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Kinetically Driven Intra- and Interchain Association of Hydrophobically and Hydrophilically Modified Poly(acrylic acid) in Dilute Aqueous Solutions

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ABSTRACT: Effects of pH, dodecyl, and PEO contents as well as the method of preparing the solution on the formation of the unimolecular micelles (unimer micelle) or aggregates made of poly(acrylic acid)-*graft*-poly(ethylene oxide)-*graft*-dodecyl (PAA-*g*-PEO-*g*-dodecyl) and PAA-*g*-dodecyl have been studied by a combination of static and dynamic laser light scattering (SLS and DLS). It revealed that: in most cases, these copolymers tend to form interchain associates; while low pH value, proper high dodecyl content and fast switch rate of solvent quality promote intrachain association. These phenomena of the system being trapped in a metastable state can be mainly attributed to its kinetic pathway: the factors mentioned earlier can enhance the initial intrachain contraction, leading to τ_c (interaction time) $\ll$ τ_e (entanglement time) for the two interaction intrachain globules. So they behave like tiny "elastic balls" and their further merge/fusion become nearly impossible during their interaction time (τ_c). In this way, the copolymer system is trapped in the metastable, unimer micelle state. The interplay of τ_c and τ_e in the formation of metastable unimer micelles or stable aggregates has been discussed in detail.

Introduction

The associations of amphiphilic copolymer have attracted many scientific and industrial interests for several decades.[1−8] They have been widely used as rheological modifiers in water-based paint formulations, stabilizers in emulsions, gelling agents in food, and dispatchers of active substance in drug or pesticide formulations[9−12] and in enhanced oil recovery.[13]

The amphiphilic copolymers containing hydrophobic and hydrophilic segments in aqueous solution can give rise to two distinctly separated parts: hydrophobic inner core and hydrophilic outer shell. And the direct driving forces for association include hydrophobic and electrostatic interaction, metal complexation, and hydrogen bonding.[10,13−18] It is found that the self-association of amphiphilic copolymer can occur either within a single polymer chain or among many polymer chains, or both.[19,20] For the association of diblock or triblock amphiphilic copolymer in selective solvent, the micelle is formed through multichain association, because single chain only have one or two associative segments. On the contrary, graft polymer has many associative side chains, and it can form micelle with less chains or even single polymer chain.[21,22] Wu et al. reported that a linear poly(*N*-isopropylacrylamide) chain grafted with poly(ethylene oxide) (PNIPAM-*g*-PEO) in water can form a stable single chain core−shell nanostructure when the temperature is revealed higher than 33 °C.[23] Yamamoto et al. studied the intra- and interchain association of poly (sodium 2-(acrylamido)-2-methylpropanesulfonate-*co*-dodecylmethacrylamide(P(AMPS-*co*-DodMAM)), and they found that DodMAM content is critical to the association behavior of these copolymers.[20] Many of these studies clearly indicate that the nature of hydrophilic and hydrophobic segments, copolymer composition, sequence distribution and spacer between the hydrophobe and polymer backbone are main architectural parameters to determine the self-associative properties of the polymers.[24,25] Besides the nature of copolymers, the solution preparation procedure can also influence the association behavior of polymers. Itakura et al. studied the solvent composition dependence of the association of poly(*N*,*N*-dimethylacrylamide)-*graft*-poly(methylmethacrylate) (PDMA-*g*-PMMA) in a methanol−water mixture and found that a quick switch of solvent quality from good to poor could lead to smaller aggregates while a slow change procedure results in larger aggregates.[21]

Most theories about associations are based on equilibrium thermodynamics. However, it can not explain the formation of unimer micelle, because smaller particle with larger surface area and higher free energy should be less stable. This counterintuitive phenomenon can be resolved from the competition between intermolecular interaction time and entanglement time.[26−28]

In order to take advantage of this phenomenon to encapsulate hydrophobic agrochemical active agents, we designed terpolymers with three distinct functions: (1) a pH-dependent amphiphilicity function, (2) the complexation function with hydrophobic agrochemical active agents, and (3) the ability to mediate the colloidal stability in aqueous solutions. Each of these functions can be addressed individually by the different components of a terpolymer. In the present work, the option of a pH-sensitive poly(acrylic acid) (PAA) backbone with grafted blocks of a hydrophilic and dispersing PEO component as well as blocks of

