Formation of Mesoglobular Phase of Amphiphilic Copolymer Chains in Dilute Solution: Effect of Comonomer Distribution

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermally sensitive polymer with a lower critical solution temperature (~32 °C) in water. Its copolymerization with hydrophilic vinylpyrrolidone (VP) at temperatures higher and lower than its LCST respectively resulted in segmented and random VP distributions. As the solution temperature increases, PNIPAM changes from hydrophilic to hydrophobic at ~32 °C so that copolymer P(NIPAM-*co*-VP) becomes amphiphilic in water at higher temperatures. The association of two pairs of such copolymers with a similar chain composition and length, but different comonomer distributions, in water at temperatures higher than 32 °C was studied by laser light scattering. A limited number of neutral P(NIPAM-*co*-VP) chains can associate to form narrowly distributed stable mesoglobules existing between single-chain collapsed globules and macroscopic precipitates. The copolymer chains with a segmented VP distribution aggregate more readily to form larger mesoglobules than their counterpart with a random VP distribution. The formation of mesoglobules is related to a competition between intrachain contraction and interchain association. Besides thermodynamic consideration, the formation of a stable mesoglobular phase is also affected by chain viscoelasticity inside each aggregate, even in dilute solution. A proper variation of the chain structure and association temperature can result in mesoglobules with different sizes, molar masses, and structures.

Introduction

It is well-known that polypeptide or protein chains can assemble into different ordered and stable quaternary structures without macroscopic precipitation under the proper conditions.[1] Such a limited aggregation induced by a variation of experimental conditions, such as temperature, salt concentration, pH, and cosolvent, has attracted much attention.[2−9] For example, Aymard et al.[6] showed that the presence of some specific restructurable protein binding sites can initiate the association of proteins when electrostatic interaction is properly screened out. On the other hand, it is also known that the interior of a biological cell could be extraordinarily crowded and contains different kinds of proteins. How they are packed inside is still not completely understood.[3]

In polymer research, amphiphilic copolymers prepared from hydrophilic and hydrophobic monomers with different comonomer distributions are often used to mimic protein chains, especially in computer simulation. For example, Timoshenko et al.[7−9] simulated the collapse and aggregation of copolymers with an identical comonomer composition, but different comonomer distributions on the chain backbone. For a given composition, statistical random and block (diblock or triblock) copolymers are two extreme cases. Their association in selective solvents have been extensively studied. In contrast, the association of segmented amphiphilic copolymers in solution is much less understood. Timoshenko et al. showed that even without any added stabilization, a limited number of neutral copolymer chains with a proper comonomer distribution could associate to form narrowly distributed stable globules instead of individual collapsed polymer chains or macroscopic precipitates. The average aggregation number increased with the length of hydrophobic segment. This is because the activation energy of moving away from the mesoglobular phase is so high that the aggregates can be stable for a long time after they are trapped in such a metastable state. However, the formation of such a stable mesoglobular phase has not been experimentally established.[7]

Experimentally, the preparation of a pair of copolymers with a similar comonomer composition and chain length, but different comonomer distributions, is rather difficult. However, Volpert et al.[10,11] prepared a series of acrylamide polymers modified with a small amount of alkylamides by micelle copolymerization. Their results showed that for a given copolymer concentration the solution of a segmented copolymer was more viscous than that of a statistical random copolymer. Tenhu et al.[12,13] studied the influence of the number and distribution of the grafts on thermal properties of poly(*N*-isopropylacrylamide)-*g*-poly(ethyl oxide) in aqueous solutions. It is generally known that the distribution of hydrophobic comonomers on an amphiphilic copolymer chain can affect its thickening ability, but the detail is missing. It is known that statistical random and block copolymers as two extreme cases are not as effective as a segmented copolymer with the same chain composition and length in thickening a solution. What is then the optimal length of hydrophobic segments for a given chain composition and length? Such a question is not only a scientific curiosity but also important for industrial applications because it is necessary to maximize the effect/cost ratio.

