*Chinese Journal of Polymer Science Vol. 30, No. 1, (2012), 63−71*

***Chinese Journal of Polymer Science***
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2012

# ASSOCIATION BEHAVIOR OF PORPHYRIN PENDANTS IN pH-SENSITIVE WATER-SOLUBLE POLYMER

Ke-wei Ding[a, b], Fei Wang[a, b] and Fei-peng Wu[a*]
[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China,*
[b] *Graduate University of Chinese Academy of Sciences, Beijing 100049, China*

**Abstract** A novel tripyridylporphyrin monomer, 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-l0,l5,20-tris(4-pyridyl)porphyrin (TrPyP), was synthesized and polymerized with acrylamide (AM) to prepare the hydrophobically associating water-soluble polymer PAM-TrPyP. The aggregation behavior of porphyrin pendants was investigated by UV-Visible and fluorescence spectra. The polymer displays a strong tendency of hydrophobic association even in dilute solutions. With increasing the concentration, the maximum absorption wavelength of Soret band changes from 416 nm to 407 nm, and the fluorescence corrected for the inner filter effect exhibits moderate concentration quenching. All the results indicate that π-π interaction of porphyrin pendants plays a key role in association of PAM-TrPyP, and H-aggregates of porphyrins are mainly formed in the concentrated solution. On the other hand, dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to follow the changes in size and structure of the macromolecular assemblies with the concentration increase. The polymer aggregation conformation changes from loose "vesicle-like" morphology to solid globule accordingly. When pH value of solution decreases to 4.3, pyridine moieties on porphyrin pendants could be protonated and the H-aggregates formed in macromolecular matrix are destroyed by electrostatic repulsion interactions.

**Keywords:** Porphyrin; Water-soluble polymer; π-π Interactions; H-aggregate; pH-sensitivity.

## INTRODUCTION

Porphyrin assemblies are of fundamental importance in supramolecular science since they are used not only as building blocks for the construction of functional molecular devices, but also to mimic the natural systems[1, 2]. The π-π interactions in aromatic systems are ubiquitous in the fields of chemistry and biology and play an important role in supramolecular science. Porphyrins have a well-extended π-conjugated system and are expected to form H-aggregates through strong intramolecular π-π interactions[3]. Porphyrin H-aggregates have potential advantages for unidirectional transport of excitation energy and electric charge along the axis of molecular stacking, which play crucial roles in electronic devices, for example, organic solar cell.

More and more porphyrin architectures with well-defined structure and ingenious function are self-assembled in organic solvents, but these media are largely different from the microenvironment in nature. In living systems, water is not only the universal solvent, but also acts as a surrounding medium for lots of biological macromolecules[4]. Meanwhile, it is an effective pH buffer and a reactant in some biological reactions, such as photosynthesis. For future application water is also a cheap and harmless solvent. Recently, a large body of investigation has been devoted to porphyrin aggregates induced by association in some heterogeneous systems like micelles[5, 6] formed by surfactants in aqueous environment. In addition, some polymer-linked porphyrins through either covalent bond[7] or electrostatic interaction[8] have been prepared to construct the

---

[*] Corresponding author: Fei-peng Wu (吴飞鹏), E-mail: fpwu@mail.ipc.ac.cn

Received January 26, 2011; Revised March 16, 2011; Accepted March 17, 2011
doi: 10.1007/s10118-012-1104-8

porphyrin assemblies. The modulation of aggregation behavior of porphyrins in these self-organized microphases by external conditions, for example, pH value, ionic strength and concentration, has attracted much attention.

Hydrophobically associating water-soluble polymer could provide another heterogeneous model to investigate the aggregation behavior of porphyrin pendants in aquatic environment[9]. The water-soluble polymer containing a small mole fraction of hydrophobic porphyrins can be considered as a kind of macromolecular surfactant. The porphyrin pendants self-associate in macromolecular matrix by some intermolecular interactions, and they also serve as endogenous probes to reveal detailed information about macromolecular assemblies due to their sensitive and plentiful spectroscopic properties.

A lot of polymers containing a small amount of porphyrin units as pendant groups have been studied[10–13], among which the derivatives of tetraphenylporphyrin were used most frequently. In this work, a novel tripyridylporphyrin monomer, 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin (TrPyP) (Fig. 1), was synthesized and polymerized with acrylamide to prepare water-soluble polymer containing a small mole fraction of porphyrins, which is abbreviated as PAM-TrPyP. The pyridyl groups make the aggregation of porphyrin pendants sensitive to the pH value of the media. The flexible spacer between rigid porphyrin groups and polymer backbone can alleviate steric hindrance and reduce the entropy loss in association of pendants[14]. UV-Vis absorption spectra, emission spectra, DLS and TEM were used to investigate the association behavior and morphology of polymer at various concentrations. The effects of π-π interactions among porphyrin rings and electrostatic repulsion interactions from pyridinium moieties on the self-association of porphyrin pendants were also discussed.

