Charge Selective Encapsulation by Polymeric Micelles with Cationic, Anionic, or Zwitterionic Cores

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ABSTRACT: Polymeric micelles showing charge selective and pH-reversible encapsulation are reported. It is found that for a guest mixture of organic cationic–anionic dyes, a unimolecular micelle (PEI@PS) with a polystyrene (PS) as shell and a hyperbranched polyethylenimine (PEI) as core can exclusively entrap the anionic one; and a physical micelle consisting of brush-like macromolecule (mPS-PAA) with multi PS-b-polyacrylic acid (PAA) as grafts can exclusively entrap the cationic one. A covalent micelle (PEI-COOH@PS) bearing a zwitterionic core, that is, PEI covalently derived with dense carboxylic acids, can undergo highly pH-switchable charge selective and pH-reversible encapsulation. Both PEI@PS and mPS-PAA can be used for highly charge-selective separation of ionic dyes but the pH-reversibility of the encapsulation is relatively limited. In contrast, PEI-COOH@PS is less effective to differentiate the anionic–cationic dyes but is well recyclable. A physical micelle obtained from the self-assembly of PEI and mPS-PAA shows similar property to PEI-COOH@PS. The combination of these micelles in mixture separation can enhance the recyclability of the micelle and widen the spectrum of mixtures that can be well separated. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1342–1350, 2012

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INTRODUCTION The recognition (selective encapsulation) of common molecules by a polymeric host is evoking much interest now. It is known that traditional molecular recognition is exclusively promoted by specific interactions such as multiple hydrogen-bonding and topological trapping, but application of such a strategy is limited in two aspects. One is specific interaction is only available for a well-defined host which is rigorously tailored in size, morphology and electronic motif, and only a few cases allow the synthesis of such a host via a usually laborious route; the other is only a narrow spectrum of guest molecules which are topologically and electronically featured can be well recognized. For most common molecules, specific recognition remains a general challenge. Generally speaking, a polymeric micelle bears irregular and dynamic cavities in the core, thus rarely offers a topological selectivity, and most polymeric micelles show wide guest affinities with a few exceptions. In the early stage, high generation dendrimers showing size-selective encapsulation were found, where the selectivity stems from the congested periphery of these dendrimers. Hyperbranched polymers are now readily available for their large scale production but have rarely shown size selectivity upon guest encapsulation. However, it was recently found that with an appropriately crosslinked surface, a derivative of hyperbranched polymer could undergo size-selective encapsulation, where the crosslinking provided a relatively robust framework and the crosslinking degree offered a topological selectivity. More recently, a polymeric nanotube with a similarly crosslinked surface was proved to be highly selective upon extraction of topologically different neutral macromolecules or charge-different molecules.

Charge selective encapsulation have been used for separation, transport, delivery of small molecules, even for the separation of charge-different peptides. In this area, polymeric micelles derived from hyperbranched polymer play an important role due to its cost-effective production. Selective encapsulation of an ionic dye by a polymeric micelle oppositely charged in the core was recently reported by a number of research groups, and thus some anionic–cationic binary mixtures of dyes were well separated. However, experiments proved that many anionic–anionic binary mixtures of dyes can be separated as well by a cationic host,
indicating elementary interactions other than ionic bonding contribute greatly to the encapsulation too. 22–24 It was shown that a rational combination of the elementary interaction styles could lead to effective separation of very similar dyes, and this mechanism was termed supramolecular fuzzy recognition 32–34 based on Zadeh's theory of fuzzy recognition. 35 In previous work, it was shown that PEI-based, core–shell amphiphilic macromolecules (CAMs) could entrap anionic dyes rather than cationic ones. For example, a CAM could exclusively entrap the anionic methyl orange (MO) from a cationic methylene blue (MB), and at high pH, complete release of MO was found. 21 This pH-reversible encapsulation is related to the reversible protonation of the PEI amines, and such a recyclable property renders the CAM an ideal separating agent for certain mixtures. However, this strategy is proved to be effective only for limited guest species. It was later found that for many anionic dyes, especially those which are stiff or highly hydrophilic, encapsulation by a CAM fails; 24 and for some dyes, encapsulation is still feasible but pH-stimulated release is not or only partly available. Once again, the fact that a micelle under neutral state is reluctant to release an ionic guest suggests that host–guest interactions other than ionic–bonding play an important role in the encapsulation. With these limitations, the separation of many cationic–anionic mixtures becomes impossible. Here in this work, we show that a polymeric micelle with a negatively charged core can highly selectively entrap a cationic guest and leaving the anionic one intact, while that with a
positive core can exclusively entrap an anionic dye; for a micelle with a zwitterionic core, it is not favorable for mixture separation but showing pH-switchable charge selectivity and highly pH-reversible encapsulation. The combination of these micelles is much favorable for convenient separation of ionic mixtures.

