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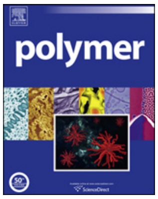

Shell–core–corona aggregates formed from poly(styrene)-poly(4-vinylpyridine) block copolymer induced by added homopolymer via interpolymer hydrogen-bonding

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The solution behavior of poly(styrene)-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer with added poly(4,4′-oxydiphenylenepyromellitamic acid) (POAA) homopolymer in DMF is studied by dynamic light scattering (DLS), nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM). It is found that coaggregation takes place when mixing PS-*b*-P4VP block copolymer and POAA homopolymer in DMF due to the strong interpolymer hydrogen-bonding between POAA chains and P4VP blocks. The coaggregation is a diffusion-controlled process and the complexation-induced aggregates are very stable. NMR measurements demonstrate that the resultant aggregates are much more swollen compared with typical amphiphilic block copolymer core–shell micelles. DLS measurements with Eu^{3+} as a probe combined with TEM observation, are employed to study the structure of the aggregates. Results reveal that the formed aggregates are core–shell spheres with the P4VP/POAA complexes as core and the PS blocks as shell when the weight ratio of POAA to PS-*b*-P4VP is lower. However, a core–shell–corona structure forms with a thin layer of POAA chains adsorbed on the initial core–shell aggregates with increasing weight content of POAA to 60%. Finally, possible mechanisms of the structural transitions are proposed.

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1. Introduction

The self-assembly of diblock copolymer in solution have attracted considerable attention not only owing to their variety of aggregate structures, including spheres, cylinders, rods, worms, lamellae, or vesicles [1–6], but also because of their potential applications in many areas, such as supports for catalytic devices, drug delivery carriers, separation technology, and lithographic templates and so on [7–15]. Currently, there are mainly two ways to trigger micellization. One method involves micellization of diblock copolymers in block selective solvents which has been well studied in the past decades [16]. The microphase precipitation of the insoluble blocks and the affinity of the soluble blocks to the solvent give rise to micelles where the insoluble blocks form a core which is surrounded by a corona containing the soluble blocks. Another method to trigger micellization consists in introducing additional non-covalent interaction, such as electrostatic interaction [17], hydrogen-bonding [17b,18], or metal–ligand coordination bond [19], etc, in an initially soluble block copolymer. The non-covalent complexes resulting from these interactions should be insoluble, thus further aggregates into micellar cores stabilized by the uncomplexed blocks. Compared with micellization of amphiphilic diblock copolymers in block selective solvents, this method to prepare micellar aggregates by comicellization of two polymers through non-covalent interaction is more facile by just simply mixing the two components in their common solvents.

Recently, coaggregation of different polymers or block copolymers driven by ionic or hydrogen-bonding has received more and more focus because the resultant micelles contain a core or shell composed of different polymer blocks, and the architecture of the micelles could be further modified to meet the needs of application [20]. Liu and coworkers [21] mixed different block copolymers that were tailor-made to contain “gluey” core blocks in a solvent to prepare mixed micelles with segregated corona chains. Gao et al. [22] have formed vesicles by mixing poly(ethylene oxide)-block-polybutadiene and poly(acrylic acid) in a solvent mixture of THF and n-dodecane. Xiong et al. [23] have prepared worm-like

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aggregates with a POAA/P4VP complex core and a PEG/PNIPAM mixed shell in ethanol by the comicellization of poly(ethylene glycol)-block-poly(acrylic acid) (PEG-*b*-PAA) and poly(N-isopropylacrylamide)-block-poly(4-vinylpyridine) (PNIPAM-*b*-P4VP) through hydrogen-bonding. Han et al. [24] have described the formation of fibril like aggregates from the self-assembly of block copolymer mixture of (polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA)) via interpolymer hydrogen-bonding in nonselective solvent. Gohy et al. [25] formed spherical core–shell structure by mixing poly(styrene)-block-poly(4-vinylpyridine) (PS-*b*-P4VP) and poly(acrylic acid) (PAA) homopolymer, and studied systematically the influence of length of the interacting blocks as well as solvent used on the complexation and on the size of the formed micelles.

To the best of our knowledge, most of the previous studies concerning the complex micelles mainly focused on the micelle formation and control of exterior morphology of core–shell structure, while studies on the core–shell structure and solution behavior of complex micelles are really scarce. In this work, coaggregation of poly(styrene)-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer and poly(4,4′-oxydiphenylenepyromellitamic acid) (POAA) homopolymer via interpolymer hydrogen-bonding was studied. Stable spherical micelles induced by hydrogen-bonding complexation between P4VP blocks and POAA chains, were detected by dynamic light scattering (DLS). The core–shell structure and solution behavior of the co-aggregates in DMF were studied by transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) and dynamic light scattering (DLS) measurements with Eu^{3+} as a probe. Compared with typical amphiphilic block copolymer core–shell micelles, the resultant aggregates are much more swollen. Furthermore, it was found that stable core–shell structure with P4VP/POAA complexes as core and PS blocks as shell were formed when POAA was added; however, with increasing weight ratio of POAA to PS-*b*-P4VP, excessive POAA chains were adsorbed onto the initial core–shell aggregates, leading to the formation of core–shell–corona structure.