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Table 1. Characteristics of PAA-*g*-PEO-*g*-dodecyl and PAA-*g*-dodecyl

copolymer	wt % PEO[a]	no. of PEO grafts in each copolymer	wt % dodecyl	no. of dodecyl grafts[b] in each copolymer	M_w of copolymer[c]/ 10^5 g moL^{-1}
PAA-D4			4	56	2.6
PAA-D10			10	146	2.8
PAA-D16			16	259	3.0
PAA-D26			26	465	3.4
PAA-D34			34	697	3.8
PAA-D40			40	906	4.2
PEO7-D12	7	9.4	12	206	3.0
PEO7-D19	7	9.4	19	365	3.3
PEO7-D34	7	9.4	34	785	4.1
PEO13-D10	13	18.5	10	178	3.1
PEO13-D25	13	18.5	25	518	3.7

[a] The content of PEO is defined as the PEO weight percent in PAA-*g*-PEO precursors. [b] The dodecyl grafts should be randomly distributed along the PAA backbone. [c] The molecular weights are examined by ^{1}H NMR: the sum of molecular weight of PAA segment, PEO and dodecyl segments (the M_w/M_n after the grafting reaction is approximated to be unchanged).

a hydrophobic and complexing dodecyl component is being pursued. However, it turned out that not all the three functions are distinct; the components interact with each other, and make the system more complicated as a result. Similar to what we have previously reported that the double hydrophilic PAA-*g*-PEO showed a tendency for interchain association in aqueous solution through hydrogen-bonding,[29] the aqueous solution of PAA-*g*-PEO-*g*-dodecyl, in which both hydrogen-bonding and hydrophobic interactions lead to the association of terpolymer.

In this study, the effects of pH values, dodecyl content, PEO content, and solution preparation procedure on the association behavior of graft copolymers PAA-*g*-dodecyl and PAA-*g*-PEO-*g*-dodecyl in aqueous solution have been investigated. Although interchain associations are dominant in most cases, with a high enough hydrophobicity of polymer chain and a preparation procedure to achieve fast switch rate of solvent quality, the formation of unimer micelle can be obtained. The variation of association behavior with conditions has been explained from thermodynamic and kinetic point of view.

Experimental Section

Materials. Poly(acrylic acid) (PAA) aqueous solution (weight fraction 35%, $M_w = 2.5 \times 10^5$ g mol^{-1}) from Sigma–Aldrich, 2-chloro-4,6-dimethoxy-1,3,5-triazine ethyl (CDMT) from Beijing F&F Chemical Co., Ltd., *N*-methylmorpholine (NMM), dodecylamine from Sinopharm Chemical Reagent Co. Ltd., and tetrahydrofuran (THF) from Beijing Chemical Works were used as received. *N*,*N*-Dimethylformamide (DMF) from Beijing Chemical Works was purified by distillation with CaH_2 under reduced pressure. Water used in this study was purified with a milli-Q system from Millipore. Dialysis bag (regenerated cellulose, cutoff molecular weight = 1.4×10^4 g mol^{-1}) from Beijing Jingkehongda Biotechnology Co., Ltd. was pretreated by successively boiling in ethanol/water (1:1 v/v), 0.01 M $NaHCO_3$ and 0.001 M 2-[2-(bis-(carboxymethyl)amino)ethyl(carboxymethyl)amino]acetic acid (EDTA) aqueous solution.

Synthesis of 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium Chloride (DMTMM). First, 8.8 g CDMT was dissolved in 120 mL of THF, and then 5.5 mL of NMM was added as droplets. The mixture was kept stirring at room temperature for 30 min and then filtrated. The resultant precipitate was washed with THF. The product has been characterized by ^{1}H NMR in DMSO-d_6 (dimethyl sulfoxide).[30−32]

Synthesis of PAA-*g*-PEO-*g*-dodecyl and PAA-*g*-dodecyl. PAA-*g*-PEO was prepared as reported before (PEO is grafted to PAA backbone, the M_w of PEO is 2.0×10^3 g moL^{-1}).[29] PAA-*g*-PEO-*g*-dodecyl and PAA-*g*-dodecyl were synthesized according to the classical reaction of amino with carboxylic groups in the presence of DMTMM. Typically, the reaction was carried out according to the procedure as followed. First 2.5 g of PAA-*g*-PEO or PAA was dissolved in 140 mL of water/THF (1/2.5 in volume), and then 0.5 g of dodecylamine was added. After 30 min, 1.5 g of DMTMM was added, and the reaction lasted for 18 h. Most THF was removed by rotary evaporation. The remaining solution was dialyzed against water for 4 days and then freeze-dried. To remove unreacted dodecylamine, the crude product was dialyzed against ethanol/water (acidic) mixture for 4 days, and then dialyzed against water. The final product was obtained by freeze-drying. The composition of the copolymer was examined by ^{1}H NMR. Several samples with different dodecyl contents were obtained following this procedure. The details are listed in Table 1. These copolymers were named as PAA-*g*-PEO-*x*-*g*-dodecyl-*y* (*x* and *y* stand for PEO content and dodecyl content respectively) or PAA-*g*-dodecyl-*y* (y stands for dodecyl content), and shortened as PEO*x*-D*y* or PAA-D*y*, respectively.[33] The weight average molecular weight (M_w) of PAA segment is 2.5×10^5 g moL^{-1} (the degree of polymerization: about 3470), and the M_w of these graft polymers range from 2.6×10^5 to 4.2×10^5 g moL^{-1} as listed in table 1.