RESULTS AND DISCUSSION

Synthesis

The chemical structures of the mPS-PAA, physical micelle of mPS-PAA/PEI, covalent micelle of PEI@PS and PEI-COOH@PS are outlined in Scheme 1. mPS-PAA is obtained via a previously reported process. PEI@PS [PEI_{232}@(PS_{21})_{35}, the nomenclature means 35 chains of polystyrene (with a polymerization degree of 21) are attached to one PEI which has 232 repeat units] is synthesized by alkylation of the amino groups of PEI with epoxy polystyrene via a similar process previously reported. PEI-COOH@PS was synthesized by treating PEI@PS in sequence with 2-hexadecyloxymethyloxirane and succinic anhydride, and the polymer was purified by dialysis. 1H NMR analysis showed that 0.2 eq. of 2-hexadecyloxymethyloxiranes were attached to one PEI, and molar mass increase indicated 0.6 eq. of succinic anhydride were attached to the PEI. 1H NMR of the resulting PEI-COOH@PS [PEI_{232}-(COOH)_{139}@(PS_{21})_{35}] is shown in Figure 1, which supports the expected structure. The physical micelle was prepared simply by mixing the respective chloroform solution of PEI and mPS-PAA.

Unimolecularity Versus Aggregate of the Micelle

The aggregation behavior of these micelles in apolar chloroform is studied by dynamic light scattering (DLS) technique. At very low concentration (10^{-5} M), scattering intensity is too low to obtain a data for PEI and neither is the physical micelle of mPS-PAA. At a higher concentration, data are available. Figure 2(A) shows that at 10^{-5} M, PEI exists as small aggregate in chloroform, with a diameter of D_h = 10.7 nm (single PEI showed D_h = 4.5 nm). 16 mPS-PAA also exists as aggregate with D_h = 19 nm, and the mixture of mPS-PAA/PEI (N: COOH = 1: 0.3) shows a monomodal size trace with D_h = 22.7 nm, which should be an aggregate with multiple core. It was previously proved that an aliphatic acid such as lauric acid and PEI could self assemble into a supramolecular micelle due to the acid–base interaction, and the resulting micelle could transfer anionic, water-soluble dyes into apolar organic solvent. Here, a similar micelle maybe formed between mPS-PAA and PEI. DLS data [D_h = 10.7 nm within 1 x 10^{-6} to 5 x 10^{-6} M, as shown in Fig. 2(B)] suggests that the covalent micelle of PEI@PS exists as unimolecular micelle, further experiment shows that within this concentration range, MOs encapsulated by one PEI@PS remains the same: 8.0 MOs per PEI@PS, indicating that PEI@PS is a unimolecular micelle. But after the introduction of carboxyl groups, the micelle PEI-COOH@PS tends to exist as aggregate (D_h = 177.1 nm), perhaps due to the enhanced polarity of the core. If further saturated with dye of RB at pH 5.4, the size of the aggregate is further enhanced to D_h = 234.7 nm, obviously still as physical aggregate.

Charge Selective Encapsulation by mPS-PAA and PEI@PS

It is found that mPS-PAA is readily soluble in chloroform, and upon shaking with certain amount of aqueous cationic MB (Chart 1, 10^{-4} M in buffered water of pH = 7.4), the chloroform phase is colored while the aqueous phase becomes colorless, indicating the complete transfer of MB from the aqueous phase to the chloroform phase. The encapsulating capacity is measured to be about 14 MB per molecule of mPS-PAA (COOH: MB = 18: 1), as measured in a
titration-like manner. In the absence of mPS-PAA, still trace MB can be detected in the chloroform phase, only when the concentration of MB is reduced to below $10^{-6}$ M, no MB is detectable in the organic phase. The concentration-dependent organosolubility of MB is perhaps related to its dimerization.\(^{40}\) It is found that mPS-PtBA [PtBA: poly(tert-butyl acrylate)], the precursor of mPS-PAA before hydrolysis, can hardly transfer any MB, supporting that the transfer is due to the carboxylic acid groups populated in mPS-PAA. UV-vis measurement shows that after being transferred to the organic phase, MB shows a spectral blue shift from 664 to 651 nm [Fig. 3(A)], further supporting the encapsulation of MB by mPS-PAA. Further test with similar cationic dye of azure I [Fig. 3(B)] and azure A [Fig. 3(C)] shows spectral blue shift too. Moreover, changes in spectral feature are observed as well, which may be related to the dimerization of these dyes.