2. Experiment section

2.1. Materials

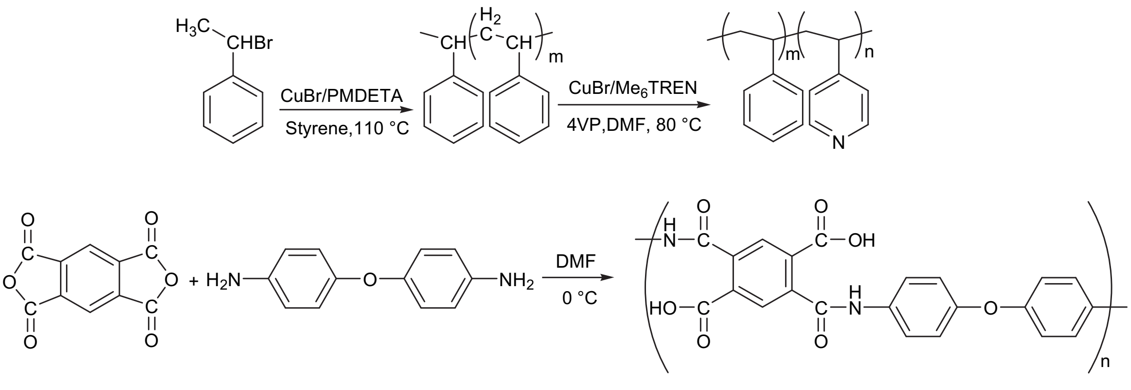
All reagents were purchased from Tianjin Chemical Reagents Company unless noted. Styrene was firstly extracted three times with 5% aqueous NaOH, and then washed with distilled water and dried over CaH_2, finally distilled under reduced pressure (40 °C, 14.5 mmHg). 4-vinylpyridine (96%, Alfa Aesar) was dried over CaH_2 and distilled under reduced pressure (55 °C, 18 mmHg). CuBr and CuCl was purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. N,N-dimethylformamide anhydrous (DMF) was dried over CaH_2, and then distilled under reduced pressure. Tris(2-dimethylaminoethyl) amine (Me_6TREN) was prepared according to the previous report [26]. Pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA) (98%, Alfa Aesar), 1-phenylethyl bromide (1-PhEtBr) (97%, Alfa Aesar), Tetrahydrofuran (THF), diethyl ether were used as received.

2.2. Synthesis of PS_{102}-*b*-$P4VP_{162}$ and POAA homopolymer

The diblock copolymer PS-*b*-P4VP was prepared by an ATRP method involving two steps. The first step involves the macroinitiator PS–Br, synthesized according to the procedures given in previous report [27]. In the second step, 0.04 g of CuCl (0.4 mmol), 5 mL of DMF, and 0.09 g of Me_6TREN (0.4 mmol) were added to a dry three-neck rounded bottom flask with a stir bar. The mixture were stirred for 30 min until the solution become deep green in color, then 1.0 g of PS–Br (0.1 mmol), 6.4 g of 4-vinylpyridine (60 mmol) were added to the flask. The flask, containing reactants, was fully degassed with three freeze–pump–thaw cycles and conducted under purified argon. It was subsequently immersed in a thermostated oil bath at 80 °C under stirring to allow polymerization of 4-vinylpyridine. The reaction continued for 8 h after which the system was cooled down to room temperature. The production was dissolved in 10 mL of DMF, passing through an alumina column to remove the Cu complex. 100 mL of distilled water was poured into the solution to precipitate PS-*b*-P4VP, which was dried at 80 °C under vacuum for 48 h.

POAA homopolymer was prepared by solution polymerization in DMF. Into a reaction flask fitted with a mechanical stirrer and Ar inlet were charged 1.675 g of ODA and 30 g of DMF. Stirring was begun, and after the ODA has dissolved, 1.861 g of PMDA powder was added gradually to the stirring solution of the diamine over 40 min. The reaction mixture was reacted at 0 °C for 24 h in Ar atmosphere to yield a viscous poly(4,4′-oxydiphenylenepyromellitamic acid) (POAA) solution.

The successful preparation of PS–Br, PS-*b*-P4VP and POAA were verified by FT-IR spectra and ^1H NMR spectra (Supplementary information). The composition and molecular weight distribution of PS-*b*-P4VP were characterized by ^1H NMR and GPC. The weight-averaged molar mass (M_w) of POAA and PS-*b*-P4VP were measured by static light scattering (Supplementary information). In this way, we determined $M_w(POAA)_{SLS} = 4.5 \times 10^4$, $M_w(PS\text{-}b\text{-}P4VP)_{SLS} = 4.8 \times 10^4$, $M_w/M_n(PS\text{-}b\text{-}P4VP)_{GPC} = 1.21$, and the composition of this diblock copolymer can be approximately formulated as PS_{102}-*b*-$P4VP_{162}$. The synthetic procedure of PS-*b*-P4VP and POAA are shown in Scheme 1.



Scheme 1. Synthetic procedure for PS-*b*-P4VP block copolymer and POAA homopolymer.

2.3. Preparation of the micellar complexes

The block copolymer PS-*b*-P4VP and POAA homopolymer was firstly dissolved in DMF respectively, then POAA/DMF solution was added dropwise into the copolymer solution to get a series of solutions with weight content of POAA in the mixture ranging from 0.2 to 0.7 and total polymer concentration being 3.0 g/mL. The mixture was stirred for more than 24 h at room temperature.

