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Novel Highly Branched Polyester Nanoparticles(Ⅱ)* —— Interactions Between Anionic HBPN Particles and Cationic Surfactant, Cetyltrimethylammonium Bromide

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The interactions between highly-branched anionic polyester nanoparticles (HBPN) and the oppositely charged surfactant (cetyltrimethylammonium bromide, CTAB) in a buffer (pH = 12) were investigated by means of dynamic laser light scattering. Our results indicate that CTAB molecules first form micelles and then the micelles are attracted to the anionic surface of HBPN to form a HBPN/CTAB complex. HBPN anionic surface has provided a certain amount of ions so that CTAB micelles at HBPN surface are more thermodynamically stable. Therefore, one CTAB micell can attract more HBPN to form larger aggregates wherein a number of HBPN is interconnected by CTAB micelles

Keywords Surfactant/polyelectrolyte interaction, Dynamic light scattering, Nanoparticle

Introduction

Polyelectrolytes can adsorb oppositely charged surfactant molecules to form various polyelectrolyte/surfactant complexes. These complexes have found important application mentioned in previous paper. There has been a growing interest in studying polymer/surfactant systems recently, especially the detail of the interaction between a given polyelectrolyte and a surfactant. A better understanding of the interactions between a polyelectrolyte and a surfactant on the molecular level is essentially important to their application and further development.

The studies in the past were concentrated on the linear polyelectrolyte chains and oppositely charged surfactant in diluted aqueous solutions. Various models were proposed for the interactions between polyelectrolytes and surfactants[1]. The interactions were viewed from surfactant micelles. The transfer of the hydrophobic section of a given polymer chain into the micelle was considered in terms of free energy or chemical potential. Experimentally, the formation of a different complex for a different polyelectrolyte/surfactant system was observed and no consistent picture has been obtained so far.

We selectively studied the interactions between rigid highly branched polyester nanoparticles (HBPN) and the oppositely charged surfactant. Dynamic light scattering (DLS) was used to mornitor the complex formation[2]. Another objective of choosing the spherical-like

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HBPN clusters is to find how polyelectrolytes can interact with the oppositely charged surfactant when the chain flexibility is eliminated. In the previous paper, we characterized the HBPN clusters and here we will concentrate our attention on the interactions between HBPN and(CTAB).

Experimental

1 Sample Preparation

The detail of preparing highly branched polyester nanoparticles was described in the previous paper(I). Since the anhydride groups were in excess in the reaction mixture, the end groups on the periphery of HBPN were carboxyls and became anionic in an alkaline solution, *e. g.*, in the buffer(pH≥12) the protons in carboxyls were removed so that HBPN could be considered as a micro sphere with negative charges on its periphery. In this way, HBPN could adsorb other cationic molecules or particles.

Cetyltrimethylammonium bromide (CTAB) from EASTMAN was used without further purification. The buffer solution (pH=12) was prepared using a standard procedure (FIXAMAL Riedel-deHa(n). The buffer solution was prepared as follows: At first, a proper amount of HBPN was dissolved in the buffer (pH=12), and then different amounts of CTAB were added only after HBPN was completely dissolved in the buffer solution. All buffer solutions of HBPN/CTAB were clarified by a Millipore 0.2 μm PTFE filter to remove dust. The filter was treated with methanol before use.

2 Laser Light Scattering(LLS)

The LLS apparatus, conditions of measurement and the treatment of samples are the same as those in paper(I). The intensity-intensity time correlation function was measured. The correlation functions were analyzed by a Laplace program CONTIN equipped with the correlator. The obtained characteristic line-width distribution $G(\Gamma)$ can be converted into the translational diffusion coefficient distribution $G(D)$ by using $\Gamma = Dq^2$, where q is the scattering vector. Further, $G(D)$ can be converted to the hydrodynamic radius distribution $f(R_h)$ by using the Stokes-Einstein equation. All the experiments were carried out at $t=25$ ℃. The details of LLS experiments and instrumentation can be found elsewhere[3,4].

Results and Discussion

Fig. 1 shows a comparison of two hydrodynamic radius distributions of the HBPN/CTAB complex formed in the buffer solution (pH=12) at different standing time (t) after mixing HBPN and CTAB, where $t=25$ ℃, $c_{HBPN}=2$ mg/mL and $c_{CTAB}=3$ mg/mL. The circles show $f_z(R_h)$ for about 2 h after adding CTAB into the HBPN buffer solution; and the diamonds show $f_z(R_h)$ for about 4 days. It is clear that initially only single peak located at *ca.* 13 nm was observed. After about 4 days, a second peak appeared at *ca.* 400 nm and at the same time the first peak shifted to *ca.* 5 nm. In comparison with the HBPN size (about 4.3 nm), it is clear that some large HBPN/CTAB complex was formed even at the initial stage. Later, we will come back to how the HBPN/CTAB complex is formed.