When any of the anionic dyes shown in Chart 1 is used in place of MB, no transfer by mPS-PAA is observed even in the presence of excess mPS-PAA, indicating the encapsulation is highly charge selective. With our continuous efforts in mixture separation,\(^{21-24,32-34}\) we want to know whether this charge selective property can be used for separation of organic anionic-cationic dyes. In an experiment, aqueous anionic EB and cationic MB is mixed ([positive charge] = [negative charge]), and the mixture is shaken with pure chloroform (equal volume). Strangely, though EB alone is insoluble in chloroform and MB is very slightly soluble in chloroform, their mixture becomes considerably soluble in chloroform, as shown in Figure 4. In further test, the anionic EB is replaced with EY, TCFR, MO, and FA for similar test, and all the binary anionic–cationic mixtures are more or less organosoluble (Fig. 4), though none of these anionic dyes alone is soluble in chloroform. It is also found that an anionic-anionic mixture or a cationic–cationic mixture shown in Chart 1 is hardly soluble in chloroform. Therefore, the organosolubility should be due to the ionic neutralization (complexation) between the oppositely charged dyes. Experiments prove that if the concentration of the dyes is reduced to below $10^{-6}$ M, organosolubility is greatly reduced or no longer detectable. Regardless of the fact that complexation between the cationic dye and the anionic dye results in greatly enhanced organosolubility, upon the addition of mPS-PAA, the cationic MB migrates to the organic phase while the anionic dye migrates to the aqueous phase. When certain amount of mPS-PAA is reached, the anionic dyes completely reside in the aqueous phase and no MB is detectable in this phase, that is, completely charge selective separation is realized. The separation efficiency is detected by UV-vis measurement. As shown in Figure 4, the featured spectral peak of MB hardly overlaps that of the anionic dyes in the aqueous phase, so the detection is convenient (attention! The separating efficiency is only well detectable from the aqueous phase). The separation is available in a wide pH range at least within 5.4–9.4. In the above tests, if MB is replaced by

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**FIGURE 2** A: DLS data of PEI ($2 \times 10^{-5}$ M), mPS-PAA ($0.24 \times 10^{-5}$ M), and their mixture mPS-PAA/PEI ($1 \times 10^{-5}$ M, [COOH]/[N] = 0.3) in chloroform. B: DLS data of PEI@PS ($5 \times 10^{-6}$ M), PEI-COOH@PS ($5 \times 10^{-6}$ M), and PEI-COOH@PS saturated with RB ($5 \times 10^{-6}$ M, pH 5.4) in chloroform. Condition: pH 7.4 unless stated otherwise.

**CHART 1** Chemical structures of several organic water-soluble dyes.
It was previously shown that a CAM with PEI as core and dodecyl or hexadecyl as shell usually existed as aggregate and could entrap anionic dyes. Here, PEI@PS is found to exist as unimolecular micelle but also can entrap such anionic dyes as MO, TCFR, RB, EB, and EY but cannot entrap CR and FA. Moreover, PEI@PS shows highly charge selective encapsulation too, when any of the anionic MO, TCFR, RB, EB, EY is mixed with MB, azure I or azure A in water, PEI@PS in chloroform can exclusively extract the anionic one and leads to 100% separation from the cationic one, as detected by UV-vis via a method described previously. The encapsulation of MO and TCFR is completely pH-reversible, but for RB, EB, and EY it is only partly reversible. In case of FA/MB or CR/MB, no separation is possible by PEI@PS, only mPS-PAA can separate them.

