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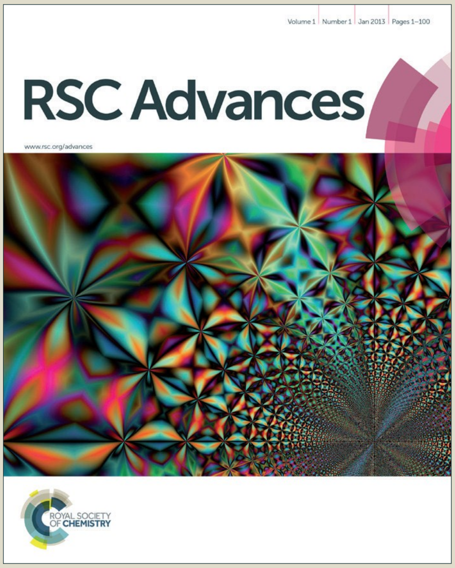

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Association Behaviors of Carbazole-Labeled Polyacrylamide in water Studied by Fluorescence Spectroscopy

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In this work association behaviors of a carbazole labeled hydrophobically modified polyacrylamide were studied by fluorescence spectroscopy in order to reveal the aggregation induced spectral features. Both emission and excitation spectra reveal three distinct regimes upon the association process of carbazole-labeled polyacrylamide with increase in concentration. In regime Ⅰ, there is only a linear relationship between fluorescence intensity and concentration which was ascribed to unimer regime without aggregation. While intense change in spectral shape could be observed in regime Ⅱand Ⅲ beyond the critical aggregation concentration. In regime Ⅱthere is an aggregation induced red shift in the excitation spectra and a decrease in 0-0 transition in emission spectra. In regime Ⅲ aggregation induced quenching was observed. These spectroscopy features of the excitation and emission spectra imply imply formation of disordered J-aggregates by carbazole unites during the association process, which could be employed to analysis the structural transition of hydrophobically modified polyacrylamide solution.

Introduction

Hydrophobically modified water-soluble polymer (HMWSP) is a kind of polymer with a small amount (<2%) of hydrophobic units introduced to the hydrophilic backbone, which is of great importance in industry such as food,[1] coatings[2] as well as enhanced oil recovery.[3,4] Its most important solution structure is associative networks resulting from the aggregation of hydrophobic unites, when the concentration is above a critical value.[5,6] Thus the association of HMWSP in water determines its performance in various applications. Due to the high viscosity of HMWSP solution, characterization of the association behaviours of HMWSPs in water is not easy as that for common block copolymer system because electron microscopy is limited by the difficulty in sample preparation. For this reason fluorescence spectroscopy becomes one of the most powerful tools to study the hydrophobic micro-domains according to either the sensitivity of chromophore to the polarity[7-9] or a diffusion controlled process-excimer formation.[7, 10-13] In most relevant researches pyrene and its analogues were adopted as labeled molecules because of its well-known fluorescence characteristics.[14] As to the emission spectrum of pyrene, the ratio I_I/I_3 of the intensities of the first and third vibronic peaks is a sensitive indicator of the polarity of the pyrene microenvironment, which was widely used to detect micelle formation resulted from change in pH,[7] concentration[9] and so forth. In addition relative excimer emission I_E/I_M has also been introduced to study the influence of polymer concentration[12-13] or surfactant[15] on the hydrophobic aggregates.

However multisteps synthesis was required on pyrene-labeled monomer design for such pyrene-labeled HMWSPs.[16-18] In order to simplify the synthesis a novel fluorescent label vinyl-carbazole might be employed. Since the HMWSPs could be labelled simply by copolymerization of such commercial monomer. Unfortunately those spectroscopy features in pyrene-labeled system could be hardly generalized to other system because the fluorescence characteristics of organic molecular aggregates varied from system to system. Quantum yields or detailed spectra might be influenced differently by aggregation process due to new excited species formation upon aggregation such as excimers[7] or different kinds of aggregates[8-11]. For instance aggregation usually induced quenching of fluorescence while aggregates of some non-emissive monomers could exhibit fluorescence with high quantum yields due to aggregation-restricted intramolecular rotation,[19] which is so-called aggregation induced emission phenomenon reported by Tang et al.[20-21] Although the interesting fluorescence of poly(N-vinylcarbazole) (PNVC) has attracted considerable attention for a long time,[22-28] fluorescence spectral signatures in association of carbazole unites were rarely reported. It could be found that two

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structured emission peaks transformed to a broad structureless band once the monomers were polymerized.[23-25] Such phenomenon has also been observed in several copolymers of N-vinylcarbazole (NVC) systems without detailed investigation on transition process.[26-28] So far all the carbazole containing copolymers studied were totally hydrophobic and the media was organic solvent named good solvent for carbazole units and to our known carbazole labelled HMWSPs haven't been reported. As a result little is known on the fluorescence characteristics of association behaviors of carbazole unite in water, which is of significance in fluorescence analysis for such new labelled system.