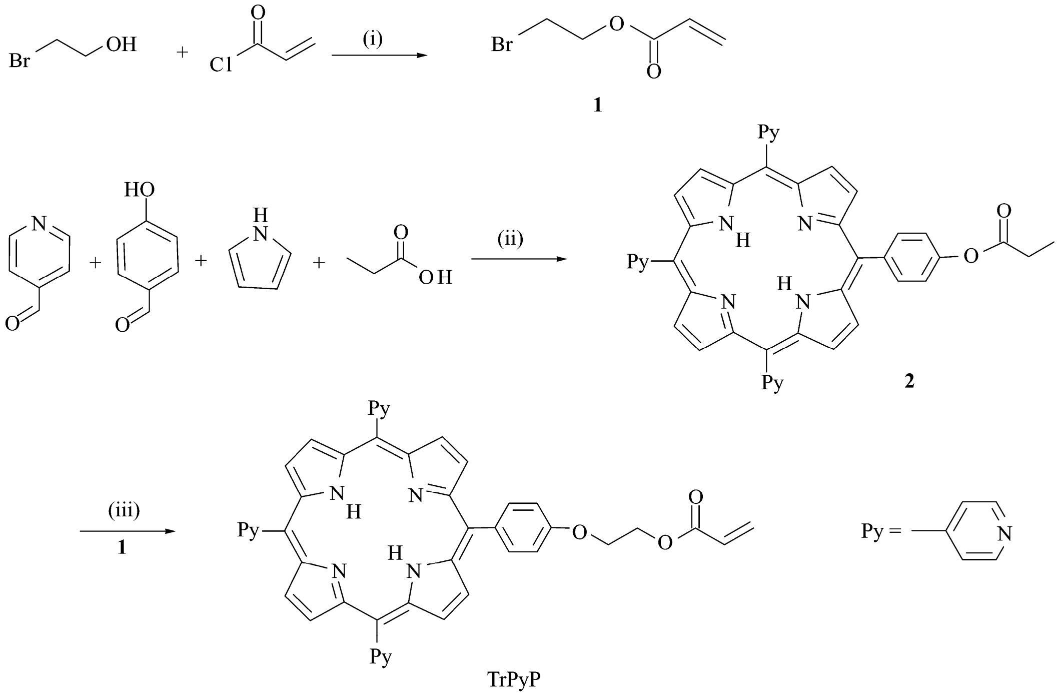

**Fig. 1** Preparation of porphyrin TrPyP, (i) $CH_2Cl_2$, TEA, 4 h, (ii) Propionic acid, $Ac_2O$, reflux, 3 h and (iii) DMF, NaOH, 3 h, rt

## EXPERIMENTAL

### *Materials*

All reagents not explicitly referenced were obtained from commercial sources and used as received. 2-Bromo-1-ethanol, pyridine-4-carboxaldehyde and acryloyl chloride were purchased from Alfa Aesar Company. Pyrrole was purchased from Sinopharm Chemical Reagent Co., Ltd and distilled before use. Acrylamide (AM) was purchased from Jiangxi Changjiu Biochemical Engineering Corporation. Acetic anhydride, *p*-hydroxybenzaldehyde, *n*-propanoic acid, triethylamine (TEA), 2,2′-azobis (isobutyronitrile) (AIBN)，pyridine, *N*,*N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), acetic acid and other A.R. grade reagents were obtained from Beijing Chemical Works. The aqueous solution was prepared by deionized water.

### *Synthesis of 2-Bromoethyl Acrylate (1)*

To a $CH_2Cl_2$ (25 mL) solution of 2-bromo-1-ethanol (4.25 mL, 60 mmol) and triethylamine (8 mL, 60 mmol), a $CH_2Cl_2$ (35 mL) solution of acryloyl chloride (4.9 mL, 60 mmol) was added dropwise at 0°C and then the reaction mixture was stirred at room temperature for 4 h. The white suspension (triethylamine hydrochlide) appeared in the reaction was filtered off and the light yellow filtrate was washed with water[15]. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure, which was then subjected to column chromatography ($SiO_2$, $CHCl_3$/hexane = 1:3) to give **1** as yellow oil (6.7 g, 62%). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 6.46 (dd, $J$ = 17.3, 1.3 Hz, 1H), 6.15 (dd, $J$ = 17.3, 10.5 Hz, 1H), 5.88 (dd, $J$ = 10.5, 1.3 Hz, 1H), 4.46 (t, $J$ = 6.2 Hz, 2H), 3.55 (t, $J$ = 6.2 Hz, 2H).