**pH-Switchable Charge Selectivity and pH-Reversible Encapsulation by PEI-COOH@PS and mPS-PAA/PEI**

It is found that within the pH range of 3–11, mPS-PAA never entrap any of the anionic dyes listed in Chart 1, and PEI@PS never entrap the cationic dyes but can entrap most of the anionic species. Regardless of the high charge selectivity, mPS-PAA and PEI@PS are limited in recyclability, that is, upon the pH change, sufficient release of the encapsulated guest is not possible for certain guest species. In this aspect, PEI-COOH@PS appears to be unique. In an experiment for single dye transfer, it is found at low pH, PEI-COOH@PS resembles PEI@PS and can entrap anionic dyes; at high pH, PEI-COOH@PS resembles mPS-PAA and can encapsulate the cationic dyes. As far as we know, PEI-COOH@PS is the first polymeric host that can undergo pH-switchable charge selective encapsulation. This property should be related to the protein-like core of PEI-COOH@PS, which exists as anionic at high pH and as cationic at low pH. Interestingly, the encapsulation of some dyes by PEI-COOH@PS shows a process-dependent behavior. If PEI-COOH@PS is fully deprotonated at pH 11 before exposure to the guest CR, CR can’t be encapsulated; while if PEI-COOH@PS is fully exposed to CR at pH 7, CR is encapsulated, and with the pH switched to 11, no release is found at least within the tested time of one week. This behavior indicates the encapsulation of CR is a kinetic-controlled process, not a thermodynamic-controlled process. It is known that CR is a rigid, relatively large molecule, so its release may require considerable conformation change of the host. RB, EB, and EY show a similar behavior to CR but the release is observed within several days. For TCFR and MO, it appears to be mainly a thermodynamic-controlled process.

Strangely, PEI-COOH@PS is not a good charge-selective agent. It is found that at pH 11 (buffered water), PEI-COOH@PS can hardly entrap any RB, but in the presence of MB, a small amount of RBs are entrapped along with major MBs, indicating a synergic encapsulation exists. And at pH 4, minor MBs are encapsulated along with the major RBs. Similar phenomena were found for EY, TCFR and MO, therefore, PEI-COOH@PS is not ideal for charge selective separation. The physical micelle of mPS-PAA/PEI resembles PEI-COOH@PS very much in guest encapsulating behavior.
The pH-responsive releasing ability of PEI-COOH@PS is greatly improved than PEI@PS and mPS-PAA. As shown in Figure 5(A), mPS-PAA can completely transfer the MB from aqueous phase to the organic phase at pH 9.4, the encapsulation is irreversible because washing the organic layer with fresh water leads to no detectable release of MB at this pH value, while when the pH is switched to 5.4, about 53.5% of the MB returns into the water phase, as measured by UV–vis spectra (data not shown). For PEI@PS, RB can be irreversibly transport to the organic phase at pH 5.4, and at pH 9.4, about 38.7% RB is released into the water phase. For the zwitterionic PEI-COOH@PS, either MB or RB can be encapsulated, depending on the pH value. At pH 9.4, MB can be irreversibly transport to the organic phase, and with the pH switching to 5.4, at least up to 95% of MB can be released (if the concentration of MB is lower, the release is almost 100%), much larger than that of mPS-PAA. RB is tested at pH 5.4 and can be irreversibly transported to the organic phase by PEI-COOH@PS, with the pH switched to 9.4, up to 91% of RB can be released, much higher than that in case of PEI@PS. It is worth to notice that when the pH is around 7.4, encapsulation of either RB or MB alone is found but are both reversible, that is, upon washing with fresh water, the guest can be completely released. Obviously, the combination of these micelles of PEI@PS, mPS-PAA, PEI-COOH@PS can greatly widen the spectrum of guest mixtures and also enhance the recycle of the micelles. For example, it is experimentally found that the aqueous MB/RB can be treated in sequence with chloroform solution of mPS-PAA (at pH 6–10) and PEI-COOH@PS (at pH < 8) and leads to complete decoloration of the water, and both mPS-PAA and PEI-COOH@PS can be recycled.