For this purpose a novel labelled HMWSP was prepared by copolymerization of acrylamide and N-vinyl carbazole in this work. Carbazole unites were introduced into hydrophilic polyacrylamide main chain, which play a role of both hydrophobic unites and fluorescence label. A concentration dependent association process of this carbazole-labelled polyacrylamide in water has been investigated by light scattering and fluorescence spectroscopy. The spectroscopy features of the excitation and emission spectra reveal three distinct regimes upon the association process, which could be employed to analysis the structural transition of carbazole-labelled HMWSPs.

Experimental section

Materials

AM was purchased from Jiangxi Changjiu Biological and Chemical Corp. (China). N-vinylcarbazole was purchased from Xiya Chemical Corp. (China). Ceric ammonium nitrate and sodium bisulfite were purchased from Kelong Chemical Corp. (China). All the chemicals were used without purification.

Synthesis of carbazole-labeled polyacrylamide

The carbazole-labeled polymers were synthesized by dispersion polymerization. Settled amounts (Table 1) of N-vinylcarbazole and acrylamide were dissolved in ethanol at first and the redox initiation system composed of Ceric ammonium nitrate and sodium bisulfite was adopted to initiate the copolymerization at room temperature (~25 ℃) for 10 hrs. The products were obtained by filtration of the reaction solution. For further purification the polymers were washed by ethanol to remove the unreacted monomers and dried in vacuum for 24 hrs at 50 ℃.

Characterization

Characterization of the carbazole-labeled polyacrylamide. The molecular weight and its distribution of carbazole-labeled polyacrylamide were determined by gel permeation chromatography (GPC) on a Waters e2695 instrument equipped with waters 2414 refractive index detector and three columns (ultrahydrogel 500,1000 and 2000) in series. Sodium polyacrylate and 0.05 M sodium nitrate solution are adopted as standards and eluent respectively and the flow rate is 0.5 ml/min. The relative mole fraction was calculated from the ^{1}H NMR data recorded on a Bruker AV-400 with D_2O as solvent.

Preparation and characterization of the polymer solution. All the investigated solutions were prepared by dissolving polymers at the concentration of 200 kppm in pure water and diluting to the settled concentration and stirring for 12 hrs and then aging for another 12 hrs in order to reach the equilibrium state.

Dynamic light scattering (DLS) experiments were performed on a commercial laser light scattering spectrometer (Brookhaven BI-200SM) equipped with a digital time correlator (BI-9001) and a cylindrical 35 mW He-Ne laser (λ = 532 nm, uniphase) as light source. The decay rate (Γ) of the aggregates was obtained by Contin analysis[29] of the experimental correlation function. Combining the equation $\Gamma = Dq^2$ and Stocks–Einstein equation $R_h = k_bT/(6\pi\eta D)$ size as well as its distribution of the aggregates could be obtained, where (the scattering vectors $q = (4\pi n/\lambda)*\sin(\theta/2)$, where n , λ ,and θ are the solution refractive index, wavelength of the incident light, and the scattering angle, while k_b, T , η , D , and R_h are the Boltzmann constant, absolute temperature, viscosity of the solvent, diffusion coefficient, and hydrodynamic radius of the aggregates respectively). The scattering angle was fixed at 90°.

All the excitation and emission spectra were recorded on fluorescence spectrometer (Horiba–Jobin–Yvon, Fluoromax-4). Band pass used for recording fluorescence and fluorescence excitation spectra was 1 nm.