Besides the effect of comonomer distribution, the changing rate of the solvent quality from good to poor in the phase transition can also influence the formation

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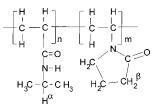
Table 1. Characterization of Poly(*N*-isopropylacrylamide-*co*-vinylpyrrolidone) Copolymers



samples	NIPAM-*co*-VP/60/5	NIPAM-*co*-VP/30/5	NIPAM-*co*-VP/60/10	NIPAM-*co*-VP/30/11
$T_{synthesis}$/°C	60	30	60	30
area of δ_H				
H^{α}	0.874	0.875	0.775	0.745
H^{β}	0.042	0.042	0.075	0.085
[VP]/mol %	4.8	4.8	9.7	11.4
M_w/(g/mol)	2.9×10^6	4.2×10^6	5.6×10^6	7.9×10^6

and structure of mesoglobules. Peng et al.[14] revealed a competition between interchain association and intrachain contraction in a laser light scattering study of the calcium-induced aggregation of poly(acrylamide-*co*-sodium acrylate) in water. Such a competition can be influenced by the quality or by dilution. Our previous study showed that individual poly(*N*-isopropylacrylamide-*co*-vinylpyrrolidone) (P(NIPAM-*co*-VP)) chains can undergo a coil-to-globule transition to form collapsed single chain globules stable in a very dilute solution even at temperatures far above the lower critical solution temperature (LCST, ~36 °C), and the copolymer chains prepared at higher temperatures can "remember" their parent collapsed state.[15] In the present study, we focused on whether neutral amphiphilic copolymer chains can form a predicted stable mesoglobular phase instead of macroscopic precipitation and how the comonomer distribution affects the formation of such mesoglobules.

Experimental Section

Sample Preparation. *N*-Isopropylacrylamide (NIPAM) was purified by recrystallization in a benzene/*n*-hexane mixture. 1-Vinyl-2-pyrrolidone (VP) comonomer was distilled at reduced pressure prior to use. Potassium persulfate (KPS) was purified in a mixture of water and methanol. Other chemicals were used as received. P(NIPAM-*co*-VP) copolymers with 5 or 10 mol % of VP were respectively prepared at 30 and 60 °C by free radical polymerization in water. KPS/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) redox was used as initiator. Each copolymer was harvested by precipitation, i.e., pouring the reaction mixture into an equal volume of methanol. Each resultant copolymer was further purified by four cycles of redissolution in water and precipitation in methanol to remove residual monomers. The final product was dried under reduced pressure at 40 °C. The copolymer was further fractionated by precipitation from a mixture of acetone solution and *n*-hexane at room temperature. The chain composition was characterized by ^{1}H NMR (DPX 300 NMR spectrometer). The ratio of the peak areas of the methine proton of the isopropyl group in NIPAM and the two protons neighboring to the carbonyl group in VP was used to determine the VP content. The results are summarized in Table 1. It shows that the composition of each copolymer was close to the feeding monomer ratio prior to the copolymerization. For each pair of the chains, there are small difference in the chain length. The nomenclature used hereafter for these copolymers is NIPAM-*co*-VP/*x*/*y*, where *x* and *y* are the copolymerization temperature (°C) and the VP content (mol %), respectively. All the solutions with a concentration of 4.0×10^{-5} g/mL were clarified with 0.45 μm Millipore Millex-LCR filter to remove dust before the LLS measurement. The resistivity of deionized water used was 18.0 MΩ cm.

Laser Light Scattering. A slightly modified spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlation (ALV5000) and a cylindrical 22 mW UNIPHASE

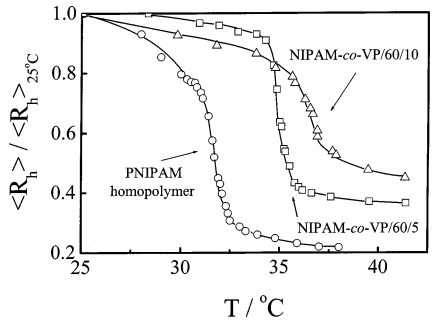


Figure 1. Typical temperature dependence of relative average hydrodynamic radius of individual PNIPAM homopolymer and P(NIPAM-*co*-VP) copolymer chains in water during the coil-to-globule transition, where $C = 6.7 \times 10^{-7}$ g/mL and 3.0×10^{-6} g/mL, respectively.

He−Ne Laser ($\lambda_0 = 632$ nm) as the light source was used. In static LLS,[16] we can measure the weight-average molar mass (M_w) and the *z*-average root-mean-square radius of gyration (written as $\langle R_g \rangle$) of scattering objects in a very dilute solution ($C \rightarrow 0$) from the angular dependence of the excess absolute scattering intensity, known as Rayleigh ratio $R_{vv}(q)$, i.e.

$$\left(\frac{KC}{R_{vv}(q)}\right)_{c\rightarrow 0} \cong \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2\rangle_z q^2\right) \quad (1)$$

where $K = 4\pi^2 n^2 (dn/dC)^2/(N_A \lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dC, n, and λ_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light in a vacuum, respectively.