Preparation of Polymer Micelle. Micelle solutions were prepared by adding graft copolymer solution in DMF (1 wt %) dropwise to excessive amount of aqueous NaCl solution (0.025 M) under stirring. The obtained solutions were then dialyzed against aqueous NaCl solution for 24 h to remove the small amount of DMF. A specific part of samples were prepared in a reverse procedure: an excessive amount of aqueous NaCl solution was slowly added into stirring copolymer solution in DMF (0.2 wt %), and then dialyzed against aqueous NaCl solution. The pH of newly prepared solutions is 4.0, and it can be adjusted to other pH values if needed. The final polymer concentration in this study is 2.7×10^{-4} g mL^{-1} with 0.025 M NaCl.

Laser Light Scattering. A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He−Ne laser (λ_0 = 632.8 nm) was used. The LLS cell is held in a thermostat index matching vat filled with purified and dust-free toluene, with the temperature controlled to within 0.1 °C. The details of LLS instrumentation and theory can be found elsewhere.[34−36] In static LLS (SLS), the angular dependence of the excess absolute time-averaged scattered intensity, i.e., the Rayleigh ratio $R_{vv}(q)$, of a very dilute dispersion can lead to the weight-averaged molar mass M_w and the *z*-averaged root-mean-square radius of gyration $\langle R_g^2 \rangle_z^{1/2}$, (or written as $\langle R_g \rangle$) of scattering objects by using Zimm plot (according to eq 1) or Berry plot (eq 2).[37,38]

$$\frac{Kc}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1+\frac{1}{3}q^2\langle R_g^2\rangle\right)+2A_2c \qquad (1)$$

$$\left[\frac{Kc}{R_{vv}(q)}\right]^{1/2} \approx \left(\frac{1}{M_w}\right)^{1/2}\left(1+\frac{1}{3}q^2\langle R_g^2\rangle\right)+A_2Mw^{1/2}c \qquad (2)$$

where $K = 2\pi^2 n^2 (dn/dc)^2/(N_A \lambda_0^4)$ and q is the scattering vector ($q = (4\pi n/\lambda_o)\sin(0/2)$) 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 this study, the solution was so dilute that the extrapolation for $c \rightarrow 0$ was not necessary. So we extrapolated for $q \rightarrow 0$ according to eq 1 or 2 omitting the c term, and got the $M_{w,app}$ from the intercept. For high molecule weight structures (above several million g moL^{-1}), eq 2 was used to analyze the experimental data; otherwise eq 1 was used.

In dynamic LLS (DLS), the intensity–intensity time correlation function $g^{(2)}(t,q)$ in the self-beating mode was measured, where t is the decay time. $G(\tau)$ can be calculated from the Laplace inversion of the measured $g^{(2)}(t,q)$.[39] In this study, the CONTIN program supplied with the correlator was used. $G(\tau)$ can be inverted to a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{q\rightarrow 0, C\rightarrow 0} = D$, so that $G(\Gamma)$ can be converted to a translational diffusion coefficient distribution $G(D)$ or further to a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = k_B T/6\pi\eta_0 D$, where k_B, T, and η_0 are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

Results and Discussion

The association of PAA-*g*-dodecyl and PAA-*g*-PEO-*g*-dodecyl in aqueous solution has been investigated. Since water is the poor solvent for dodecyl, in PAA-*g*-dodecyl aqueous solution, it is the hydrophobic interaction induces the copolymer association. As demonstrated by many studies, PAA-PEO or PAA/PEO can from intermolecular hydrogen-bonding complexes in aqueous solution.[29,40–42] So in PAA-*g*-PEO-*g*-dodecyl aqueous solution, besides the hydrophobic interaction, there also exists hydrogen bonding between PAA segments and PEO segments, which together leads to the association of copolymer.