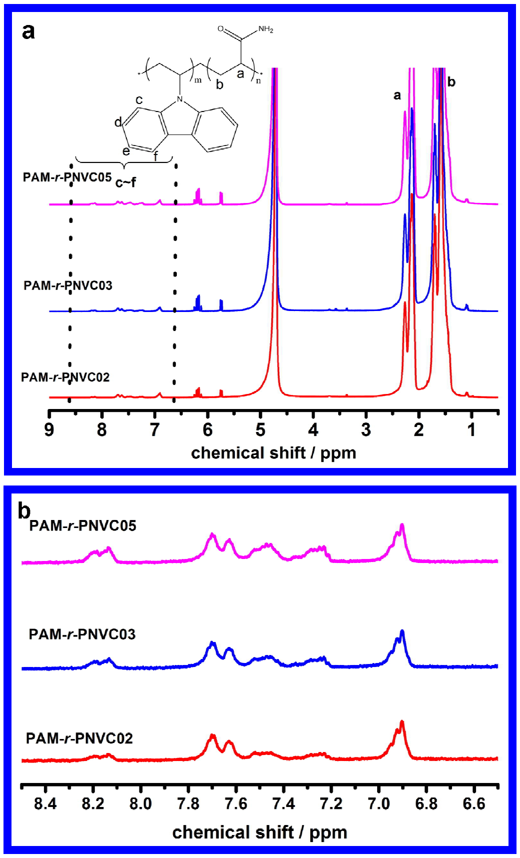

Figure 1. ^{1}H NMR spectra of the copolymers of acrylamide and N-vinylcarbazole (a) and a close-up view of the characteristic peaks of carbazole unites (b).

Table 1. Polymerization conditions and characterization of carbazole-labeled PAMs.

Sample	AM/g	NVC/g	Ethanol/g	M_w[a]/kDa	PDI[a]	f_{nvc}	F_{pnvc}[b]
PAM-r-PNVC02	25	0.2	55	145.9	2.32	0.45%	0.28%
PAM-r-PNVC03	25	0.3	55	145.8	2.13	0.55%	0.42%
PAM-r-PNVC05	25	0.5	55	132.7	2.19	0.61%	0.70%

[a] The relative molecular weight (M_w) and polydispersity index (PD.I) were analyzed by GPC.

[b] The mole fraction of PNVC (F_{pnvc}) was analyzed by ^{1}H NMR.

Results and discussion

Synthesis and characterization of carbazole-labeled polyacrylamide.

As a matter of fact copolymers of NVC and AM were less reported due to two difficulties of the copolymerization. First NVC is a typical kind of non-conjugated monomer which was thought to be hardly copolymerized with conjugated monomer such as styrene, AM et al by radical polymerization.[30-31] However latest research[32] demonstrated that NVC was not so less active as thought and its copolymers with other conjugated monomers might be synthesized. The second difficulty is the mismatch of solubility. AM as well as corresponding polymers are water soluble therefore water is most adopted reaction media for polymerization of AM. Contrarily NVC and PNVC could be hardly dissolved in water. For this reason ethanol was adopted as reaction media to dissolve both monomers NVC and AM in our experiments. Because high molecular weight PAM exhibits limited solubility in ethanol, the ultimate copolymers would precipitates from the reaction solution.

From the NMR results in Figure 1a it could be convinced that the NVC had been copolymerized with AM successfully according to the characteristic peaks of PNVC (aromatic protons of carbazole unites at 8.3 to 6.8 ppm in Figure 1b). Based on the calculation and comparison of peak areas of different characteristic peaks from the two components, we can find that the copolymer exhibits a higher mole fraction of PNVC when the fraction of NVC in monomers was increased. In addition there is a slight effect of the monomer composition on the molecular weight from the GPC results in table 1. All the three samples are with nearly the same molecular weight. The possible reason might that this molecular weight is the upper limitation for solubility. Although mole fraction of carbazole unites is rather low (<1%) obvious associative behaviors could be found when certain amounts polymer was dissolved in water. Meanwhile efforts have been made to increase the mole fraction of carbazole unites, while higher contents of carbazole unites would worsen the modified PAM solubility in water due to the extremely hydrophobicity of PNVC. It should be stressed that the N-vinylcarbazole is copolymerized instead of blending in the sample, which is supported by the emission peaks of vinylcarbazole monomer instead of the structureless peaks of aggregates (in section 3.3) and comparison between the emission spectra of the copolymer and that of NVC monomer in water (S1).

Concentration dependent association process.