Fig. 2 shows the time dependence of the averaged hydrodynamic radius $\langle R_h \rangle$ of the larger peak(the higher in Fig. 1, which has a smaller averaged size), where the experimental conditions are identical to those in Fig. 1. As we stated before, the larger peak in Fig. 1 represents the HBPN/CTAB complex. Therefore, it is very clear that the HBPN/CTAB com-

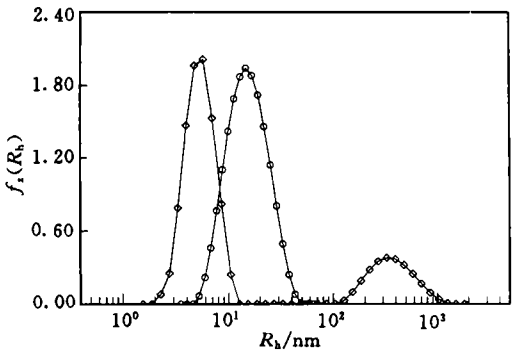

Fig. 1 Typical hydrodynamic radius distributions $f(R_h)$ of the HBPN/CTAB complex.
(○) $t\approx2$ h; (◇) $t\approx101$ h. The c_{HBPN} and c_{CTAB} are 2 mg/mL and 3 mg/mL, respectively.

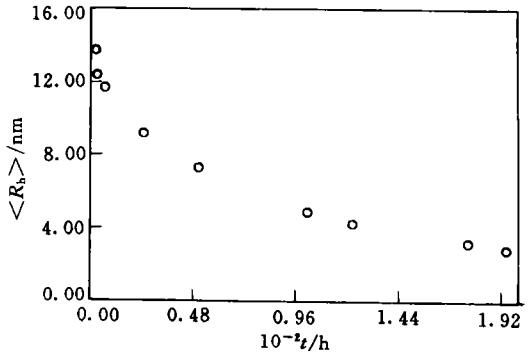

Fig. 2 Plot of the average hydrodynamic radius $\langle R_h \rangle$ of the larger peak with a smaller average size in Fig. 1 *versus* time.

plex is not stable and the averaged hydrodynamic radius decreases with time after the mixing even though at the same time some larger species were formed in the solution (shown in Fig. 1). It is worth noting that the final hydrodynamic radius approached that of the CTAB micelle (*ca.* 2.5 nm). This indicates that at the initial stage CTAB molecules were attached to HBPN to form some HBPN/CTAB complex and gradually individual HBPN clusters came together to form some larger aggregates (with the assistance of CTAB) because we have known HBPN alone in the buffer is stable according to our previous study. At the same time, the CTAB micelles were detached from HBPN, freely going into the solution.

Fig. 3 shows the time dependence of the area ratio (A_L/A_S) of the two peaks shown in Fig. 1, where the subscripts L and S represent the peaks in Fig. 1 with a larger and a small averaged size, respectively. A_L/A_S increased with the increase of time after mixing CTAB with HBPN and finally reached a stable value of *ca.* 0.45 after *ca.* 8 days. It should be pointed out that the area under each peak is proportional to the light scattered from the cor-

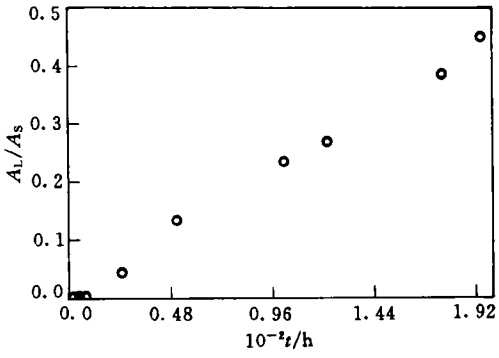

Fig. 3 Plot of the area ratio (A_L/A_S) as a function of time after mixing CTAB with HBPN in the buffer (pH=12).

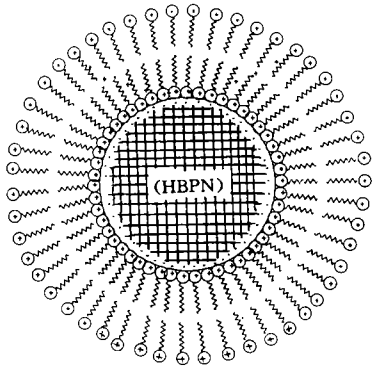

Fig. 4 Schematic of the previous double CTAB layer vesicle model, where one HBPN is encapsulated in its hollow center.

responding species (individual HBPN/CTAB complex particle or the larger aggregate) and the scattering intensity is further proportional to the mass of the scatterer. Therefore, the actual number of the larger aggregates should be very small because the aggregates are much larger than HBPN, CTAB micelles and even the initial HBPN/CTAB complex. The increase of A_L is attributed to both the size and amount increases of the aggregates.