2.4. Dynamic light scattering (DLS)

The hydrodynamic diameter, D_h, of the micellar complexes were measured by dynamic light scattering (DLS). The experimental autocorrelation function, $g(t)$, is commonly expressed in the form of cumulant expansion:

$$g(t) = \exp\left[-\Gamma_1 t + \left(\frac{\Gamma_2}{2!}\right)t^2 - \left(\frac{\Gamma_3}{3!}\right)t^3 + \cdots\right]$$

Where Γ_i is the ith cumulant and $\Gamma_1 = Dq^2$, where D is the translation diffusion coefficient and q is the absolute value of the scattering vector. The diffusion coefficient is related to the hydrodynamic radius $\langle R_h \rangle$ by using the Stokes–Einstein equation:

$$R_h = \frac{k_B T}{6\pi\eta D}$$

Where k_B is the Boltamann constant and η is the viscosity of the solvent.

DLS experiments were conducted on a Malvern Zetasizer Nano ZS equipped with a He–Ne laser with a wavelength, λ, of 632.8 nm. The temperature was set to 25 °C and the angle of measurement was 173°. All the samples were diluted and filtered through 0.45 μm Millipore filters to remove dust before measurements.

2.5. Transmission electron microscopy (TEM)

The aggregate morphologies were visualized with a regular TEM. For transmission electron microscopy (TEM) measurements, droplets of solutions at a concentration of 0.3 mg/mL were dropped onto a copper grid with holey carbon film for a few minutes, DMF was allowed to evaporate from the grids at atmosphere pressure and room temperature, and finally dried in a vacuum. Iodine was employed as staining agent to selectively contrast POAA chains and P4VP blocks. The samples were placed in vapors of iodine crystals for 2 h at 35 °C. Bright-field TEM measurements were performed on a JEM 2010 transmission electron microscope operating at an accelerating voltage of 200 kV.

2.6. Nuclear magnetic resonance (NMR)

The ^{1}H NMR studies were carried out on a NMR instrument operating at 400 MHz and using DMF-d_7 as solvent.

2.7. Dynamic light scattering (DLS) with Eu^{3+} as a probe

DLS experiments were conducted on a Malvern Zetasizer Nano ZS. A solution of Eu^{3+}/DMF with Eu^{3+} concentration of 4.75×10^{-2} M was prepared by dissolving $EuCl_3 \cdot 6H_2O$ in DMF. During the experiment, Eu^{3+}/DMF solution was added dropwise into PS-*b*-P4VP/POAA/DMF solution, then the size of aggregates were measured directly. The total polymer content for each sample was kept the same.

3. Results and discussion

3.1. Formation of aggregates

When POAA/DMF was added dropwise into the DMF solution of PS-*b*-P4VP, the bluish hue appeared right away, which implies that the POAA chains have interacted with PS-*b*-P4VP diblocks by strong hydrogen-bonding to form aggregates. Fig. 1 shows the size distribution of POAA, PS-*b*-P4VP, and their solution blends in DMF with different POAA/PS-*b*-P4VP ratios. As is known, DMF is a good solvent for PS-*b*-P4VP and POAA, so pure PS-*b*-P4VP and POAA can dissolve in DMF molecularly with the average diameter, $\langle D_h \rangle$, of ~10 nm. When the block copolymer PS-*b*-P4VP and POAA homopolymer were mixed, the size distributions shifted to higher values, with $\langle D_h \rangle$ of ~100 nm, which indicated that larger aggregates formed. Since PS blocks have no specific interactions with POAA, and all the mixed solutions at different POAA/PS-*b*-P4VP ratio are optically transparent and stable, it is reasonable to consider that the insoluble POAA/P4VP complexes formed the core surrounded by soluble PS blocks as shell.

Fig. 2 shows that after the complexation, dilution had nearly no effect on $\langle D_h \rangle$ of the PS-*b*-P4VP/POAA (3:7 wt/wt) complex micelles in the range of 0.05–0.5 mg/mL. It implies that dilution exerts little influence on the spatial rearrangement of chains involved in complex aggregates, and the aggregates are kinetically frozen once the core–shell structures form. On the other hand, Fig. 3 reveals that for the solution blends of PS-*b*-P4VP and POAA prepared with different initial concentration but at a fixed ratio, the size of the complex aggregates decreased as the initial concentration decreased. From results of Fig. 2 and Fig. 3, it is clear that the complexation process is kinetically controlled and there is no

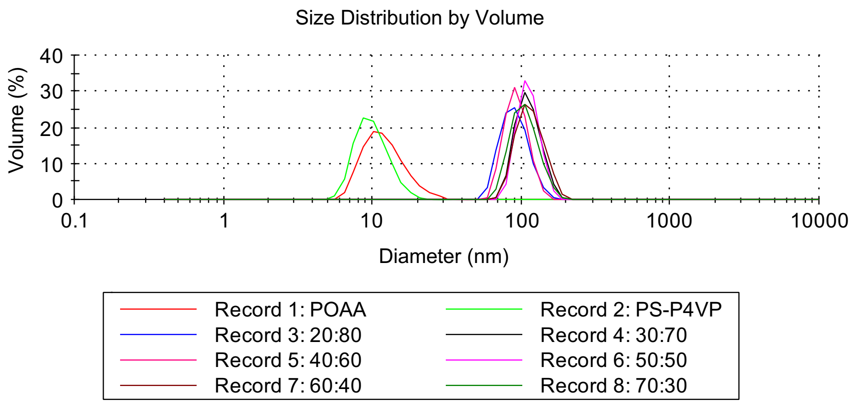


Fig. 1. Size distribution of POAA, PS-*b*-P4VP, and their solution blends in DMF with different ratio of POAA: PS-*b*-P4VP. The total polymer concentration is 3 mg/mL.