Concentration induced association might be the most notable character of amphiphilic polymers including HMWSP, which was widely studied by various groups.[1-2, 5-6, 17] For HMWSP when the concentration was beyond the critical micellization concentration unimers of the HMWSP would associate to form micelles. Further increase in concentration would induce formation of links between different micelles which might result in distinct rise in viscosity.[33] This concentration induced association also held true for our carbazole-labeled PAM. From DLS results in figure 2 it could be found that this kind of HMWSP (PAM-*r*-PNVC05) form aggregates in water when the concentration is above 1000 ppm. At lower concentration it is difficult to obtain reliable correlation function because of the rather low scattering intensity. Thus we can determine the critical concentration for PAM-*r*-PNVC05 is near 1000 ppm. According to the size distribution in figure 2, it could also be

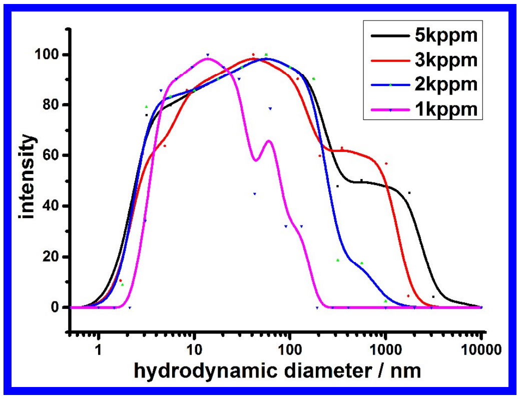

Figure 2. hydrodynamic diameters as well as its distribution of PAM-r-PNVC05 at different concentrations obtained from DLS.

concluded that the larger aggregates were formed at higher concentration. The averaged diameter is about 28.1 nm at the concentration of 1000 ppm while the value increases to 86.7 nm, 172.9nm and 251.9 nm when the concentration increases to 2000ppm, 3000ppm and 5000ppm respectively. Therefore different from that in block copolymers and some other associative polymers, an open association model might more suitable to describe the aggregation behaviours of PAM-*r*-PNVC05, which means the association level or in other words the aggregation number is determined by the concentration.

Fluorescence study of the aggregation process

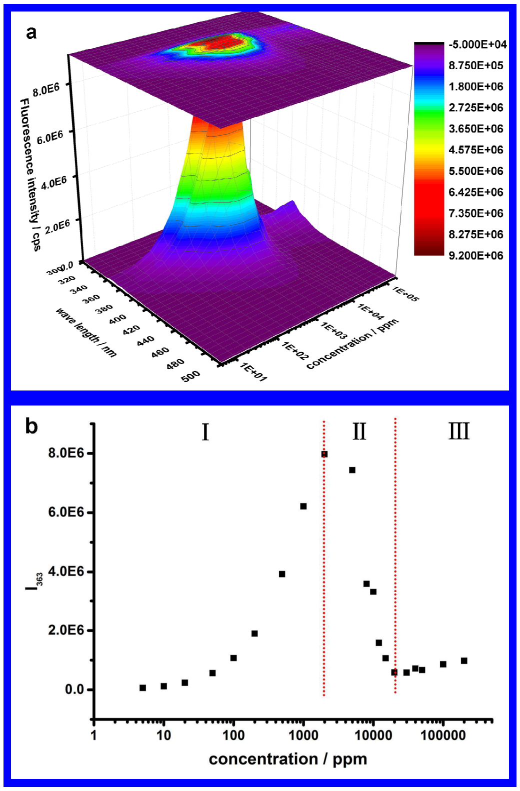

Figure 3. (a) 3D plot and projection of emission spectra and (b) the intensity of the second emission peak (λ=363nm) of PAM-r-PNVC05 in water at different concentrations.($\lambda_{excitation}$ =291nm)

As the concentration dependent aggregation behaviour was well established in this system, fluorescence study of the association process of PAM-*r*-PNVC05 was executed to reveal the fluorescence spectral features of carbazole unites upon aggregation. Figure 3a gives the overall emission spectra of PAM-*r*-PNVC05 at a large range of concentration covering from 5 ppm to 200 kppm. The excitation wave length was fixed at $\lambda_{excitation}$ =291nm, because the highest intensity could be acquired at this wave length according to either the literature[24, 27-28] or our experiment at dilute solution. However it seems too complicated to summary the variation of the spectra in one or two words, because it is sensitively dependent on the concentration. At different concentration regimes, different laws govern the change of emission spectra. For simplicity the intensity of the second emission peak at 363nm (0-1 transition) in the spectra was plotted versus concentration in figure 3b. According to the variation tendency in figure 3b, the overall concentration range was divided into three different regimes roughly. In regime (Ⅰ), the emission intensity increases monotonously to a maximum, while it decreases intensively to a minimum in regime (Ⅱ), followed by a slight increase in regime (Ⅲ).