### *Synthesis of 5-[4-[(Ethylcarbonyl)oxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin (2)*

It was synthesized by a slightly modified Adler-Longo method[16] and confirmed by $^1$H-NMR and MS. MS (ESI) calcd for $M^+$ 689.2539, found 690.2640 (M + 1).

### *Synthesis of 5-[4-[2-(Acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin (TrPyP)*

To a solution of **2** (0.3 g, 0.43 mmol) in dry DMF (25 mL) under nitrogen was added powdered sodium hydroxide (0.09 g, 2.2 mmol), and the mixture was stirred at room temperature for about 1.5 h (the color of the solution changed from purple to green). Formation of the phenolate form of **2** was checked by TLC. The 2-bromoethyl acrylate (**1**) (0.42 g, 2.3 mmol) was added to the solution and the mixture was stirred for 3 h at room temperature. The pH of the reaction mixture was then adjusted to 7 with 1 mol/L HCl and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and the organic phase was washed twice with water, dried over $Na_2SO_4$, and evaporated to dryness. Products were purified by column chromatography on silica with $CH_2C1_2$ as the eluent and precipitated from a mixture of dichloromethane-hexane to give TrPyP as a purple solid (0.24 g, 75%). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 9.08 (dd, $J$ = 4.4, 1.5 Hz, 6H), 8.97 (d, $J$ = 4.7 Hz, 2H), 8.87 (s, 4H), 8.84 (d, $J$ = 4.8 Hz, 2H), 8.19 (dd, $J$ = 4.4, 1.5 Hz, 6H), 8.14 (d, $J$ = 8.6 Hz, 2H), 7.36 (d, $J$ = 8.6 Hz, 2H), 6.59 (dd, $J$ = 17.3, 1.4 Hz, 1H), 6.31 (dd, $J$ = 17.3, 10.4 Hz, 1H), 5.98 (dd, $J$ = 10.4, 1.4 Hz, 1H), 4.75 (t, $J$ = 6.1 Hz, 2H), 4.55 (t, $J$ = 6.1 Hz, 2H), –2.86 (s, 2H). MS (ESI) calcd for $M^+$ 731.2645, found 732.2731 (M + 1).

### *Preparation of Polymer PAM-TrPyP*

The 285.0 mg acrylamide (AM) and 14.5 mg TrPyP were poured into 10 mL DMSO, and the mixture was stirred at room temperature until they were dissolved. 6.0 mg AIBN was then added to the solution as initiator. The polymerization was performed in a sealed tube at 60°C for 24 h after purging with nitrogen for 20 min. After the polymerization, the resultant solution kept homogeneous and it was poured dropwise into 1 L acetone with stirring to precipitate the polymer. The precipitates formed in this process were filtered off and dried in vacuum at 45°C. The polymer was redissolved gradually in a little amount of $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent with stirring, and then precipitated again. The purification process was repeated several times until the porphyrin in filtrate could hardly detected by UV-Vis absorption spectrum, and IR band of C＝C bond (1636 $cm^{-1}$) of the unsaturated ester was not found in the IR spectra of polymer. 170 mg product was obtained (57% yield).

### *Measurements*

$^1$H-NMR spectrum was obtained on a Bruker DPX400 spectrometer. Mass spectrum was obtained on a Bruker APEX-IV. Static light scattering (SLS) measurement of polymer was performed *via* a Wyatt DAWN EOS. Dynamic light scattering (DLS) measurement was performed with a Wyatt DynaPro Nanostar at 25.0°C. FT-IR spectra were obtained from a Varian Excalibur 3100 infrared spectrometer in KBr disks. UV-Vis absorption spectrum was recorded with a Hitachi UV-3900 UV-Vis spectrophotometer. Fluorescence emission spectrum was performed on a Hitachi F-4500 fluorescence spectrophotometer. A 1 mm colorimetric ware was applied in the test of spectroscopic properties of the sample with high concentration. The morphologies were observed using a JEOL JEM-2100 transmission electron microscope (TEM) with an accelerating voltage of 200 kV and the samples were stained with saturated aqueous solution of uranyl acetate before observation.

## RESULTS AND DISCUSSION

### *Properties of Polymer PAM-TrPyP*

The synthesized porphyrin monomer TrPyP has a Soret band at 419 nm and Q bands at 515, 550, 590 and 645 nm (spectrum a in Fig. 2), which is similar to that of its precursor (**2**) (see Fig. 1). So the introduction of polymerizable unit has no influence on the absorption of the porphyrin ring. TrPyP exists as monomeric form in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent and obeys the Beer's law well, as shown in the inset of Fig. 2. The molar extinction coefficient ($\varepsilon_M$) of TrPyP at 419 nm is estimated to be $4.0 \times 10^6$ $mol^{-1}$ L $cm^{-1}$.