**EXPERIMENTAL**

**Materials**

PEI \( [M_n = 1 \times 10^4, M_w/M_n = 2.5, \text{degree of branch (DB)} = 60\%] \) was purchased from Aldrich. Rose Bengal (RB), erythrosine B (EB), eosin Y (EY), tetrachlorofluorescein (TCFR, Alfa Aesar), Fushion acid (FA), Methylene blue (MB), azure I, azure A, methyl orange (MO), and congo red (CR), all the chemicals were purchased from Sinopharm Chemical (China) unless stated otherwise. A buffer solution with pH 7.4 was prepared by mixing 2.2 g Na2HPO4, 0.1 g NaH2PO4, and 8.5 g NaCl with deionized water to form a 1000 mL solution; a buffer solution with pH 5.4 was prepared by mixing NaAc (0.2 M, 86 mL) with HAc (0.3 M, 14 mL); a buffer solution with pH 9.4 was prepared by mixing Na2CO3 (0.1 M, 20 mL) and NaHCO3 (0.1 M, 80 mL); and a buffer solution with pH 11 was prepared by mixing Na2CO3 (0.1 M, 9 mL) and NaHCO3 (0.1 M, 1 mL). 4-Glycidyloxy-2,2,6,6-tetramethyl-piperidine-1-oxyl (GTEMPO) was synthesized on literature.41

**Synthesis**

mPS-PAA (PMMA152-g-[PAA18-PS21]16: polymethyl methacrylate (PMMA) with 16 grafts, where each graft was a block copolymer of polyacrylic acid (PAA) with a polymerization degree of 18 and polystyrene (PS) with a polymerization degree of 21) was synthesized exactly as previously
reported. Physical micelle of mPS-PAA/PEI was prepared in a typical way as follows, for COOH/N = 0.3, a solution of PEI (2 mL, 2 \times 10^{-6} M, [N] = 4.64 \times 10^{-4} M) in chloroform and a solution of mPS-PAA (2 mL, 0.24 \times 10^{-6} M, [COOH] = 1.4 \times 10^{-3} M) in chloroform were mixed to form a solution with [mPS-PAA/PEI] = 1 \times 10^{-6} M. 4-glycidyl-2,2,6,6-tetramethylpiperidine-1-oxyl-PS (epoxy PS) was synthesized as follows. A mixture of GTEMPO (0.54 g, 2.368 mmol), AIBN (0.233 g, 1.4 mmol), styrene (7.4 g, 71 mmol) was degassed by bubbling with nitrogen for 15 min, sealed, heated at 70 °C for 2 h, followed by heating at 125 °C for 40 h. The polymer was recovered by dilution with chloroform and precipitation in ethanol, purification was carried out by repeated dissolving in chloroform and precipitating in ethanol (95%), and finally dried in vacuum oven at 60 °C for 12 h. 5.66 g (71%) white powder was obtained. $M_n$ (GPC) = 2250, $M_w/M_n = 1.25$.

PEI@PS with a structure of PEI$_{232}$(PS$_{21}$)$_{35}$ (nomenclature: 35 chains of polystyrene with polymerization degree of 21 were attached to one PEI, which had 232 equivalent repeat units) was prepared by alkylation of PEI with epoxy PS: a solution of PEI (0.04 g, 0.93 mmol eq. repeat of CH$_2$CH$_2$NH), epoxy PS (0.31 g) in DMF (1.5 mL) was stirred at room temperature for 11 days. The polymer was recovered by precipitating in ethanol (95%) and purified by repeated dissolving in chloroform and precipitating in ethanol, and finally dried in vacuum oven at 60 °C for 12 h. A quantitative yield was obtained. $^1$H NMR (CDCl$_3$, δ/ppm): 6.8–7.4 (2205 H), 6.2–6.8 (1470 H), 1.1–2.4 (2205 H), 2.4–4.5 (1410 H). The chains of PS attached to one PEI polymer could be calculated by the equation: $(1160 \times l_{1.1-2.4}/l_{2.4-4.5})/(637 \times l_{1.1-2.4}/l_{2.4-4.5})$. $M_n$ (cald) = 88750; $M_n$ (GPC) = 32.5 \times 10^4, $M_w / M_n = 1.55$.

**PEI-COOH@PS**

In Step 1, to a solution of PEI@PS (8.35 g, 0.094 mmol) in chloroform (50 mL), 2-hexadecyloxymethyloxirane (2.41 g, 8.1 mmol) was added and the solution was stirred for another 3 days. The solution was dialyzed against chloroform (Dialysis tube: Spectro/Por, MWCO 2000) for 2 days. After removing the chloroform, 9.6 g white polymer was obtained. $^1$H NMR (CDCl$_3$, δ/ppm): 6.8–7.4 (2205 H), 6.2–6.8 (1470 H), 1.1–2.4 (3420 H), 0.8–1.0 (560 H), 2.4–4.5 (1730 H). The number of hexadecyl chains introduced onto one PEI@PS could be calculated by this equation: 490 × $(I_{0.8-1.0/I_{2.4-4.5}})$–140, where $I_{0.8-1.0/I_{2.4-4.5}}$ represented the signal intensity between 0.8 and 1.1 ppm, and $I_{2.4-4.5}$ represented the signal intensity between 2.4 and 6.8 ppm. $M_n$(cald) = 102,500.