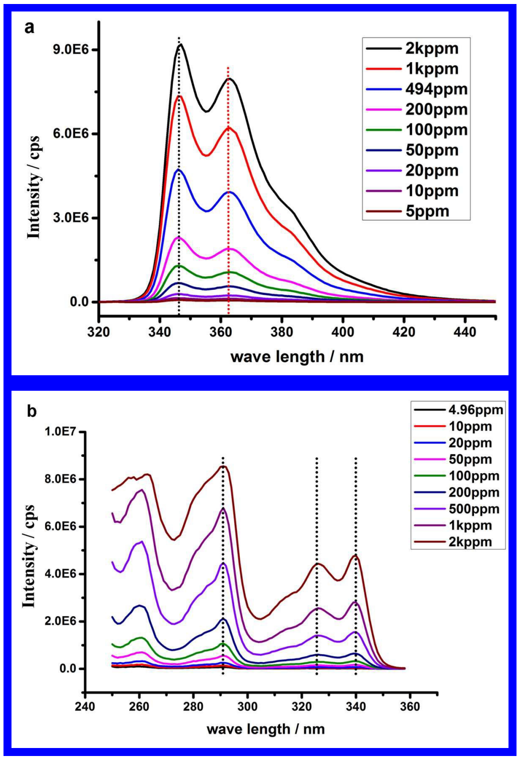

Figure 4. emission spectra ($\lambda_{excitation}$=291nm) (a) and excitation spectra ($\lambda_{emission}$=363nm) (b) of PAM-r-PNVC05 in water at different concentrations in regime (Ⅰ).

Regime (Ⅰ): unimer regime. In regime (Ⅰ) the investigated concentration range covers from 5 ppm to 1000 ppm. The emission spectra in figure 4a exhibit two structured emission peaks and an obscure shoulder peak (385 nm), which coincided with the spectral characteristics of carbazole monomers. The emission peak at 346 nm represents 0-0 transition while the peak at 363 nm corresponds to the 0-1 transition. By comparing the emission spectra of the copolymer with that of blends of N-vinylcarbazole and PAM, it convinced the copolymerization of the two monomers, because emission peaks of carbazole monomer could hardly be observed in water due to its hydrophobicity (S1). On the other hand, the difference of the spectra resulting from concentration is only the fluorescence intensity. Not only the emission spectra but also the excitation spectra in figure 4b hold the same trend. Three obvious absorption bands could be found in figure 4b. The band from 300 nm to 350 nm might be

$S_0 \rightarrow S_1$ absorption and band from 250 nm to 300 nm might be $S_0 \rightarrow S_2$ absorption. Unfortunately the real absorption spectra in this regime (c<1000 ppm) could hardly be obtained due to relatively weak signals and low detection accuracy of UV spectroscopy.

In order to analyse the intensity variation, the intensities of corresponding characteristic peaks in emission spectra and excitation spectra were plotted versus concentration. In both figure 5a and 5b, a linear relationship between the intensity and concentration could be found at low concentration regime. Because both the emission and excitation is only related to the number of the chromophore, we speculate that only unimers exist in this regime, which also coincides with the results from DLS. From figure 5a, the intensity deviates from the linear relationship when the concentration is beyond 500 ppm. Similar deviation from Linear law is also found from the characteristic peak at λ=291nm in figure 5b, while the linear relationship covers a wider range for the lower energy peaks. According to the analysis regime (Ⅰ) is assigned to unimer regime at the concentration lower than 1000 ppm.

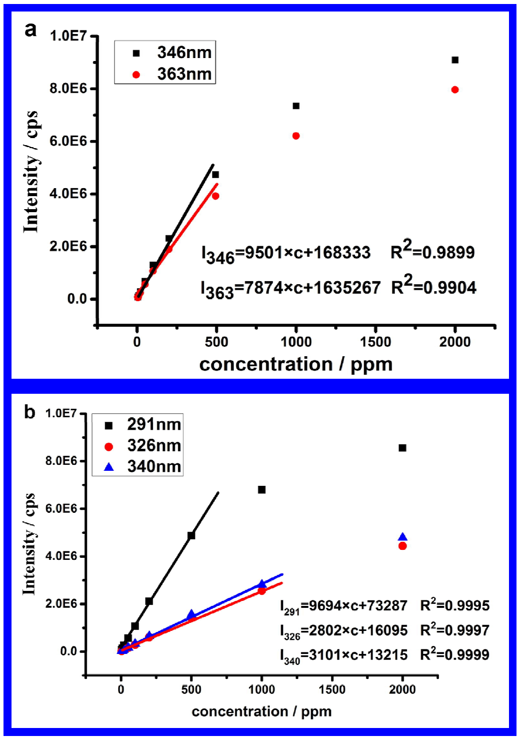

Figure 5. intensity of characteristic peaks in emission spectra (a) and excitation spectra at various different concentrations in regime (Ⅰ).