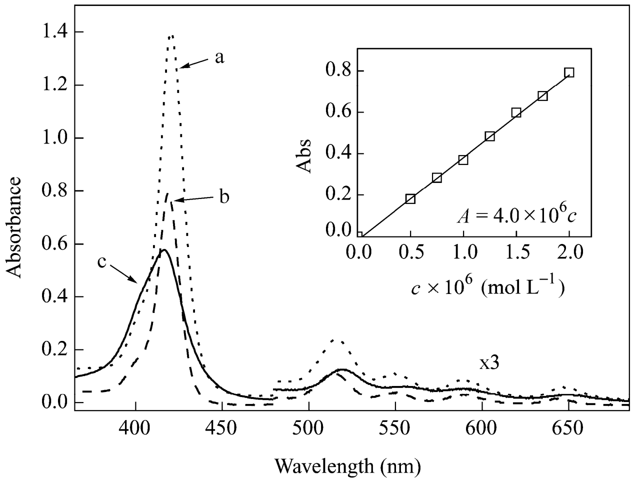

**Fig. 2** UV-Vis absorption spectra of the porphyrin monomer TrPyP and polymer PAM-TrPyP in different solvents: (a) TrPyP in $H_2O$-DMSO (1/9 *V*/*V*), (b) PAM-TrPyP in $H_2O$-DMSO (1/9 *V*/*V*), (c) PAM-TrPyP in water
Inset gives the plot of absorption of TrPyP at 419 nm versus concentration in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent.

The polymer PAM-TrPyP was prepared in DMSO by random copolymerization. It displays very similar UV-vis absorption spectrum to that of TrPyP in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent, indicating the radical polymerization has no additional effect on the porphyrin ring as reported[11]. The content of porphyrin units in the polymer is estimated from quantitative absorption spectra in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent setting $\varepsilon_M$ of TrPyP as a standard and the result is showed in Table 1. Compared to that in feed, the proportion of porphyrins in polymer is considerably small, which shows that the polymerization rate of the porphyrin monomer is much lower than that of AM. The lower polymerization rate may be ascribed to the steric repulsion of the porphyrin rings. The molecular weight of the polymer was also investigated by static light scattering (SLS) in water. The content of porphyrin units in the polymer PAM-TrPyP is very low and the polymer exhibits good solubility in water. The sequence distribution of porphyrin pendants in polymer is random.

**Table 1.** Polymerization of AM (M1) with TrPyP (M2)

| Polymer | In feed | | In polymer | | $M_w \times 10^{-4}$ |
|---|---|---|---|---|---|
| | [M1]+[M2], mol/L | [M1]:[M2] | [M2], wt% | [M1]:[M2] | |
| PAM-TrPyP | 0.4 | 200:1 | 2.3 | 433:1 | |

### Steady-state Absorption Spectra of PAM-TrPyP in Aqueous Solution

The porphyrins display strong hydrophobic property due to their macrocyclic structure, so the porphyrin pendants exhibit obvious association in dilute solution, in spite of very low content of porphyrins in the polymer. The spectrum c in Fig. 2 illustrates the steady-state absorption spectra of polymer PAM-TrPyP in dilute aqueous solution. Compared to that in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent (spectrum b), the baseline rises a little, and the Soret band is blue shifted and becomes much wider obviously (the half-band width changes from about 15 nm in line 2 to more than 35 nm in spectrum c). The above phenomena reflect that porphyrin pendants self-aggregate in aqueous solution as a result of the hydrophobic interaction, and the system becomes heterogeneous to some extent due to the formation of some small aggregates. Moreover, the broad Soret band originated from exciton coupling in loose hydrophobic microdomains suggests that the relative orientation of pendant porphyrins is close to random distribution. The hydrophobic association between porpyrins can be destroyed by DMSO, and PAM-TrPyP can dissolve thoroughly in $H_2O$-DMSO (1/9 *V*/*V*) mixed solvent.

Upon close examination of the absorption spectra of PAM-TrPyP in water as a function of concentration, a shoulder (407 nm) on the high-energy side of the Soret band is found and it gets higher and higher as shown in Fig. 3(a). Finally, the maximum absorption wavelength of Soret band changes from 416 nm to 407 nm. To observe this variable process clearly, Fig. 3(b) shows the absorption ratio of 407 nm over 416 nm as a function of concentration, which rises sharply at the beginning and then comes to a steady stage. The absorption ratio exceeds 1.0 at last. Different spectroscopic evidence indicates that different types of porphyrin aggregates coexist in hydrophobic microdomains. According to the Kasha's exciton theory[17], the blue shift of the maximum absorption wavelength of Soret band indicates that the proportion of H-aggregates increases as the concentration rises, and 407 nm can be safely assigned to the Soret band of these ground-state aggregates[18]. The tendency of the formation of face-to-face aggregate is due to the π-π stacking interactions of porphyrin rings, which act as a major driving force in aggregation in concentrated solutions.