Fig. 4 shows a model assumed for the HBPN/CTAB complex, namely a double CTAB layer vesicle with an HBPN encapsulated in its center. If ever, according to this model, the hydrodynamic radius of the HBPN/CTAB complex formed in the buffer solution should be *ca.* 9 nm, *i.e.*, $R_{h,\,complex}=R_{h,HBPN}+2R_{h,\,CTAB}$, because $R_{h,\,HBPN}\approx 4$ nm and $R_{h,\,CTAB}\approx 2.5$ nm. Moreover, such formed HBPN/CTAB should be very stable in the solution. However, our results clearly contradict this model. Firstly, the initial size (*ca.* 13 nm) of the HBPN/CTAB complex is much larger than that of the complex suggested in Fig. 4; secondly, the complex is instable in the buffer solution. After a careful consideration, a new model was suggested for the formation of the complex between HBPN and CTAB.

Fig. 5 shows the model proposed in this study, wherein CTAB first forms stable CTAB micelles and later these CTAB micelles are attached to HBPN by means of electrostatic attraction. According to this new model, the hydrodynamic radius of the HBPN/CTAB complex formed in the buffer solution should be 11 nm or larger because $R_{h,\,complex}=R_{h,CTAB}+2R_{h,\,HBPN}$, which is close to the initial size of the HBPN/CTAB complex. Moreover, we can use this model to explain all the experimental results in Figs. 1—3. According to this new model, the formation of the CTAB micelle is more favorable than the formation of the double layer vesicle and the HBPN/CTAB complex is formed *via.* the electrostatic attraction between HBPN and the CTAB micelles. However, the simple calculation on the basis of the concentration and molecular weights of HBPN and CTAB shows that the surface of the CTAB micelle is much bigger than a complete coverage of HBPN cluster and on average, each CTAB micelle attracts *ca.* 5 HBPN clusters. Further interconnection or aggragation of these HBPN/CTAB complexes aggregates are possible because such two HBPN/CTAB complexes can come together with one CTAB micelle as a bridge between them. This might explains why the initial hydrodynamic radius (*ca.* 13 nm) of the HBPN/CTAB complex was slightly larger than the ideal value (*ca.* 11 nm) predicted by the model in Fig. 5.

Thermodynamically, after formation of the complex the anionic surface of HBPN provides a certain amount of ions for the CTAB micelle so that the CTAB micelle becomes more stable, thus one CTAB micelle will attract HBPN as much as possible. On the other hand, the solution is so dilute that to reach a true thermodynamic equilibrium takes time. This is why the second peak representing the larger aggregates did not appear initially, but the aggregates gradually increased with the increase of time and finally reached a stable state wherein a number of HBPN clusters were interconnected by CTAB micelles to form larger aggregates and the surface of the aggregate was covered with CTAB micelles so that further aggregation was stopped. During this process, the excessive CTAB micelles were released into the buffer solution and became free and individual CTAB micelles. This explains not only two peaks in Fig. 1, but also the shift of the first peak to the smaller size direction.

Fig. 6 shows typical a c_{CTAB} dependence of the initial averaged hydrodynamic radius $\langle R_h\rangle$ of the HBPN/CTAB complex in the buffer, where we fixed c_{HBPN} to be 2 mg/mL. It clearly shows that the hydrodynamic radius decreases from *ca.* 13 nm to *ca.* 2.8 nm as c_{CTAB} increases from 3 mg/mL to 14 mg/mL. If the model in Figure 4 was correct, we would expect that

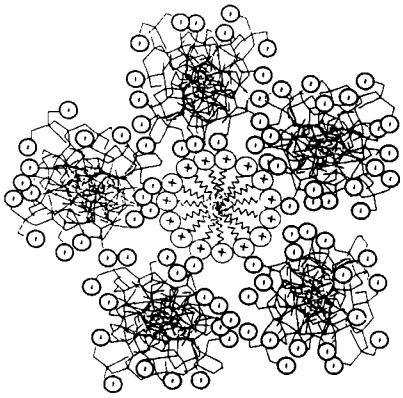

Fig. 5 Schematic of the new HBPN/CTAB complex model wherein individual CTAB molecules first form the CTAB micelles and then these CTAB micelles adsorbed on the anionic surface of HBPN.

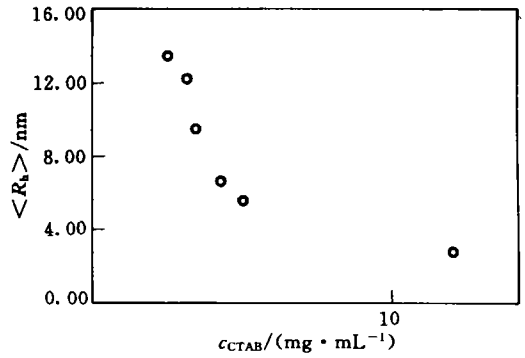

Fig. 6 The CTAB concentration dependence of the average hydrodynamic radius of HBPN/CTAB complexes.

the HBPN/CTAB complex becomes more stable as c_{CTAB} increases. However, our results show that the increase of c_{CTAB} actually speeds up the decrease of $\langle R_h \rangle$ of the HBPN/CTAB complex. In contrast, the results in Fig. 6 can be explained by means of the model in Fig. 5. More CTAB will make the aggregation fast individual CTAB micelles are released, so that the initial size decreases with the increase of c_{CTAB} increase.

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