In dynamic LLS,[17] the Laplace inversion of each measured intensity−intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode leads to a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $\Gamma/q^2 = D$ so that $G(\Gamma)$ can be converted into a translational diffusion coefficient distribution $G(D)$ or a hydrodynamic radius distribution $f(R_h)$ via the Stokes−Einstein equation, $R_h = k_B T/(6\pi\eta D)$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. Normally, the cumulant analysis of $G^{(2)}(t)$ for a narrowly distributed sample is sufficient to result in an accurate average line width ($\langle\Gamma\rangle$).

Results and Discussion

Figure 1 shows a typical intrachain collapse of the coil-to-globule transition of an individual PNIPAM homopolymer and P(NIPAM-*co*-VP) copolymer chains in an extremely dilute aqueous solution. Note that the lower critical solution temperature (LCST) shifts to a higher temperature and the extent of chain contraction decreases after the incorporation of a few mol % of VP comonomer. This is understandable because VP is hydrophilic in the temperature range studied. Figures 2 and 3 show the temperature dependence of the association of P(NIPAM-*co*-VP) copolymers in water in terms of the changes of weight-average molar mass (M_w) and average hydrodynamic radius ($\langle R_h \rangle$) of the resultant copolymer aggregates. Both M_w and $\langle R_h \rangle$ increase as the time elapses and approach corresponding constants after a certain time. Such formed aggregates were stable for a long time, indicating that the interchain association was stopped at a certain stage. A comparison of Figures 2 and 3 shows that $\langle R_h \rangle_{t\rightarrow\infty}$ decreases as the aggregation temperature ($T_{aggregation}$) increases, while $(M_w)_{t\rightarrow\infty}$ increases when $T_{aggregation} < \sim 37$ °C but increases when $T_{aggregation} > 37$ °C. The fact that stable aggregates formed at 36 °C have a smaller M_w, but a larger $\langle R_h \rangle$, clearly indicates that they have a loose

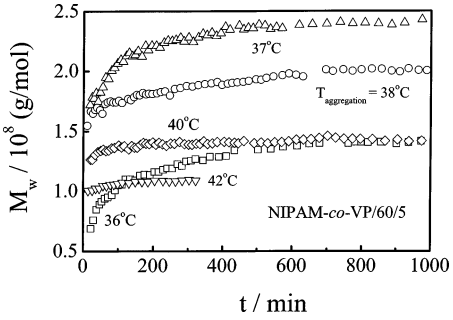


Figure 2. Time dependence of weight-average molar mass (M_w) of mesoglobules formed at different aggregation temperatures, where $C = 4.0 \times 10^{-5}$ g/mL.

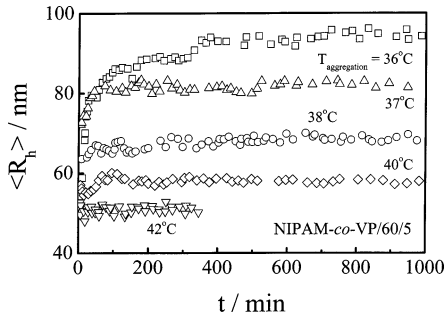


Figure 3. Time dependence of average hydrodynamic radius ($\langle R_h \rangle$) of mesoglobules formed at different aggregation temperatures, where $C = 4.0 \times 10^{-5}$ g/mL.

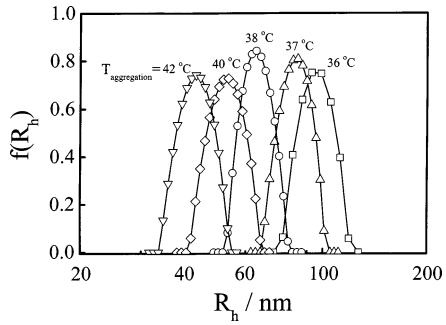


Figure 4. Typical hydrodynamic radius distributions ($f(R_h)$) of resultant stable NIPAM-*co*-VP/60/5 mesoglobules formed at different aggregation temperatures.

structure. This is because the copolymer chains are only partially collapsed at 36 °C. It should be noted that for each pair of copolymer chains the small difference in the chain length should have an effect much less than the comonomer distribution. Experimentally, it is rather hard to obtain the chains with an identical length.