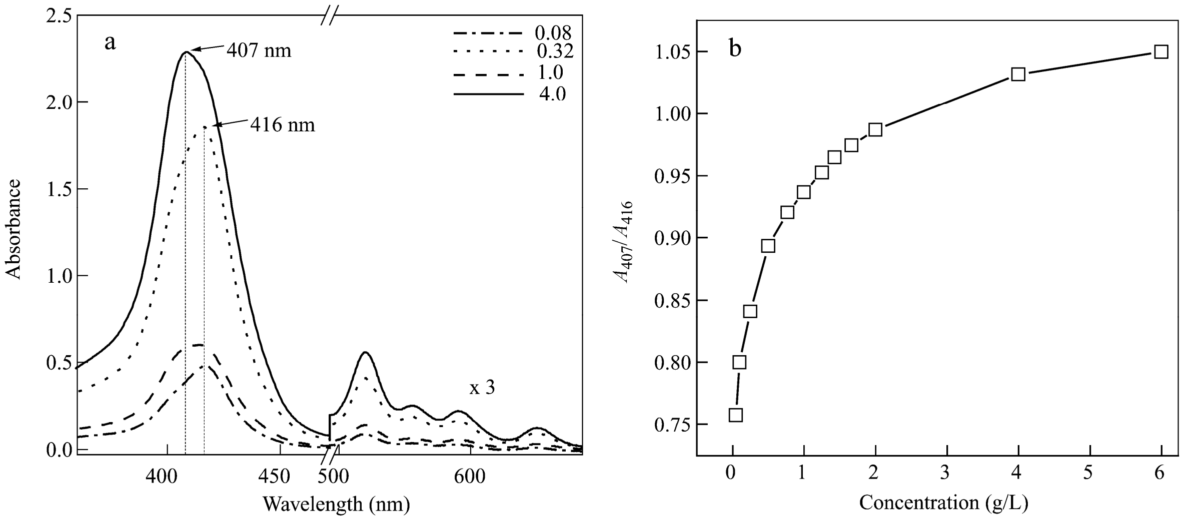

**Fig. 3** (a) UV-Vis absorption spectra of PAM-TrPyP in aqueous solutions of different concentrations (g/L) (The samples with the concentration 1.0 and 4.0 g/L were measured in 1 mm cuvette, while other samples were measured in 1 cm cuvette.); (b) The absorption ratio of 407 nm over 416 nm as a function of concentration

### Fluorescence Emission Spectra of PAM-TrPyP in Aqueous Solution

The fluorescence emission spectra of PAM-TrPyP also indicate the same process. Figure 4(a) shows the fluorescence emission spectra of PAM-TrPyP with different concentrations. The spectra were measured in 1 cm cuvette with excitation wavelength at 520 nm, and fluorescence intensity was obtained at 712 nm, where the copolymer had almost no absorption. All the samples were purged with nitrogen for 20 min before measurement. The samples also exhibited typical fluorescence spectra of free base porphyrin and no new emission band was found at long wavelength direction. So there was no evidence for the formation of excimer.