1. The Effects of pH on the Association of PAA-*g*-dodecyl and PAA-*g*-PEO-*g*-dodecyl in Dilute Aqueous Solution. At pH 4.0, the degree of neutralization, α, of the carboxylic acid groups of PAA segment is about 0.1–0.15, i.e. most of them are protonated; at pH 10.0, they are almost fully ionized (α≈1.0); and at pH 7.0, α is 0.2–0.9, the carboxylic acid groups are partially ionized depending on modifications of PAA chain and the exact conditions.[37,43] Figure 1 shows the pH dependence of characteristic relaxation time distributions and apparent molecular weight of (a) PAA-*g*-PEO-7-*g*-dodecyl-12, (b) PAA-*g*-PEO-13-*g*-dodecyl-10, and (c) PAA-*g*-PEO-13-*g*-dodecyl-25 in aqueous solutions (note: the $M_{w,app}$ in all figures are referring to the apparent weight average molecular weight of associates). Within the studied pH range, there are two groups of relaxation modes, and the corresponding apparent weight average molecular weight ($M_{w,app}$) obtained from SLS is in the range of 6.2×10^6 to 2.7×10^7 g moL^{-1}. Furthermore, as shown in figure 2, the plots of the average characteristic relaxation rate (Γ) of fast mode and slow mode of PAA-*g*-PEO-13-*g*-dodecyl-25 vs q^2 under different pH conditions are straight lines and the extrapolation at $q \rightarrow 0$ passes through the origin. It clearly reveals the diffusive character of the two modes (they are diffusive for the other samples too, which is not shown here). Each slope leads to a $\langle D \rangle_0$, and further to a $\langle R_h \rangle$. The $\langle R_h \rangle$ (in the following part of this paper, R_h is used for simplicity) of fast modes are in the range 10–30 nm, while the R_h for slow modes are in the range 100–300 nm. The above DLS and SLS data indicate that the interchain association is dominant in these PAA-*g*-PEO-*g*-dodecyl aqueous solutions within all studied pH ranges. And there are about 20–100 single polymer chains in each associate. At pH 4.0, the R_h of associates are around 100 nm; but at pH 7.0 and 10.0, the R_h increase to 200–300 nm. That is because the α of PAA segments as well as its hydrophilicity increases with pH. So, at pH 4.0, the associates are more compact than those at higher pH.[44]

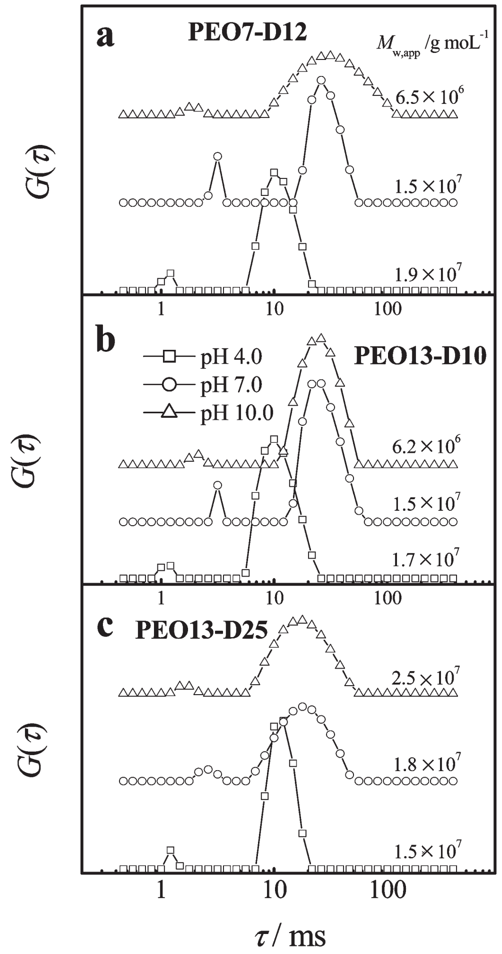

Figure 1. pH dependence of characteristic relaxation time distributions and corresponding apparent molecular weight of associates: (a) PAA-*g*-PEO-7-*g*-dodecyl-12; (b) PAA-*g*-PEO-13-*g*-dodecyl-10; (c) PAA-*g*-PEO-13-*g*-dodecyl-25 aqueous solutions at 20 °C. $C_{polymer} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{NaCl} = 0.025$ M.

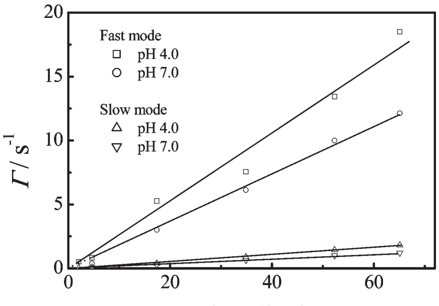

Figure 2. Scattering vector (q) dependence of average characteristic relaxation rate (Γ) of fast and slow relaxation modes for PAA-*g*-PEO-13-*g*-dodecyl-25 aqueous solutions with pH 4.0 and 7.0, 20 °C, $C_{polymer} = 2.7 \times 10^{-4}$ g mL^{-1}, and $C_{NaCl} = 0.025$ M.