Figure 4 shows that resultant stable aggregates are narrowly distributed. Similar results were also obtained for other three P(NIPAM-*co*-VP) copolymers. It also shows that these aggregates are relatively small, implying that they are made of a limited number of chains. It is helpful to note that no precipitation was observed even after a long time, reflecting no change in the scattering intensity. As for the structural information on these aggregates, we examined the ratio of the radius of gyration to hydrodynamic radius, $\langle R_g \rangle / \langle R_h \rangle$, as shown in Figure 5. The date points are scattered due to experimental uncertainties, especially in the measurement of $\langle R_g \rangle$ for large aggregates. However, the decrease of $\langle R_g \rangle / \langle R_h \rangle$ from ~1.5−1.7 to ~0.8 reveals a change from random-coil chains to uniform spherical aggregates, i.e., mesoglobules.[18] The mesoglobules made of NIPAM-*co*-

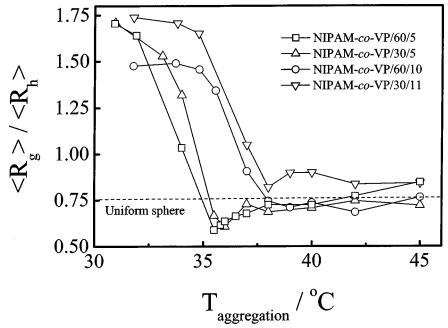


Figure 5. Aggregation temperature dependence of ratio of average radius of gyration to average hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$) of resultant stable mesoglobules made of different copolymers.

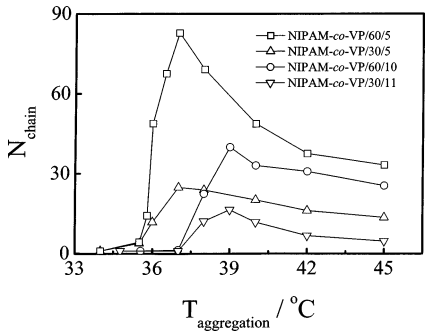


Figure 6. Aggregation temperature dependence of average aggregation number (N_{chain}) of resultant stable mesoglobules made of different copolymers, where N_{chain} is defined as $M_{w,mesoglobule}/M_{w,chain}$.

VP/30/11 have the highest ratio of $\langle R_g \rangle / \langle R_h \rangle$. This is because NIPAM-*co*-VP/30/11 have the highest hydrophobic VP content and a random distribution of VP on the chain backbone so that its contraction is hindered. We will come back to this point later. The formation of such stable mesoglobules is in accord with what was described by Timoshenko et al.[3−5] Only after confirming the formation of stable mesoglobules can we turn our attention to the effect of comonomer distribution.

Figure 6 shows the temperature dependence of the average aggregation number (N_{chain}) of the mesoglobules made of different P(NIPAM-*co*-VP) copolymers, where N_{chain} was obtained from the ratio of the weight-average molar masses of the resultant stable mesoglobules and individual copolymer chains. Note that, for the copolymers with 10 mol % VP, N_{chain} reaches its maximum at a higher temperature because they are more hydrophilic. For each pair of copolymers with a similar VP content, the mesoglobules made of the copolymer chains prepared at 60 °C have a higher N_{chain}. On the other hand, for each pair of copolymers prepared at the same temperature, the copolymer with a higher VP content has an expected smaller N_{chain} because the average length of the PNIPAM segments is shorter and the copolymers are more hydrophilic.

It is a hypothesis that the copolymer chains prepared at higher temperatures would have a more segmented structure because it is expected that most of VP monomers would be copolymerized on the periphery of collapsed PNIPAM segments.[15] In other words, the chains prepared at 60 °C would have a more segmented structure in comparison with those prepared at 30 °C. In this way, for a given VP content, the average length of the PNIPAM segments between two neighboring VP segments should be longer than that of a statistic

random copolymer prepared at 30 °C. It is expected that at high temperatures NIPAM-*co*-VP/60/y copolymers with longer PNIPAM and PVP segments can provide a stronger hydrophobic interaction as well as a stronger hydrophilic stabilization force, which have the opposite effects on the formation of the mesoglobular phase. However, the effect of hydrophobic interaction should be larger because PNIPAM is a major component and the length increase of the PNIPAM segment is much faster when the VP monomers start to group together as short segments. This explains why the copolymer chains prepared at 60 °C result in larger aggregates.