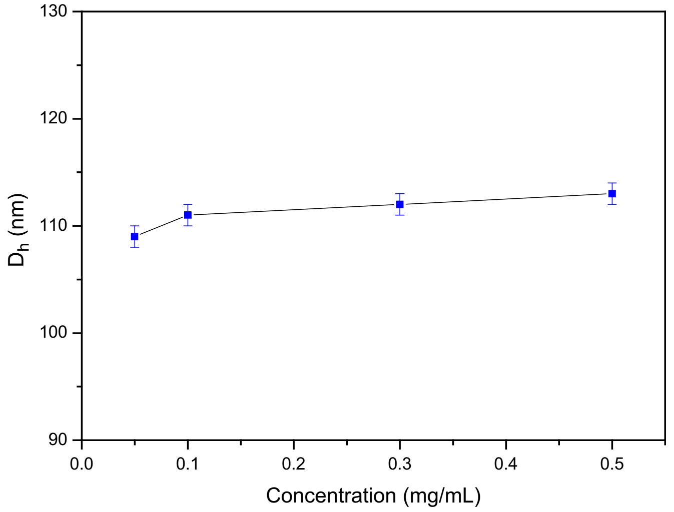


Fig. 2. Polymer concentration dependence of the average hydrodynamic diameter, $\langle D_h \rangle$ of PS-*b*-P4VP/POAA mixture solution at POAA % of 30%.

thermodynamic equilibrium between individual interchain complexes and the aggregates.

3.2. Solution behavior of aggregates in DMF

The aggregate solutions of PS-*b*-P4VP/POAA at different POAA/PS-*b*-P4VP weight ratios in DMF-d_7 were studied by ^{1}H NMR. The technique is a valuable tool to gain information about the aggregate structure [28]. For example, the signals assigned to solvated coronal chains should be clearly seen in the NMR spectrum, while the ones corresponding to the totally desolvated, solid-like, chains forming the core of the aggregate should vanish.

Fig. 4 shows the ^{1}H NMR spectra of PS-*b*-P4VP unimers and PS-*b*-P4VP/POAA solution blends at different POAA/PS-*b*-P4VP ratios in DMF-d_7. As we know, integration of a spectrum allows quantitative comparison of the numbers of different types of hydrogen, thus we can obtain the ratio of the number of H atoms (N_{P4VP}) associated with the P4VP blocks to that (N_{PS}) assigned to PS blocks by calculating as the following equation (1):

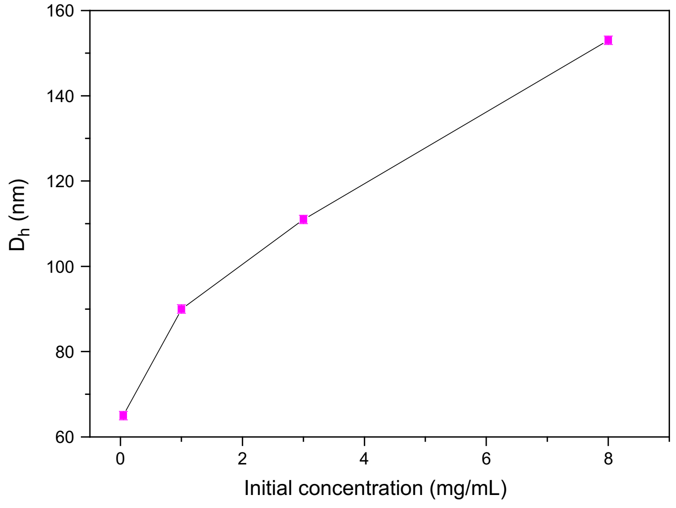


Fig. 3. Initial concentration dependence of the average hydrodynamic diameter, $\langle D_h \rangle$ of PS-*b*-P4VP/POAA mixture solution at POAA % of 30%. Before experiments, all the samples were diluted and the total polymer concentration was fixed at 0.05 mg/mL.