Figure 3 shows the plots of $KC/R_{vv}(q)$ (a) and $[KC/R_{vv}(q)]^{1/2}$ (b) versus q^2 for PAA-*g*-PEO-*g*-dodecyl aqueous solution with different compositions under pH 4.0 together with the linear fitting of the plots (see eqs 1 and 2), where the slopes of the fitted

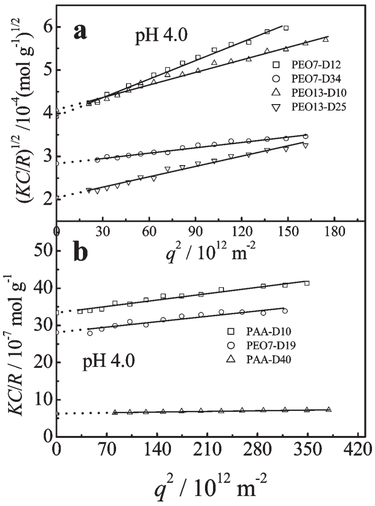

Figure 3. Angular dependence of (a) $KC/R_{vv}(q)$ and (b) $[KC/R_{vv}(q)]^{1/2}$ of PAA-*g*-PEO-*g*-dodecyl aqueous solution under pH 4.0, 20 °C, $C_{\text{polymer}} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{\text{NaCl}} = 0.025$ M.

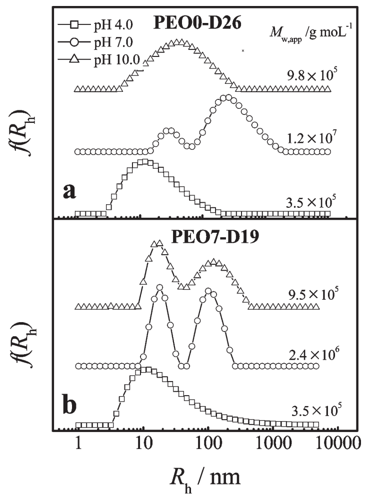

Figure 4. pH dependence of hydrodynamic radius distributions and the apparent molecular weight ($M_{w,app}$) of associates in (a) PAA-*g*-dodecyl-26 and (b) PAA-*g*-PEO-7-*g*-dodecyl-19 aqueous solutions at 20 °C, $C_{\text{polymer}} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{\text{NaCl}} = 0.025$ M.

lines give the apparent value of R_g and the intercept represents the apparent molar weight of the associates. For high molecule weight structures (above several million g mol^{-1}), the SLS experimental data was analyzed as in Figure 3a, otherwise as in Figure 3b.

Figure 4 shows that the association behaviors of PAA-*g*-dodecyl-26 and PAA-*g*-PEO-7-*g*-dodecyl-19 aqueous solutions are quite different from that mentioned above. At pH 4.0, there is only a single fast mode, with R_h around 10 nm. And $M_{w,app}$ values of associates are about 3.5×10^5 g moL$^{-1,}$ which are almost the same as that of a single polymer chain. These results indicate that intrachain association is dominant under these conditions, leading to the formation of unimer micelles. With pH increase, a slow mode emerges, which means large aggregate is formed. However, the relative amplitude of fast mode is larger than that in Figure 1, which indicates that even at higher pH, these two polymers have a strong tendency to form unimer micelle or smaller aggregates.

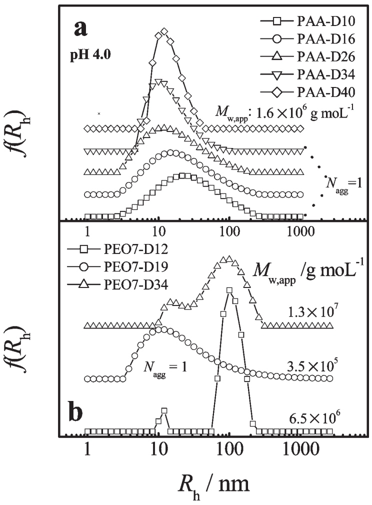

Figure 5. Hydrophobic dodecyl content dependence of hydrodynamic radius distributions and the apparent molecular weight of associates in (a) PAA-*g*-dodecyl and (b) PAA-*g*-PEO-7-*g*-dodecyl aqueous solutions at 20 °C, $C_{\text{polymer}} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{\text{NaCl}} = 0.025$ M.