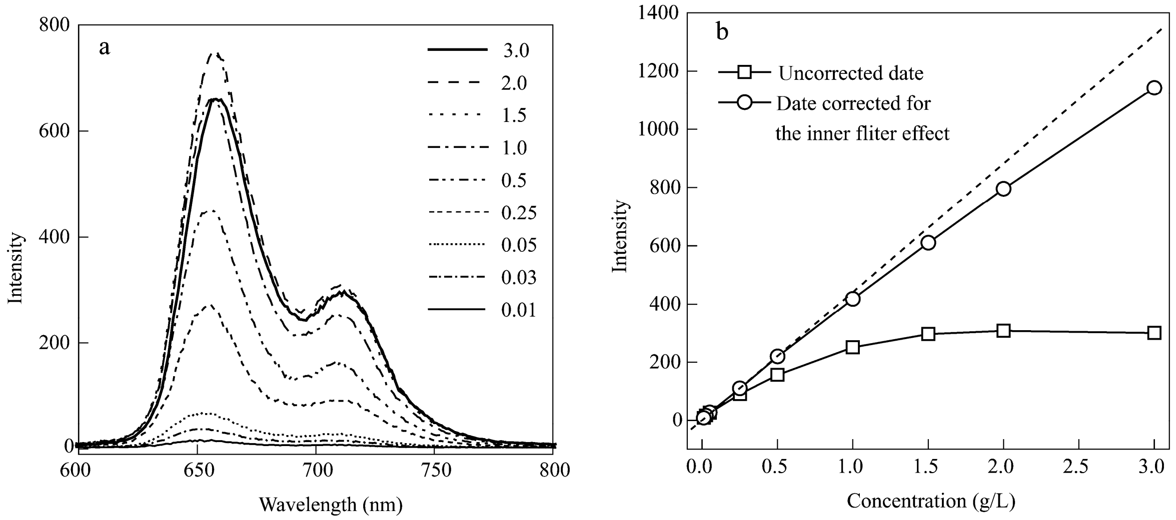

**Fig. 4** (a) Fluorescence emission spectra of PAM-TrPyP in aqueous solutions of different concentrations (g/L); (b) Fluorescence intensity at 712 nm versus concentration before and after correction for the inner filter effect

As it is well known, the recorded fluorescence intensity may not be proportional to the fluorophore concentration because of the inner filter effect. This is due to the high absorption of excitation light and reabsorption of emitted light by the sample. This effect can be roughly corrected with the following equation[19]:

$$I_{\text{real}} = I_{\text{measured}} \times 10^{A(\lambda_{\text{exc}})/2} \times 10^{A(\lambda_{\text{em}})/2} \tag{1}$$

where $A(\lambda_{\text{exc}})$ and $A(\lambda_{\text{em}})$ are absorption values of the sample at excitation and emission wavelength respectively, and $I_{\text{real}}$ is the corrected fluorescence intensity. Figure 4(b) shows the fluorescence intensity at various concentrations before and after correcting for the inner filter effect. It could be seen from this figure that the real emission intensity increases according to the increase of the concentration. The linear region at relatively low concentrations is assumed to be because of the presence of monomeric porphyrin only. However, the variety of fluorescence intensity shows obvious deviation from linearity at high concentrations. It means that the polymer PAM-TrPyP indeed displays the concentration quenching in aqueous solution. Considering the changes of Soret band in absorption spectra, the mechanism behind concentration quenching is the formation of H-type porphyrin aggregates. It is reported that the fluorescence quenching due to formation of H-aggregate is substantially weak[20], which coincides well with the little deviation of corrected intensity plot from linearity as shown in Fig. 4(b).

The above phenomenon also demonstrates that π-π interactions take effect in this process. So it is the long-range hydrophobic interactions impel the porphyrin pendants to move closer randomly, and then π-π interactions dominate the association and well-defined H-aggregates are formed mainly in hydrophobic microdomains.

### *Response of PAM-TrPyP to pH Values*

When the pyridyl groups are protonated, the porphyrin pendants contain both hydrophobic and hydrophilic moieties in the molecular architecture. It imparts them a high capacity of self-organization depending on the balance between repulsive and associative interactions. The aqueous solution of PAM-TrPyP with a concentration of 6.4 g/L was selected as substrate to study pH response of the polymer. In this case, the maximum absorption wavelength was located at 407 nm and therefore the H-aggregates were the main component. The pH value of the solution was adjusted from 7.0 to 3.6 by acetic acid, and the corresponding changes in absorption spectra are showed in Fig. 5. The maximum of Soret band changes to 422 nm finally because pyridine moieties are protonated. However, the porphyrin pendants still remain as the free base species throughout the process, which is certified by the characteristic four-band pattern in the Q-band region. The presence of isosbestic point at about 416 nm suggests the existence of the pH dependent equilibrium between protonated and non-protonated porphyrins in acidic solutions. The inset of Fig. 5 presents the absorbance at 407 and 422 nm as a function of pH values respectively. The decrement of absorbance at 407 nm indicates that the electrostatic repulsion interactions overcome the π-π associative interactions and therefore the H aggregates are destroyed drastically. The apparent pK of protonating pyridine moieties, determined by spectrophotometric titration, has a value of 4.3, which is found to be somewhat low. This is probably because that there is a pH gradient from bulk solution to hydrophobic microdomain where porphyrins are placed. The sharp change of absorbance in pH ranging from 4.6 to 3.8 makes the polymer has potential application as an optical pH sensor[21].