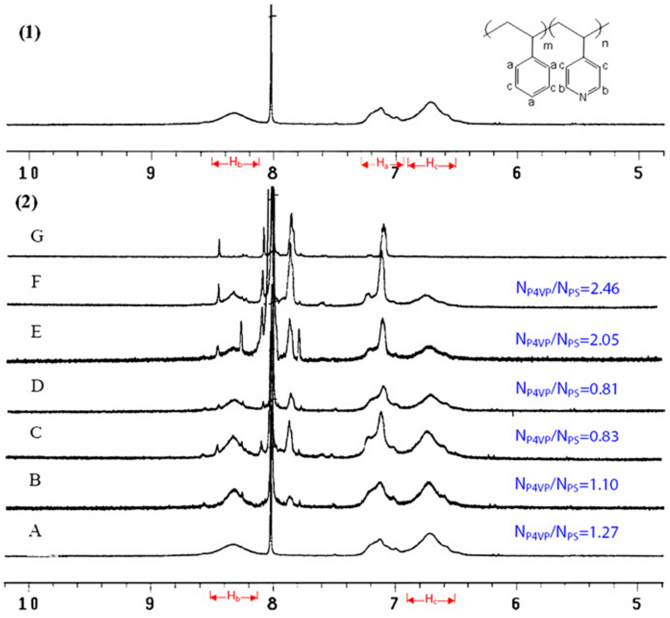


Fig. 4. ^{1}H NMR spectrum of (1) PS-*b*-P4VP unimers and (2) PS-*b*-P4VP/POAA complexes in DMF-d_7 at different ratio (PS-*b*-P4VP: POAA) values: A = ∞, B = 65:35, C = 55:45, D = 45:55, E = 40:60, F = 30:70, G = 0.

$$\frac{N_{\mathrm{P4VP}}}{N_{\mathrm{PS}}} = \frac{2H_b}{H_a + H_c - H_b} \tag{1}$$

Where H_a, H_b, H_c is integration area of different types of hydrogen (a, b, c respectively) assigned to PS-*b*-P4VP copolymer. According to Fig. 4(1), the correlation between H_b and H_a, H_c is expressed as: $H_a = 1.5 \times (H_c - H_b)$. Further, equation (1) can be described by the equation (2):

$$\frac{N_{\mathrm{P4VP}}}{N_{\mathrm{PS}}} = \frac{4H_b}{5(H_c - H_b)} \tag{2}$$

As discussed above, PS-*b*-P4VP copolymer is molecularly dissolved in DMF solution, which means that PS and P4VP blocks can move freely with total swelling by the solvent, so both the signals associated with benzene ring hydrogen for PS blocks and pyridine ring hydrogen for P4VP blocks can be detected. However, when PS-*b*-P4VP forms core–shell structure in solution, the intensity of signals for core and shell chains will be different, so the $N_{\mathrm{P4VP}}/N_{\mathrm{PS}}$ value will become higher or lower than that of pure PS-*b*-P4VP copolymer. In the present system, the addition of POAA into PS-*b*-P4VP/DMF solution induced the formation of core–shell aggregate structures, which made the $N_{\mathrm{P4VP}}/N_{\mathrm{PS}}$ value change. It should be noted that the signals of POAA overlap with that of PS-*b*-P4VP copolymer in some positions, i.e. $\delta = 8.46$, which must be deducted before calculating.

According to equation (2), the value of $N_{\mathrm{P4VP}}/N_{\mathrm{PS}}$ for PS-*b*-P4VP\POAA solution blends in DMF-d_7 at different ratios can be calculated (Fig. 4(2)). Before discussion, it should be noted that both the signals assigned to core-chain and shell-chain of all the aggregates at different POAA/PS-*b*-P4VP weight ratios can be detected, which indicates the resultant aggregates, especially the core of the aggregates are a little swollen in DMF [29]. When the weight content of POAA in mixture solution is less than 60%, the $N_{\mathrm{P4VP}}/N_{\mathrm{PS}}$ value is smaller than that of pure PS-*b*-P4VP in DMF-d_7 (1.27). It can be concluded that the core of the resultant aggregates should be formed by the P4VP/POAA complexes when POAA% is relatively low. Furthermore, with increasing POAA content in the mixture, the

N_{P4VP}/N_{PS} value decrease from 1.10 to 0.81, which reveals the aggregates induced by interpolymer complexation of P4VP/POAA become compact as more POAA chains are involved in the core–shell structure. However, when POAA% is above 60%, the value of N_{P4VP}/N_{PS} become higher than 1.27, indicating pyridine rings of P4VP blocks are more moveable than benzene rings of PS blocks. The abnormal N_{P4VP}/N_{PS} values are surprising and inconsistent with the core–shell structure discussed above.

To explore the reason for the higher N_{P4VP}/N_{PS} value for PS-*b*-P4VP\POAA solution blends at POAA% above 60%, Eu^{3+} was used as a probe to further study the core–shell structure of the aggregates. It is well known that Eu^{3+} can coordinate with ligand containing nitrogen or oxygen atoms strongly [30]. When Eu^{3+} was added to PS-*b*-P4VP/POAA/DMF micellar solution, it would coordinate with the carbonyl oxygen of the POAA and pyridine nitrogen of P4VP blocks. Since Eu^{3+} is relatively large (0.95 Å), it can attract more than six oxygen or nitrogen atoms, effectively cross-linking the chains through intra- and intermolecular coordination with the carbonyl oxygen of the POAA and pyridine nitrogen of P4VP blocks.