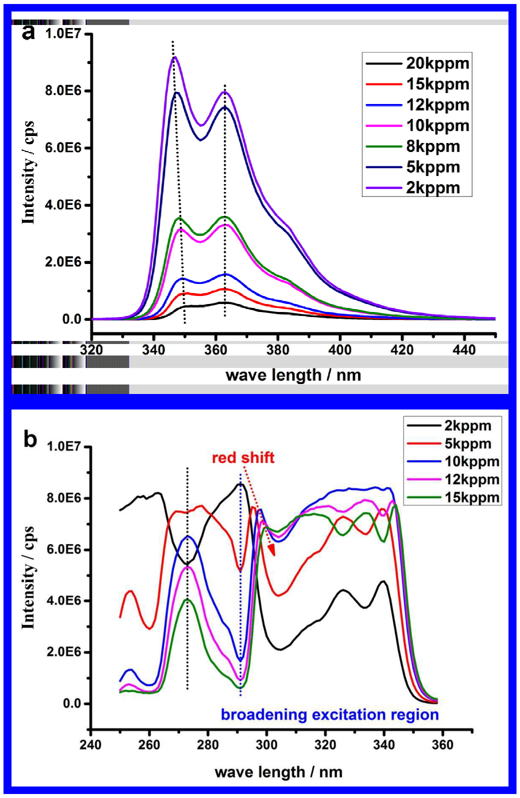

Figure 6. emission spectra ($\lambda_{excitation}$=291nm) (a) and excitation spectra ($\lambda_{emission}$=363nm) (b) of PAM-r-PNVC05 in water at different concentrations in regime (Ⅱ).

Regime (Ⅱ): slightly aggregated regime. As stated in the previous section, when the concentration is above 1000 ppm, the fluorescence intensity is not linear with polymer concentration. Meanwhile aggregates could be detected by DLS. In this regime, the system was examined from 2000 ppm to 20 kppm. Figure 6a and 6b represent the emission and excitation spectra in regime (Ⅱ). It is obvious that the fluorescence intensity decreases intensively with increase in polymer concentration from the emission spectra in figure 6a. The intensity of both two emission peaks reduce to nearly 10% from 2 kppm to 20 kppm. It might be taken for granted due to the inner filter effect at high concentration. Generally speaking, inner filter effect exists when the concentration is high enough. The inner filter effect[34] means that the incident light might be absorbed before reaching the central part of the cuvette as well as fluorescence photons emitted in the region overlapping the absorption spectrum can be absorbed, which results in a decrease in apparent fluorescence intensity at higher concentration. Unfortunately the inner filter effect can not be adopted to interpret the phenomenon showing in figure 6a according to the excitation spectra in figure 6b. Additionally the concentration for carbazole units is not too high because of ultralow mole fraction of PNVC in the copolymer. Different from that regime (Ⅰ), the change in the excitation spectra in figure 6b is extremely complicated at different concentrations. From figure 6b, it could be found that the excitation peak change to a valley in the spectrum when the concentration increased from 2 kppm to 20 kppm. Therefore the excitation spectrum change is the origin to the anomalous intensity change in figure 6a. However it should be stressed that the emission spectral shape still kept constant when it was examined at different excitation wave lengths.

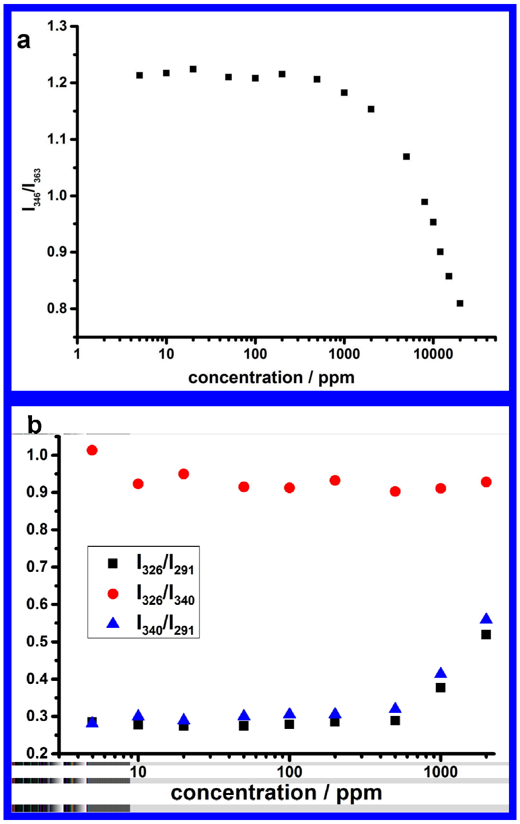

Figure 7. fluorescence intensity ratios of different characteristic peaks in emission spectra (a) and excitation spectra (b) at different concentrations.