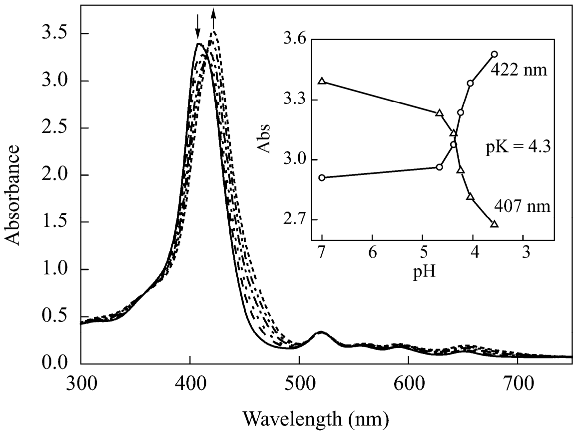

**Fig. 5** UV-Vis absorption spectra of PAM-TrPyP in aqueous solutions (6.4 g/L) with pH values decreased from 7.0 to 3.6
Inset gives the dependence of absorbance of the Soret band on the pH values.

### *Morphology of PAM-TrPyP*

Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to characterize the evolution of the geometrical parameters (the size and shape) of macromolecular assemblies both in solution (DLS) and in the solid-state (TEM), by evaporating the solvent. Figure 6 shows hydrodynamic radius ($R_H$) of macromolecular aggregates measured by DLS experiments in aqueous solutions of various concentrations. As shown in Fig. 6, two samples with low concentration (1.0 and 4.0 g/L) exhibit a unimodal size distribution and average $R_H$ of about 60 nm. However, the average $R_H$ value shifts to larger size greatly (about 251 nm) for the 15.0 g/L sample.

TEM experiments were also performed, and electron microphotographs of the PAM-TrPyP assemblies at different concentrations are showed in Fig. 7. At low concentration, they exhibit a regular vesicle-like morphology with a diameter of *ca*. 100 nm. When the concentration is up to 15.0 g/L, the aggregates are found to be solid globules with a diameter in the range of 200–500 nm, the size of which is increased obviously and becomes more polydisperse. The diameters ($2R_H$) obtained from the DLS measurements are slightly larger than those from TEM. This is possibly due to the fact that $R_H$ includes the contribution from associated water molecules whereas the radius obtained from TEM does not[22].

Hence dramatic increase of concentration made the morphology of macromolecular assemblies change obviously[23]. In view of the results discussed above, as the concentration of PAM-TrPyP increased, the approach between porphyrin pendants in hydrophobic microdomain becomes close enough. Consequently, the π-π interactions play a leading role in subsequent association and impel the porhyrins to form more compact aggregates as shown in Fig. 7(c).

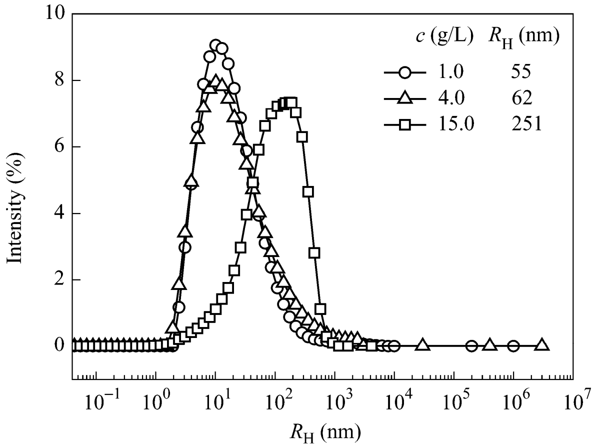

**Fig. 6** DLS size distribution functions for macromolecular assemblies in aqueous solutions of various concentrations

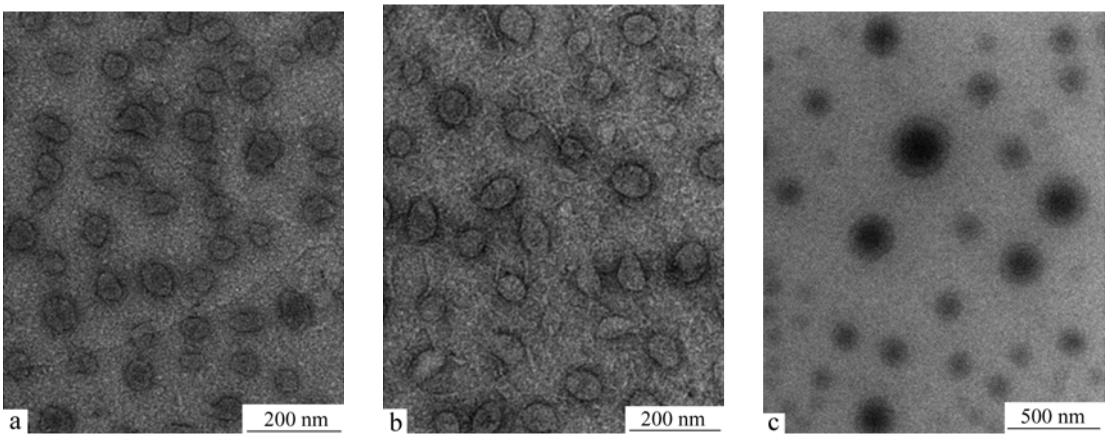

**Fig. 7** TEM micrographs of polymer aggregates for PAM-TrPyP at different concentrations: (a) 1.0 g/L, (b) 4.0 g/L and (c) 15.0 g/L