Fig. 5 shows the changes of $\langle D_h \rangle$ of aggregates from PS-*b*-P4VP/POAA mixture solution at POAA% of 30% and 60% with amount of added Eu^{3+}. For PS-*b*-P4VP/POAA mixture solution at POAA% of 30%, when 1×10^{-6} mol Eu^{3+} was added, D_h of aggregates decreased by ~10 nm, then the size of aggregates began to increase slowly with further addition of Eu^{3+}. When sufficient amount of Eu^{3+} was added, only slight change of D_h can be observed without agglomeration of aggregates (not shown in Fig. 5). It can be easily explained by the coordination of Eu^{3+} with P4VP blocks and POAA chains. Initially, the addition of small amount of Eu^{3+} compresses the core via cross-linking P4VP/POAA complexes, but when it saturates the coordination bond, excessive Eu^{3+} make the size of the aggregates increase. In the case of PS-*b*-P4VP/POAA mixture solution at POAA% of 60%, although small amount of Eu^{3+} also decrease the size of aggregates because of extrusion of DMF from core–shell structure for coordination interaction, agglomeration of aggregates was observed with sharp increase of D_h from ~100 nm to ~1000 nm when 4×10^{-6} mol of Eu^{3+} was added. Upon further addition of Eu^{3+}, obvious precipitation was observed.

TEM measurements was used to observe the aggregates morphology from PS-*b*-P4VP/POAA mixture solution at POAA% of 30% and 60% with addition of a small amount of Eu^{3+} as shown in Fig. 7. Eu^{3+} selectively absorbed in P4VP blocks and POAA chains can provide a good contrast in TEM images. For PS-*b*-P4VP/POAA mixture solution at POAA% of 30%, the aggregates show typical core–shell structure with P4VP/POAA complexes as core and soluble PS blocks as shell, which is in agreement with the result discussed above. The stable core–shell structure makes sure the addition of enough Eu^{3+} without agglomeration of aggregates due to the protection of PS shell chains (inset of Fig. 5). Fig. 7b shows the aggregates formed from PS-*b*-P4VP/POAA mixture solution at POAA% of 60%,. Differently from Fig. 7a, the aggregates contain a thin film, with a thickness of ~3 nm, coating on the surface. To avoid the influence of the added Eu^{3+} on the structure of the aggregates, the sample without addition of Eu^{3+} was placed in vapors of iodine to selectively stain P4VP and POAA chains for TEM measurement. As shown in Fig. 7d, in addition to a thin film coating on the surface, obvious core–shell structure was observed. Based on the results above, it is inferred that the thin film coating on the surface of the aggregates is a layer of POAA chains absorbed onto the initial core–shell structure. Hence, the aggregates formed by mixing PS-*b*-P4VP and POAA with POAA% of 60% consist of core–shell–corona structure with P4VP/POAA complexes as core, PS blocks as shell and a thin layer of POAA chains adsorbed on the surface. During addition of Eu^{3+} to the PS-*b*-P4VP/POAA mixture solution, coordination interaction between Eu^{3+} and POAA chains occurred on the surface of aggregates, and when enough Eu^{3+} ions were added, agglomeration of aggregates can be induced by coordination bonds of Eu^{3+} as “linking bridge” among different aggregates (inset of Fig. 5).

The same DLS experiments were also performed for other micellar solution at different weight content of POAA from 20% to 70% working at a fixed concentration of Eu^{3+} of 4×10^{-3} M. As shown in Fig. 6, before addition of Eu^{3+}, the D_h of aggregates for all the solution are ~100 nm. At a lower POAA weight content, the addition of 4×10^{-6} mol Eu^{3+} does not induce obvious changes of the D_h for the micellar solution, while the D_h apparently increases when the POAA% is above 60% in the micellar solution. The results demonstrate that core–shell structure forms at a lower POAA% less than 60%, while increasing weight content of POAA in mixture solution induces the generation of core–shell–corona structure. It should be pointed out that although obvious structural transition of aggregates occurs at POAA% of 60%, core–shell–corona aggregates coexist with core–shell ones at POAA% of 50%. The structural transition of aggregates with increasing POAA% in mixture solution

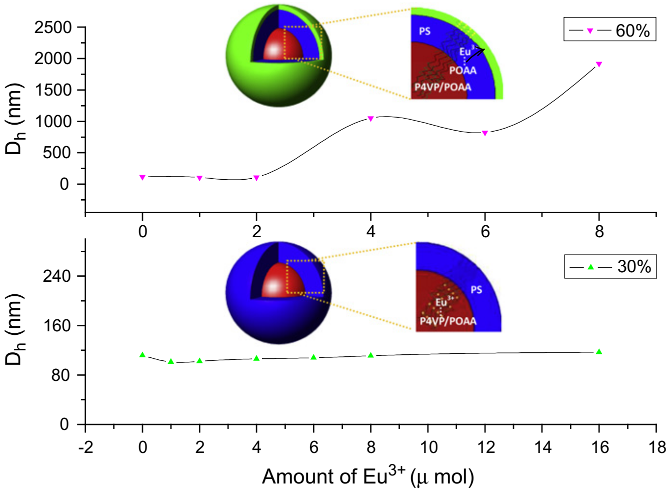


Fig. 5. Amount of added Eu^{3+} dependence of the average hydrodynamic diameter, $\langle D_h \rangle$ of PS-*b*-P4VP/POAA mixture solution at POAA% of 30% and 60%, where the total polymer concentration are both 0.3 mg/mL.