Besides the fluorescence intensity, both emission and excitation spectral shapes vary with change in concentration in this regime. For the emission spectra, there are two distinct changes. First is a slight red shift of the higher energy emission peak, from 346 nm at 2 kppm to 352 nm at 20kppm. However the lower energy emission peak keeps at 363 nm for the whole concentration range. Another obvious change in emission spectra is that the relative intensity of the higher energy emission peak decreases with the increase in concentration. From figure 7a we can find that the intensity ratio of the two emission peaks I_{346}/I_{363} (the wave length of higher energy emission peak is slightly changed according to figure 6a) keeps nearly constant at the concentration below 1000 ppm and decreases from 1.2 to 0.8 when the concentration increases to regime (Ⅱ). This ratio might be an effective parameter to estimate the aggregation of carbazole unites. As to the excitation spectra, the relative intensity of the lower energy band (300nm~350nm) increases with increase in concentration. The intensity ratios of characteristic peaks of the excitation spectra have also been plotted versus concentration in figure 7b, the intensity ratios (I_{326}/I_{291} and I_{340}/I_{291}) between the higher energy peak (270 nm ~ 300 nm) and lower energy peaks (300 nm ~ 350 nm) keep constant in the unimer regime (c < 1000 ppm) and increase when the carbazole unites began to aggregate. On the contrary the intensity ratio (I_{326}/I_{340}) of the two characteristic peaks in the lower energy band changes little. When the concentration is above 2 kppm, an obvious red shift of the higher energy absorption band could be found in figure 6a. Due to the red shift of the higher energy band and the intensity increase of the lower energy band, the two energy bands merge to form a broad excitation region (290 nm~ 350 nm), which results in a change in wave lengths corresponding to the peak and valley. In the broad excitation region the distinction between peak and valley become rather blurry especially when the concentration is above 10 kppm. Comparing with the absorption spectra in Figure 8a, we can find the absorption spectrum at lower concentration (c<2000 ppm) is nearly identical in shape to the excitation spectrum in figure 6b. While the absorption spectra and excitation spectra are no longer superimposable at higher concentration (c>2000 ppm), which usually implied that several species were present or a sole species in several existed in different forms in ground state such as aggregates.[34] Considering the DLS results, higher concentration induced larger particles, because aggregation of the fluorescence carbazole unites influences the energy level, large conjugated system makes the electron more localized.

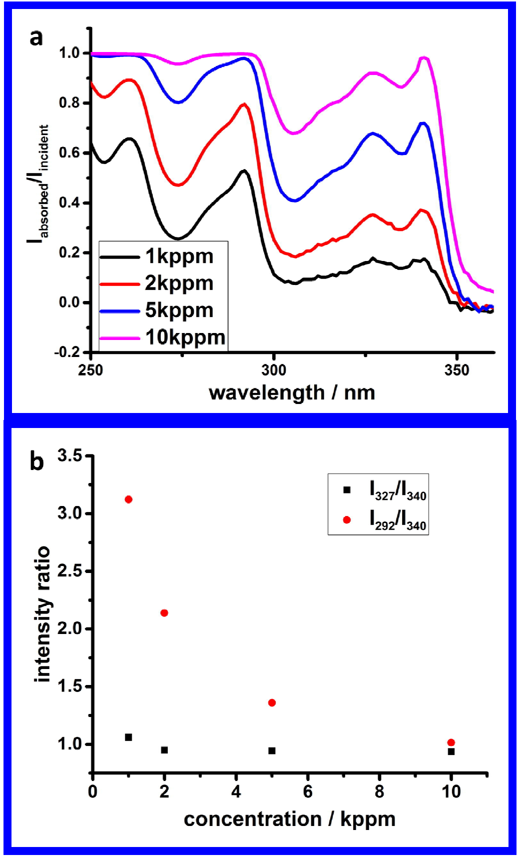

Figure 8. absorption spectral (a) and absorbed intensity ration of different characteristic peaks at different concentrations in regime (Ⅱ).