2. Effects of Dodecyl Content on the Association of Graft Polymers in Aqueous Solution. Figure 5 shows the effect of hydrophobic dodecyl content on the association of (a) PAA-*g*-dodecyl and (b) PAA-*g*-PEO-7-*g*-dodecyl in aqueous solutions at pH 4.0. For PAA-*g*-dodecyl, when the dodecyl contents (f_{Dod}) are in the range 10−34 wt %, there is only one single fast mode and the $M_{w,app}$ is similar to a single chain. So the hydrophobe associations of polymer-bound dodecyl group occur within single polymer chain, leading to the formation of unimer micelle. The R_h of unimer micelles decreases with the increase of f_{Dod}, i.e. the micelles become smaller and more collapsed. When the f_{Dod} increases to 40 wt %, there is still only one single mode, but $M_{w,app}$ is 1.6×10^6 g moL^{-1} (see Figure 3b), which means each micelle contains about four single chains.

In PAA-*g*-PEO-7-*g*-dodecyl aqueous solution, there are both hydrophobic and hydrogen-bonding interactions. At low f_{Dod}, two diffusion modes are found, and the corresponding $M_{w,app}$ is 6.5×10^6 g moL^{-1}, which means large aggregates are formed. As f_{Dod} increases to 19 wt %, only a single fast mode exists, and the $M_{w,app}$ is the same as a single chain, so intrachain association is dominant. A further increase of f_{Dod} leads to the formation of large aggregates again. These results indicate that proper high hydrophobe content is favorable for intrachain association. Additionally, comparing Figure 5a with Figure 5b, the hydrogen-bonding association of PAA−PEO segment tend to form interchain aggregates which will be discussed in detail later.

3. Effects of PEO Content on the Association of Graft Polymer in Aqueous Solution. Figure 6 shows the effects of PEO content on the association of PAA-*g*-PEO-*g*-dodecyl in aqueous solution. In Figure 6a, the f_{Dod} is fixed at around 11 wt %. When the PEO content (f_{PEO}) is 0%, i.e., for PAA-*g*-dodecyl, there is only one single fast mode. Combined with the $M_{w,app}$, the dominance of intrachain association can be obtained. With the increase of f_{PEO} to 7 wt %, two modes emerge and interchain association is dominant. The further increase of f_{PEO} to 13 wt % induces no further change. In figure 6b, the f_{Dod} is higher and fixed at around 22 wt %. When f_{PEO} is 0 and 7 wt %, intrachain association is preferred. While at $f_{\text{PEO}} = 13$ wt %, interchain association is dominant. These results indicate that the PEO chain in graft polymer tends to induce interchain association. While, as described in part 2, proper high dodecyl content is favorable for intrachain association. The competition of these two factors resulted in the formation of unimer micelle at

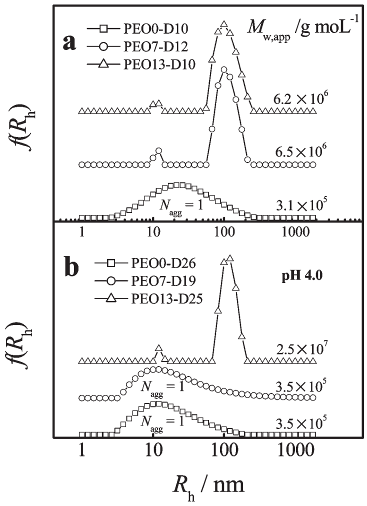

Figure 6. PEO content dependence of hydrodynamic radius distributions and apparent molecular weight of associates in PAA-*g*-PEO-*g*-dodecyl aqueous solutions at 20 °C, with dodecyl contents: (a) ~11 wt % and (b) ~22 wt %, pH 4.0, $C_{\text{polymer}} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{\text{NaCl}} = 0.025$ M.

comparably low PEO content (0, 7 wt %) and relatively high dodecyl content (19 wt %). The increase of PEO content or decrease of dodecyl content will promote interchain association.

4. Physical Explanation of the Association Behavior from Thermodynamic and Kinetic Point of View. As mentioned in parts 1−3 in this section, in most cases, slow mode coexists with fast mode, and the interchain associations dominate and the amplitude of slow mode is more than 95% (*z*-average). Thermodynamically, interchain associations are more stable because they possess larger size and smaller surface area, which lead to minor surface energy and Gibbs free energy. On the contrary, intrachain associations are in a higher Gibbs free energy metastable state (in a local potential well). Usually, the thermo-fluctuations can overcome the potential energy barrier between the metastable potential well and the thermodynamic stable, lower surface energy state, so the interchain associations can become dominant. But under some specific conditions, such as a proper hydrophobic modification of polymer backbone and a certain pH range, the potential energy well is too deep to be overcome by thermo-fluctuations; the intrachain globules cannot "escape" from the metastable wall. So the copolymer system is trapped in the metastable, unimer state. We will describe this point in kinetic detail as follows.