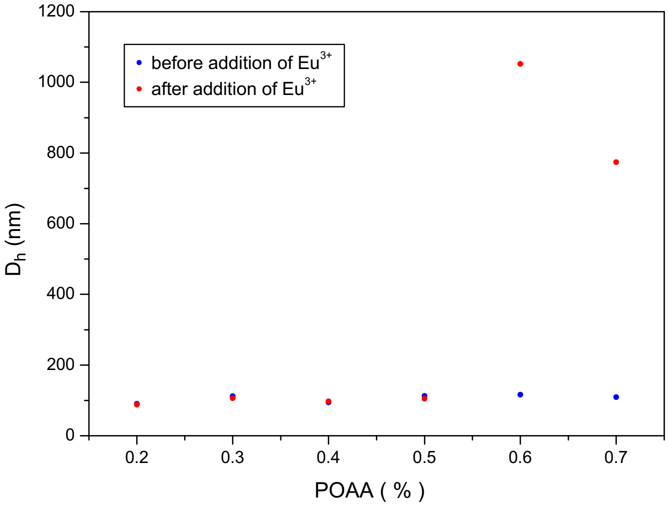
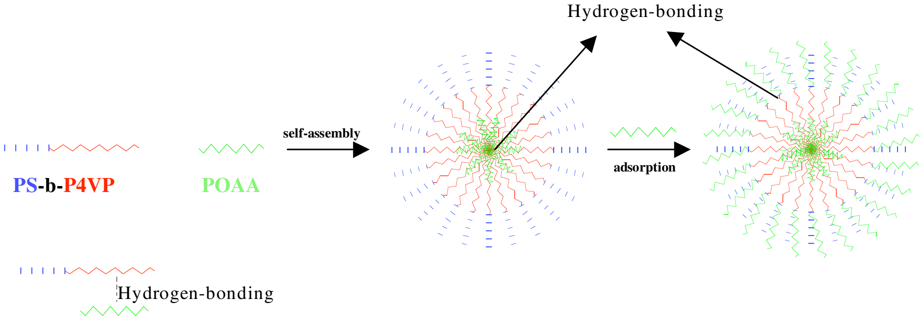


Fig. 6. The changes of average hydrodynamic diameter, $\langle D_h \rangle$ of PS-*b*-P4VP/POAA solution blends in DMF with weight fractions of POAA before and after the addition of Eu^{3+}. The total polymer concentration is 0.3 mg/mL, and the concentration of added Eu^{3+} is fixed at 4×10^{-3} M.



Scheme 2. Formation of core–shell–corona aggregates from the mixture of PS-*b*-P4VP block copolymer and POAA homopolymer via hydrogen-bonding.

is well consistent with the NMR results. For the stable core–shell structure, the value of N_{P4VP}/N_{PS} is smaller than that of pure PS-*b*-P4VP in DMF-d_7 owing to insoluble P4VP/POAA complexes, however, when core–shell–corona structure is formed, the adsorbed POAA chains are expected to penetrate into the shell of the aggregates and exclude solvent from the PS shell chains, leading to the increase of N_{P4VP}/N_{PS} value due to the weakness of the signals associated with PS blocks.

3.3. Possible formation mechanism of core–shell–corona structure

The coaggregation process of PS-*b*-P4VP block copolymer and POAA homopolymer and possible formation mechanism of the core–shell–corona structure are given in Scheme 2. When mixing PS-*b*-P4VP block copolymer and POAA homopolymer in DMF, strong interpolymer hydrogen-bonding between POAA chains and P4VP blocks induces the formation of stable core–shell structure with insoluble P4VP/POAA complexes as core and PS blocks as shell. When the weight content of POAA in mixture solution is above 60%, core–shell–corona aggregate with a layer of POAA chains absorbed onto the initial core–shell structure is formed.

The aggregates formed from PS-*b*-P4VP/POAA mixture solution with added Eu^{3+} at POAA% of 70% was examined by TEM as shown in Fig. 7c. A thin layer of POAA with the same thickness to that of aggregates from mixture solution at POAA% of 60% is observed. The independence of thickness of absorbed POAA layer on POAA weight content demonstrates POAA chains are inserted into the PS shell of the core–shell aggregates. Interestingly, an island-like outer layer as shown in Fig. 7c forms, which means that some POAA chains are