Another feature of Figure 6 is the initial sharp increase of N_{chain} followed by a gradual decrease. Note that for each copolymer the temperature at which N_{chain} reaches its maximum roughly corresponds to the temperature at which individual copolymer chains reach their fully collapsed states. It is easy to understand the increase of N_{chain} with the aggregation temperature because long PNIPAM segments become more and more hydrophobic. Before reaching the collapse temperature, less compact chains can interpenetrate with each other so that the interchain association is dominant. At higher aggregation temperatures, intrachain contraction becomes dominant and short hydrophilic VP segments tend to stay on the periphery of long collapsed PNIPAM segments to minimize the interfacial energy. In this way, the interchain association is retarded, which explains why N_{chain} decreases in the high aggregation temperature range.

Thermodynamically, the formation of stable mesoglobules instead of macroscopic precipitation requires a dedicate balance between enthalpic and entropic contributions. In comparison with macroscopic precipitation, the existence of many small mesoglobules must gain in both translational entropy ($\Delta S > 0$) and interfacial energy ($\Delta H > 0$). For a homopolymer in a poor solvent, the gain of ΔH is always larger than $T\Delta S$, i.e., $\Delta G = \Delta H - T\Delta S > 0$. Therefore, the equilibrium moves toward the direction of forming macroscopic precipitation. For amphiphilic copolymers in a selective solvent (often water), a microphase separation can occur, in which the association of hydrophobic segments leads to intrachain contraction and interchain aggregation, but hydrophilic segments tend to stay on the periphery. Under proper conditions, the gain of $T\Delta S$ can offset that of ΔH, i.e., $\Delta G = \Delta H - T\Delta S < 0$, so that further interchain aggregation stops. It is expected that more hydrophilic groups on the periphery would lead to smaller mesoglobules. However, because of the chain connectivity, a perfect arrangement to expose all hydrophilic VP components on the periphery is impossible. For a given type of copolymer with a similar composition, longer hydrophobic (i.e., short hydrophilic) segments should make the arrangement easier. As discussed before, the copolymer synthesized at 60 °C has longer PNIPAM segments than its counterpart synthesized at 30 °C for a given comonomer composition. Longer PNIPAM segments at high temperatures provide a stronger hydrophobic attraction so that the copolymer chains prepared at 60 °C have a lower LCST and a higher N_{chain} than its counterpart prepared at 30 °C.

On the other hand, we should consider the kinetic and viscoelastic effects on the formation of mesoglobules. Once the temperature is raised, the copolymer chains simultaneously undergo intrachain contraction and interchain association. The relative length of the interaction (contact) time (τ_C) of two approaching aggregates and the relaxation time (τ_R) of copolymer chains inside each aggregate will determine whether they can be fused together to form a larger aggregate. Only when $\tau_C > \tau_R$ does the merging of two colliding aggregates become possible. Otherwise, two aggregates will act as two elastic glass balls and bound away after the collision. The hydrophilic VP segments on the periphery reduce the interaction time, while the intrachain contraction increases the local concentration inside the aggregates, resulting in a longer relaxation time. A quick increase of the solution temperature above the coil-to-globule transition temperature promotes the intrachain contraction and suppresses interchain association. This is why N_{chain} decreases as the aggregation temperature increases in the range of temperatures higher than the LCST. As shown in Figures 2 and 3, M_w and $\langle R_g \rangle$ nearly instantly reach their stable values after the solution temperature was raised over 40 °C. In contrast, at lower aggregation temperatures, it took a much longer time (~10 h) to form stable mesoglobules because individual partially contracted copolymer chains have much chance to associate with each other. On the other hand, dilution is another way to reduce interchain association.

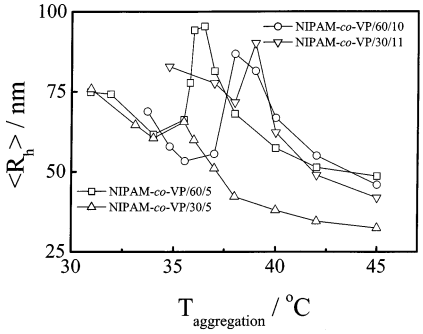


Figure 7. Aggregation temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) of resultant stable mesoglobules made of different copolymers.