## CONCLUSIONS

A novel hydrophobically associating water-soluble polymer PAM-TrPyP was prepared to investigate the aggregation behavior of porphyrin pendants and driving forces in self-association. The porphyrin pendants associates randomly even in dilute solutions. The formation of H-aggregates is preferred in the process of increasing concentration. Accordingly, the morphologies of polymer change from loose pseudo-vesicle to compact globule. Therefore, π-π interactions of porphyrin pendants dominate the association in concentrated PAM-TrPyP solutions. In the acidic solution, electrostatic repulsion interactions could destroy the H-aggregates easily. Thus, porphyrin H-aggregates could form in macromolecular matrix in aquatic media and the H-aggregates could be modulated by the external conditions. The polymer PAM-TrPyP is a good scaffold for further research on photophysical properties of porphyrin aggregates in water.

## REFERENCES

1 Beletskaya, I., Tyurin, V.S., Tsivadze, A.Y., Guilard, R. and Stern, C., Chem. Rev., 2009, 109: 1659

2 Satake, A. and Kobuke, Y., Tetrahedron, 2005, 61: 13

3 Choi, M.S., Tetrahedron Lett., 2008, 49: 7050

4 Tait, M.J. and Franks, F., Nature, 1971, 230: 91

5 Gandini, S.C.M., Yushmanov, V.E., Borissevitch, I.E. and Tabak, M., Langmuir, 1999, 15: 6233

6 Scolaro, L.M., Donato, C., Castriciano, M., Romeo, A. and Romeo, R., Inorg. Chim. Acta, 2000, 300-302: 978

7 Iida, K., Nango, M., Matsuura, M., Yamaguchi, M., Sato, K., Tanaka, K., Akimoto, K., Yamashita, K., Tsuda, K. and Kurono Y., Langmuir, 1996, 12: 450

8 Li, J.B., An, Y.L., Chen, X., Xiong, D.A., Li, Y., Huang, N. and Shi, L.Q., Macromol. Rapid Commun, 2008, 29: 214

9 Morishima, Y., Chinese J. Polym. Sci., 2000, 18(4): 323

10 Nowakowska, M., Karewicz, A., Loukine, N. and Guillet, J.E., Polymer, 2002, 43: 2003

11 Kamachi, M., Cheng, X.S., Kida, T., Kajiwara, A., Shibasaka, M. and Nagata, S., Macromolecules, 1987, 20: 2665

12 Nowakowska, M., Karewicz, A., Kłos, M. and Zapotoczny, S., Macromolecules, 2003, 36: 4134

13 Wang, R.M., He, Y.F., Lei, Z.Q., Wang ,Y.P. and Li, S.B., Chinese J. Polym. Sci., 1998, 16(1): 91

14 Zhou, Q.F., Zhu, X.L. and Wen, Z.Q., Macromolecules, 1989, 22: 491

15 Malik, S., Kawano, S.-I., Fujita, N. and Shinkai, S., Tetrahedron, 2007, 63: 7326

16 Casas, C., Saint-Jalmes, B., Loup, C., Lacey, C.J. and Meunier, B., J. Org. Chem., 1993, 58: 2913

17 Kasha, M., Rawls, H.R. and El-Bayoumi, M.A., Pure Appl. Chem., 1965, 11: 371

18 Andrade, S.M., Teixeira, C., Togashi, D.M., Costa, S.M.B. and Sobral, A.J.F.N., J. Photochem. Photobiol., A, 2006, 178: 225

19 Stella, L., Capodilupo, A.L. and Bietti, M., Chem. Commun., 2008, (39): 4744

20 Zozulya, V.N., Ryazanova, O.A., Voloshin, I.M., Glamazda, A.Y. and Karachevtsev, V.A., J. Fluoresc., 2010, 20: 695

21 Thyagarajan, S., Leiding, T., Årsköld, S.P., Cheprakov, A.V. and Vinogradov, S.A., Inorg. Chem., 2010, 49: 9909

22 Yue, B.H., Huang, C.-Y., Nieh, M.-P., Glinka, C.J. and Katsaras, J., J. Phys. Chem. B, 2005, 109: 609

23 Kim, S.Y., Lee, K.E., Han, S.S. and Jeong, B., J. Phys. Chem. B, 2008, 112: 7420