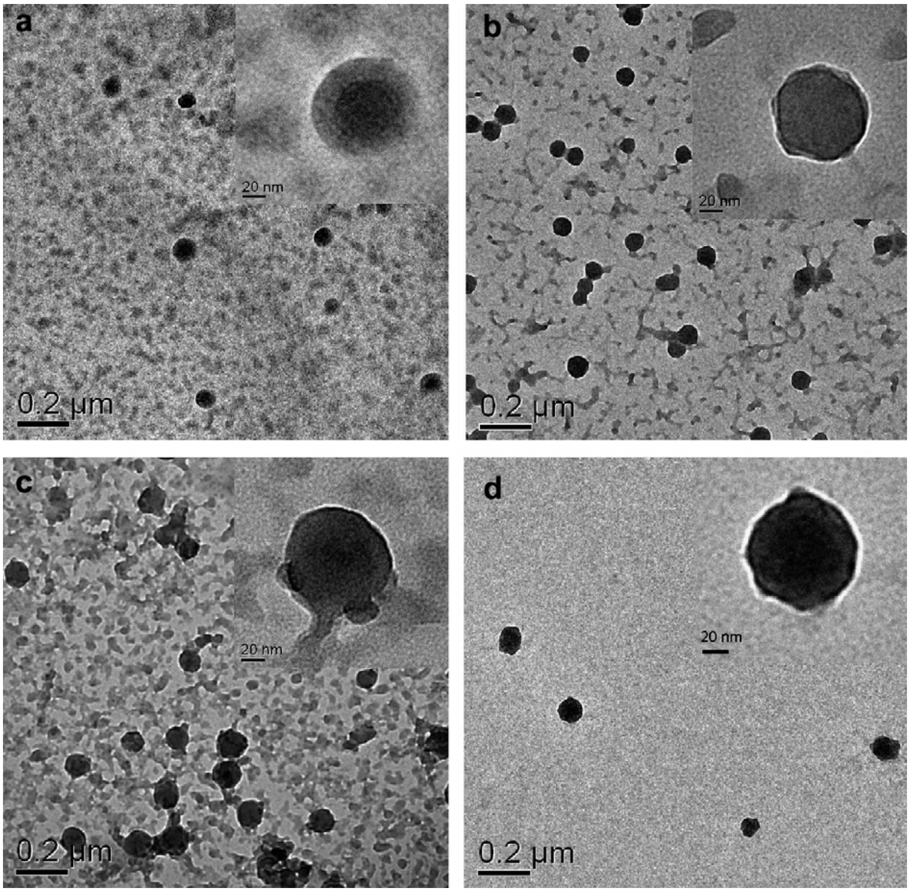


Fig. 7. TEM images of the aggregates formed from PS-*b*-P4VP/POAA mixture solution with added Eu^{3+} at different POAA weight fraction: (a) 30%; (b) 60%; (c) 70%. (d) TEM image of the aggregates formed from PS-*b*-P4VP/POAA mixture solution at POAA weight fraction of 60% after staining with iodine vapor.

adsorbed onto POAA corona component at a higher weight content of POAA in the mixture solution. The results here are quite similar to the adsorption of PNIPAM-*co*-P4VP onto core–shell PS-*co*-PMAA microspheres [31]. When an excess amount of POAA is further added, i.e. at 80% of POAA%, the POAA chains cannot be continuously adsorbed into the aggregates and remain as POAA unimers in DMF (DLS, not shown).

Usually, the driven force of adsorption or coating is due to the hydrogen-bonding [32], electrostatic affinity [33], covalent bonding [34], coordination bonding [35], hydrophilic and hydrophobic interaction [36] and a combination of these interactions between the colloid and the coating materials. Given that DMF is a good solvent for PS blocks and POAA homopolymer and there is no special interaction between them, it can be concluded that the adsorption of POAA is driven by hydrogen-bonding interactions between POAA chains and P4VP/POAA complexes. As discussed in NMR results, the resultant core–shell structure is swelled to a great degree, so POAA unimers can easily penetrate the swelled PS shell and interact with P4VP/POAA complexes by a strong hydrogen-bonding (Scheme 2). The inserted POAA chains press PS chains and extrude DMF from shell component, leading to a decrease of signal assigned to PS blocks during NMR measurements.

From a thermodynamic point of view, the formation of core–shell–corona structure is favorable. As we know, in micellar solution of block copolymer, the degree of stretching of the core-forming blocks is an important factor influencing the final morphologies of the micelles [37]. When a homopolymer is added into micellar solution from block copolymer, the incorporated homopolymer chains in core will increase the stretching of core-forming blocks, which, in turn, results in the decrease of conformational entropy and is thermodynamically unfavorable [38]. Considering the spherical aggregates formed from block copolymer, there are mainly two ways to relieve the thermodynamic disadvantage caused by the incorporation of homopolymer chains in the core of the aggregates. One is the accumulation of a small amount of homopolymer chains in the core centre without morphological changes, which effectively leads to a reduced chain stretching [38]; another involves the morphology transition from sphere to rod, where the low degree of core-chain stretching allows more chains to be incorporated into aggregates than spherical structure [39]. In our system, at POAA% of 60%, although we cannot exclude the possible existence of accumulation of POAA chains in the centre of PS-*b*-P4VP/POAA complex aggregates, the formation of core–shell–corona structure allow excessive POAA unimers inserted into the shell component, which could directly reduce the stretching of P4VP blocks.

4. Conclusions

Stable aggregates are formed when mixing POAA homopolymer and PS-*b*-P4VP block copolymer in DMF, due to complexation between POAA and P4VP block via interpolymer hydrogen-bonding. Dilution has nearly no effect on the size of aggregates, and the complexation is a diffusion-controlled process. Compared with typical amphiphilic block copolymer core–shell micelles, the resultant aggregates are much more swollen. At a lower weight content of POAA in mixture solution, the formed aggregates are core–shell spheres with the P4VP/POAA complexes as core and the PS blocks as shell, while a core–shell–corona structure formed with a thin layer of POAA chains adsorbed on the initial core–shell aggregates when the weight content of POAA increased to 60%. Since the formed core–shell structure is swelled to a great degree, POAA unimers can easily penetrate the swelled PS shell and interact with P4VP/POAA complexes by a strong hydrogen-bonding, leading to the formation of core–shell–corona structure.

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Appendix. Supplementary information

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.polymer.2009.09.028.

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