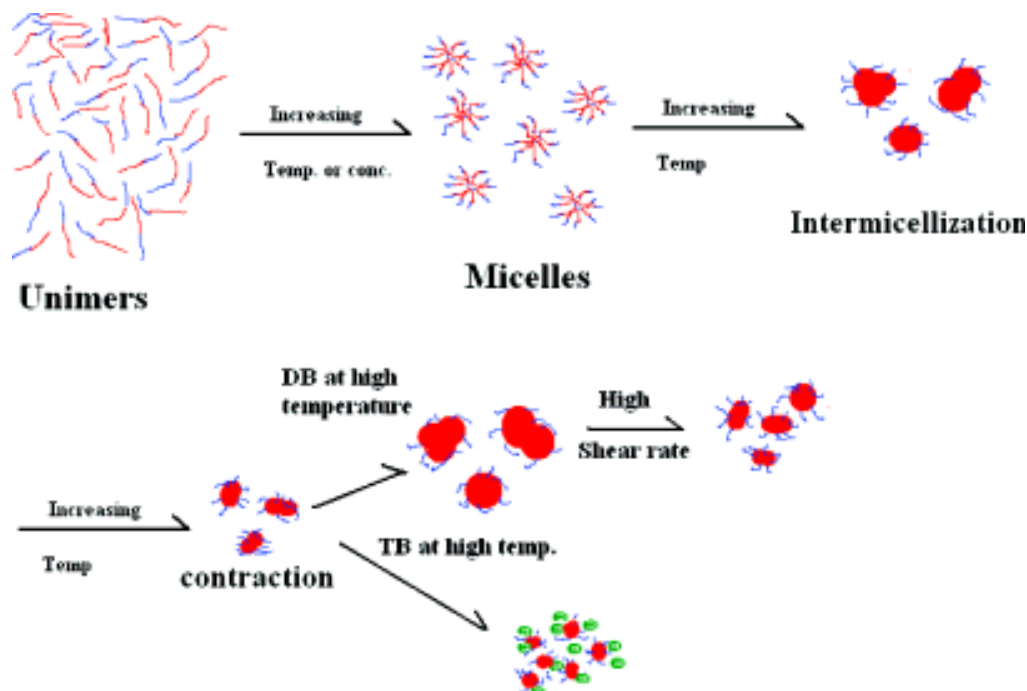
Figure 5. Schematic representation of the temperature-induced self-assemble of amphiphilic copolymer chains (blue color represents the hydrophilic part and red color represents the hydrophobic part of the polymer chains) into micelles and the formation of loose micellar clusters stabilized by hydrophilic coronal chains and the condensation of the complexes into core−shell structures. The effect of charges is illustrated, and the renewed aggregation of the uncharged diblock copolymer is depicted. The shear-induced disintegration of the association complexes is also displayed.

are shown in Figure 4. At the lowest shear rate (50 s^{-1}), a palpable transition zone is detected in the relative viscosity data at intermediate temperatures for the solution of the diblock copolymer without surfactant (Figure 4a), followed by a pronounced upturn of η_{rel} at high temperatures. As the shear rate is raised, the intermediate transition peak and the strong upturn of η_{rel} at high temperatures are gradually reduced with increasing shear rate. This finding demonstrates that the building up of big association structures is progressively suppressed as the shear flow is enhanced. At low temperatures, the relative viscosity exhibits a virtually Newtonian behavior, whereas at intermediate and high temperatures, shear thinning is found (see the inset in Figure 4a). The latter phenomenon suggests a shear-induced disruption of the loose micelle clusters. The solid curves in Figure 4a show the subsequent down-scans (0.2 °C/min); it is evident that, also in the viscosity experiments, hysteresis effects are visible, but at the highest shear rate, the hysteresis effect has practically disappeared because no large-scale structural rearrangements have occurred at this high shear rate during the heating cycle. Again, it seems to take a long time to reestablish the delicate micelle-like architecture at intermediate temperatures.

The relative viscosity for the solution of the triblock copolymer (Figure 4b), exhibits initially a moderate decrease, which probably is a harbinger of reorganization of the polymer chains prior to the formation of loose micellar complexes. At intermediate temperatures, a conspicuous transition peak appears, but the values of η_{rel} are much lower than the corresponding values for the diblock copolymer solution because the association complexes are smaller (cf. Figure 3). In contrast to the behavior of the uncharged diblock copolymer, the relative viscosity (shear rate of 50 s^{-1}) drops at high temperatures because the polyelectrolyte character of the polymer and shear flow prevent interchain aggregation; increased temperature appears to lead to further contraction of the core−shell structures. In the case of the diblock copolymer solution with

added SDS (Figure 4c), η_{rel} passes through a weak transition peak at intermediate temperatures. The reason for this indistinct transition is probably that the mixed polymer−surfactant intermicellar complexes are fragile, and they are broken-up even in the presence of a low shear rate. The solid curves in Figure 4b,c divulge also in this case hysteresis effects that again emphasize the slow structural reorganization. The inset plot in Figure 4b and the viscosity data for the diblock copolymer with added SDS show that over the considered shear rate region the viscosity behavior is virtually Newtonian, and no signs of shear thinning or shear thickening are observed. The slight upturn of η_{rel} (the inset plot) at high shear rates is ascribed to incipient turbulence.

Conclusions and Summary

The findings from this study can be summarized in the following way (cf. Figure 5). At conditions below CMC and CMT, the polymer solution consists of unimers. At low temperatures, the chains in the aqueous copolymer solutions (1 wt %) considered in this work will self-assemble into polymeric micelles. As the temperature rises in the transition region, intermicellization occurs, loose micelle clusters are formed, MPEG coronal chains stabilize the intermicellar structures, and the core consists of PNIPAAM chains. Upon further increase in temperature, interchain contraction takes place. At still higher temperatures, a renewed interpolymer aggregation of the compressed species from the uncharged diblock copolymer was generated because of enhanced sticking probability, and these structures were disintegrated under the influence of strong shear flows, whereas for the charged triblock copolymer and the diblock copolymer with added SDS, no renewed aggregation was detected. The repress of interchain aggregation for the charged triblock copolymer and the diblock copolymer with added surfactant is attributed to repulsive forces between the

compressed moieties, and the conjecture is that the surfaces of the core−shell particles are decorated by some charges (Figure 5).

The shear rate dependence of the viscosity for the uncharged copolymer divulged shear thinning in the transition areas, whereas for the solutions of the charged triblock copolymer and the diblock copolymer with added SDS, the viscosity behavior is virtually Newtonian, and no sign of shear thinning was found. Furthermore, the viscosity results indicated that weak association structures were evolved at intermediate temperatures in the polymer−surfactant mixture. The novel features presented in this investigation clearly show that temperature-induced aggregation in aqueous solutions of an amphiphilic copolymer can be significantly tuned by electrostatic interactions.

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