The competition between intrachain contraction and interchain association can be better viewed from the temperature dependence of the average hydrodynamic radius $\langle R_h \rangle$, as shown in Figure 7. A comparison of Figures 6 and 7 shows that such a temperature dependence can be roughly divided into three regions. In the lower temperature range, where N_{chain} remains constant (~1), $\langle R_h \rangle$ decreases as the solution temperature increases, reflecting the contraction of individual chains. In the middle temperature range, N_{chain} and $\langle R_h \rangle$ increase before reaching their maximum values, showing that interchain association becomes dominant. In the higher temperature range, both N_{chain} and $\langle R_h \rangle$ decrease as the aggregation temperature increases. It should be noted that the decrease of $\langle R_h \rangle$ in the lower and higher temperature ranges is caused by completely different reasons. In the higher aggregation temperature range, intrachain contraction happens prior to interchain association. The higher the aggregation temperature, the faster the contraction rate. Therefore, individual collapsed copolymer chains have a much less chance to undergo interchain association. This is why both N_{chain} and $\langle R_h \rangle$ decrease in this region.

Figure 8 shows the temperature dependence of the average chain density ($\langle \rho \rangle$) of resultant stable mesoglobules, where $\langle \rho \rangle$ is defined as $M_w/(4\pi\langle R_h \rangle^3 N_A/3)$. For all

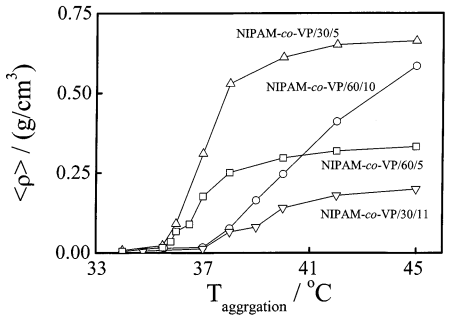


Figure 8. Aggregation temperature dependence of average chain density ($\langle\rho\rangle$) of resultant stable mesoglobules made of different copolymers, where $\langle\rho\rangle$ is defined as $M_w/(4\pi\langle R_h\rangle^3 N_A/3)$.

the copolymers studied, $\langle\rho\rangle$ always increases with the aggregation temperature. Note that intrachain folding normally results in a lower chain density than interchain penetration because the chains are not infinitely flexible. For the copolymer pair, NIPAM-*co*-VP/60/10 and NIPAM-*co*-VP/30/11, the average chain density of NIPAM-*co*-VP/60/10 mesoglobules is higher because the copolymer prepared at 60 °C has longer PNIPAM segments and tends to form stronger interchain association as discussed before. However, for the copolymer pair with a lower VP content, the average chain density of NIPAM-*co*-VP/60/5 mesoglobules is lower. On the basis of our previous study, we know that the coil-to-globule transition of individual NIPAM-*co*-VP/60/5 chains is easier.[13] The lower chain density reflects that NIPAM-*co*-VP/60/5 mesoglobules consist of many small collapsed single-chain globules; i.e., intrachain contraction is dominant in the formation of the mesoglobular phase.

Conclusion

Poly(*N*-isopropylacrylamide-*co*-vinylpyrrolidone) (P(NIPAM-*co*-VP)) copolymers are amphiphilic at higher temperatures. Using two pairs of poly(*N*-isopropylacrylamide-*co*-vinylpyrrolidone) copolymers with a similar chain composition and length, but different VP distributions, we have confirmed that a limited number of such amphiphilic copolymer chains can associate to form stable mesoglobules existing between single-chain collapsed globules and mesoscopic precipitates, even though these chains are neutral and no stabilizer is added. Further, we have shown that the comonomer VP distribution on the chain can greatly influence the formation of such a mesoglobular phase. The degree of amphiphilicity increases with the aggregation temperature, resulting in a competition between intrachain contraction and interchain association. Such a competition depends on the chain composition as well as the rate of changing the solution temperature. Specifically, our results indicate that the copolymers with a segmented VP distribution have a higher tendency to undergo interchain association. When intrachain contraction happens fast and prior to interchain association, smaller mesoglobules are formed. A proper adjustment of the rates of intrachain contraction and interchain association can lead to a desired particle size. This study provides a different view of the formation of polymeric nanoparticles in dispersion as well as a model system to imitate the aggregation of protein-like chains in solution.

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