Li et al.[45] showed that in the association process of copolymer, the faster intrachain contraction can results in smaller mesoglobules. The stability of such formed mesoglobular phase mainly depends on the coarsening dynamics. Many studies demonstrated that in the phase separation process of a polymer solution, the collision would not be effective as long as the collision (or contact) time (τ_c) is relatively smaller than the time needed to establish a permanent chain entanglement (τ_e) between two approaching globules.[46−49]

Quantitatively, Tanaka[50,51] showed that τ_c and τ_e can be roughly characterized as

$$\frac{l_0}{\langle v \rangle} < \tau_c < \frac{{l_0}^2}{\langle D \rangle} \quad \text{and} \quad \tau_e \sim \frac{{a_m}^2 {N_m}^3 {\varphi_p}^{3/2}}{D_m} \tag{3}$$

where l_0 is the interaction range, $\langle v \rangle$ and $\langle D \rangle$ are the mean thermal velocity and translational diffusion coefficient of the aggregates, respectively, φ_p is the average polymer concentration inside aggregates, and a_m, N_m, and D_m are the length, number, and diffusion coefficient of the monomer, respectively. When $\tau_c \ll \tau_e$, two collided globules have no time to stick together and they behave like two tiny nonadhesive "elastic ball". The concept of τ_c and τ_e is refined to understand the formation of unimer micelle in this complex system, although none of our polymer system goes through phase separation. In order to obtain a stable globular phase, it is necessary to decrease τ_c and increase τ_e. Equation 3 shows that, for a given polymer solution under a fixed set of experimental conditions, l_0, a_m, N_m, and D_m are constants, one can only increase $\langle D \rangle$ and φ_p to ensure $\tau_c \ll \tau_e$ in order to obtain a stable globular phase. It has been reported that long polymer chain, diluted solution, proper hydrophobicity, and fast microphase separation are favorable for achieving $\tau_c \ll \tau_e$ experimentally.[24,26−28]

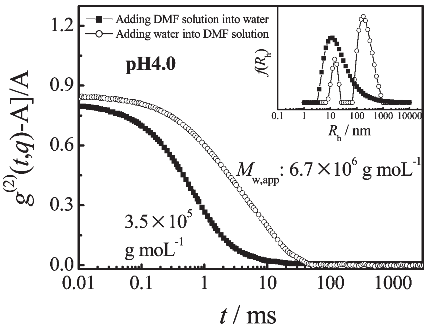

Figure 7. Intensity−intensity time correlation function [*g*(2)(*t*,*q*) − *A*]/*A* of PAA-*g*-PEO-7-*g* -dodecyl-19 in aqueous solutions prepared in two different procedures: adding a solution of copolymer in DMF into water or adding water into copolymer−DMF solution, the inset is the corresponding R_h distribution, pH 4.0, $C_{\text{polymer}} = 2.7 \times 10^{-4}$ g mL^{-1}, $C_{\text{NaCl}} = 0.025$ M, 20 °C.

In this study, the polymer aqueous solutions were prepared by adding a small amount of polymer−DMF concentrated solution into a large amount of water. When the polymer contacts selective solvent (water), it contracts intramolecularly into a globule immediately. Then these initial globules collide with each other. They can either adhere together or bounce and separate, depending on the relationship between τ_c and τ_e. Our results show that under most conditions, interchain associations are dominant; Intrachain associations only dominate at low pH values (pH 4.0) and proper high dodecyl content. Under these conditions (with high hydrophobicity), the initial graft polymer contraction will lead to denser globules. And the smaller initial globular size results in a higher $\langle D \rangle$, which leads to smaller τ_c. Meanwhile, the polymer concentration inside each globule (φ_p) increases which makes larger τ_e, i.e., the more collapsed chains are more difficult to relax. Therefore, $\tau_c \ll \tau_e$ can be achieved, leading to the formation of unimer micelle.