In Step 2, to the above product (8.56 g, 0.084 mmol) in chloroform (50 mL), succinic anhydride (2.27 g, 22.7 mmol) and 4-N,N-dimethylaminopyridine (DMAP; 1.42 g, 11.6 mmol) was added and the solution was stirred for 2 days. The solution was dialyzed against ethanol followed by chloroform (Spectro/Por, MWCO 2000), each for 2 days. The residual solution was dried to yield 9.7 g white polymer. $^1$H NMR (CDCl$_3$, δ/ppm): 6.2–7.4 (3675 H), 0.8–1.0 (560 H), 1.1–2.4 (3980 H), 2.4–4.5 (1820 H). That no signal appeared at 8.20 ppm indicated that DMAP was completely removed. The number of succinic moieties introduced onto one polymer could be calculated from the increase of mass by: $(9.7–8.56)/(100 \times 60000)$ = 0.000084. A value derived from $^1$H NMR was much lower perhaps because the limited solubility of the quaternized core in chloroform.

**Measurements**

UV/vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments). $^1$H NMR spectra were recorded on Bruker (400 MHz) with TMS as a reference. Dynamic light scatterings (DLS) were recorded on Malvern Zetasizer Nano ZS90 equipped with a 4 mW He–Ne gas laser ($\lambda = 633$ nm), measurements were conducted at a fixed scattering angle of 90°, and molecular diameters were calculated from the computed diffusion coefficient using the Stokes–Einstein equation. The CONTIN analysis method was used. The number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) of epoxy PS were determined by gel permeation chromatography (GPC) using a Waters 150-C, calibrated with standard poly(styrene); eluent: chloroform; flow rate: 1 mL/min; sample concentration: 10 mg/mL; injection volume 200 μL. For PEI@PS, the measurement conditions are as follows, eluent: DMF + 100 mM
LiCl; flow rate: 1 mL/min; sample concentration: 10 mg/mL; injection volume 200 μL.

Ionic Mixture Separation

Typically, to a solution of aqueous EB/MB (5 × 10⁻⁵ M, 4 mL, MB: EB = 1:1 in molar ratio), mPS-PAA (5 × 10⁻⁶ M) in chloroform was added. The resulting mixture was subjected to rigorous shaking and followed by long standing, and the addition was continued until no MB is detectable in the aqueous phase. When MB is completely transferred, the EB in either phase is detected by UV–vis spectroscopy and compared with the initial concentration.

Encapsulating Capacity

To learn whether a micelle exists as aggregate or as unimolecular micelle, the dependence of encapsulating capacity on concentration of the micelle was measured, where a linear relationship generally means that a unimolecular micelle exists exclusively. A stock solution of aqueous MO (5 × 10⁻³ M) was prepared, a micelle at a diversity of concentrations (10⁻⁵–10⁻⁸ M) was prepared and mixed with equal volume of the stock MO solution under vigorous shaking. After a phase balance was reached, the oil layer was separated and measured with A UV–vis spectrometer. The absorbance data were plotted against the micelle concentration, where a linear relationship suggests that unimolecular micelle existed exclusively, while a nonlinear one suggests the existence or coexistence of aggregate.

CONCLUSIONS

The covalent micelle of PEI@PS can exclusively entrap anionic dyes due to the protonated amino groups, whereas the physical micelle of mPS-PAA can exclusively entrap cationic dyes due to the dense carboxylate groups. The highly charge selective encapsulation can be used for very effective separation of ionic dyes, and the pH-reversibility is partly limited for some dye species. The covalent micelle of PEI-COOH@PS bearing a zwitterionic core shows a highly pH-switchable and pH-reversible encapsulation during liquid-liquid extraction, and this micelle is mainly useful for the reversible transport of single dye but is ineffective for charge selective separation. The appropriate combination of these micelles in mixture separation can greatly enhance the recyclability of the micelle and also greatly widen the spectrum of mixtures that can be well separated.

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