5. The Effects of Solution Preparation Procedure on the Association of Graft Polymer. Figure 7 shows the intensity−intensity time correlation function of PAA-*g*-PEO-7-*g*-dodecyl-19 in aqueous solutions prepared in two different procedures: adding a solution of copolymer in DMF dropwise into large amount of water or reverse as described in the Experimental Section. In the former case, the time correlation function only has one single relaxation mode, and the corresponding R_h is around 10 nm. As stated in part 2 of this section, intrachain association is dominant under this specific condition. The latter is prepared by adding large amount of water dropwise into copolymer solution in DMF (2.0×10^{-3} g mL^{-1}). It should be stated that at a higher initial concentration of polymer solution in DMF, such as (1.0×10^{-2} g mL^{-1}),

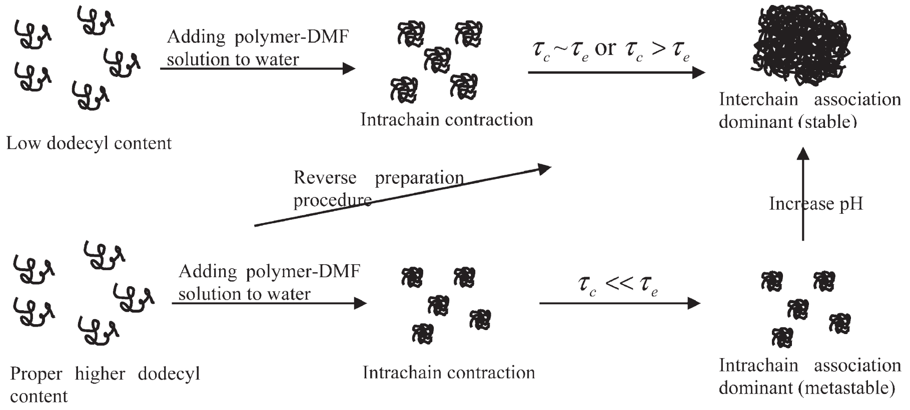

Figure 8. Schematic of competition between intrachain and interchain association in PAA-*g*-PEO-*g*-dodecyl aqueous solution with different dodecyl contents or under different conditions.

adding water into the copolymer solution in DMF results in precipitation. But a reduced initial copolymer concentration (2.0×10^{-3} g mL^{-1}) can result in a clear solution. If the copolymer aqueous solution is prepared in this procedure, as shown in figure 7, a slow mode at around 200 nm emerges, with $M_{w,app}$ of associates about 6.7×10^6 g moL^{-1}, which indicates that interchain association is dominant. Similar phenomenon has also been reported by Li et al.[45] and Itakura et al.,[21] their results showed that the aggregates obtained from a quick switch of solvent quality from good to poor are much smaller than that in a slow switching process. In the former case (adding polymer DMF solution into water), solvent quality is quickly switched from good to poor for dodecyl segments. When copolymer contacts large amount of water, it experiences immediately intense intrachain contraction, which increases $\langle D\rangle$ and φ_p simultaneously. Therefore, it is easier to attain $\tau_c \ll \tau_e$, and resulting in unimer micelle dominance. In the latter case, water is added dropwise into polymer solution in DMF, the solvent quality decreased gradually. The initial intrachain contraction is small, $\langle D\rangle$ and φ_p only increases little, while the initial polymer concentration is still high. All of these enhance the chance for polymer chains to associate with each other and form large aggregates.

All the discussion above can be schematically summarized in Figure 8. During the association of amphiphilic graft polymer in dilute solution, a competition between intrachain and inerchain association is involved. In most cases, interchain association is dominant, but under some specific conditions (low pH, proper high dodecyl content, fast switch of solvent quality), intrachain association is favored and lead to the formation of unimer micelle. This phenomenon can be explained by the competition of interaction time and entanglement time: those specific conditions can promote the initial intrachain contraction, leading to $\tau_c \ll \tau_e$, thus prohibiting the resultant unimer micelles to interpenetrate with each other to form interchain associations.

Conclusion

The association behavior of PAA-*g*-PEO-*g*-dodecyl and PAA-*g*-dodecyl in aqueous solution has been studied by DLS and SLS. We focused on the competition of intrachain and interchain association under different conditions, such as pH values, dodecyl content, PEO content and the solution preparation procedure. Our results showed that under most situations, large interchain aggregates are formed. However, in some specific cases, intrachain association is dominant, resulting in unimer micelle. It was shown that, low pH value (4.0), proper high dodecyl content and fast switch rate of solvent quality (adding polymer DMF solution into water) promote intrachain association. These phenomena can be explained by the competition between intermolecular interaction time and entanglement time: the factors mentioned above can enhance the initial intrachain contraction, which increases relaxation time (τ_e) and reduces interaction time (τ_c) of the approaching "globules", and leading to $\tau_c \ll \tau_e$. The interaction between these two intrachain globules behaves like tiny "elastic balls" and their further merge/fusion become nearly impossible during their interaction time (τ_c); thus, they can stay in the metastable state and intrachain association become dominant in the solution.

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