For this reason all these spectra changes are mainly ascribed to the slight aggregation of carbazole unites. Further analysis on the relative absorbed intensity at different bands in Figure 8b, we can find the proportion of $S_0 \rightarrow S_2$ absorption (270nm~300nm) decreases and that of $S_0 \rightarrow S_1$ absorption (300nm~350nm) increases with aggregation. The relative ratio (I292/I340) of $S_0 \rightarrow S_2$ absorption to $S_0 \rightarrow S_1$ absorption decreases from 3.2 to 1 when concentration increased from 1000 ppm to 10 kppm. It implies that the change in Figure 7b resulted from aggregation induced change in absorption bands. Additionally it should be noted that $S_0 \rightarrow S_2$ transition still absorbed more than $S_0 \rightarrow S_1$ transition but emitted much less upon aggregation. It might be might be ascribed to quenching of new formed aggregates to the unimer. However we still couldn't exclude the influence of inner effect completely.

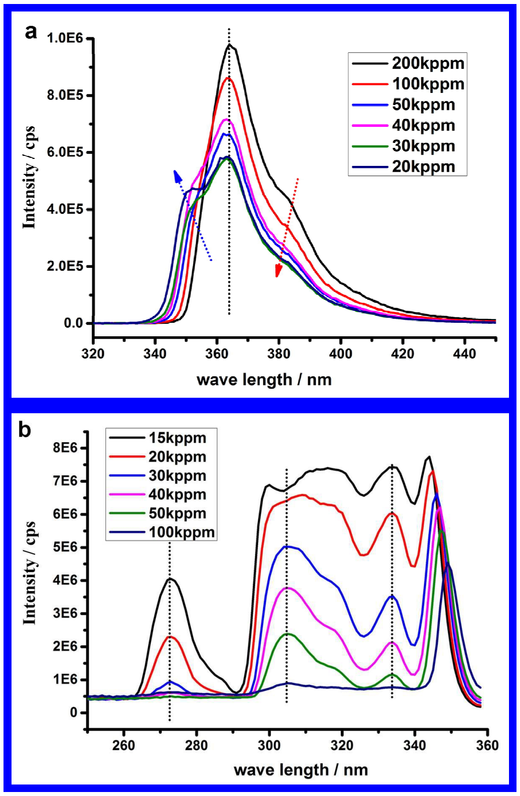

Figure 9. emission spectra ($\lambda_{\text{excitation}}$=291nm) (a) and excitation spectra ($\lambda_{\text{emission}}$=363nm) (b) of PAM-r-PNVC05 in water at different concentrations in regime (Ⅲ).

Regime (Ⅲ): intensively aggregated regime. In regime (Ⅲ), a reasonable result that higher fluorescence intensity is at higher concentration in both figure 3b and figure 9a. Regarding to the emission spectra in figure 9a, higher energy emission peak becomes a blurry shoulder peak at first and vanishes at last when the concentration increases from 20 kppm to 200 kppm. The lower energy emission peak (λ=363nm) is without any change. Contrarily it might be concluded that intense aggregation induced quenching occurred in this regime when the excitation spectra (figure 9b) were examined. The overall intensity decreases and most peaks in excitation spectra including the broad excitation region vanishes with increase in concentration in regime (Ⅲ). Only the lowest energy peak exists and there is a slight red shift of this peak during the concentration induced quenching process. Unfortunately no more information could be obtained from absorption spectra in this regime because the incident light has been absorbed completely due to high concentration and molar absorption coefficients. Undoubtedly the change in fluorescence spectra results from the intense aggregation of carbazole unites at such high concentration.

Association-induced fluorescence features of carbazole unites.

Despite the description of the spectral signatures of carbazole aggregates in last section, fluorescence features will be tried to be interpreted and understood within the scope of organic molecular aggregates.[35] Generally speaking once organic molecules become close enough to each other both absorption and fluorescence spectra might deviate from that of monomers because of the dipole-dipole coupling between the transition dipole moments of the neighboring molecules.[36] According to different orientations of the chromophores within the aggregates, the aggregates could be classified as H-aggregates and J-aggregates ideally. When the aromatic molecules pack in a side-by-side orientation to form H-aggregates, the excitonic coupling is positive leading to a blue-shift absorption and quenched fluorescence.[8, 10-11, 37-38] While in J-aggregates the molecules pack in a head-to-tail orientation and the coupling is negative resulting in a red-shift absorption.[9, 38-40] Thus from the excitation spectra of PAM-r-PNVC05 it seems that J-aggregates were formed by carbazole unites, because an obvious red-shift exists in the excitation spectra of the aggregates. Additionally in Spano's work[36] another important spectral feature of J-aggregates is that the ratio of the oscillator strengths in the A_1 to A_2 bands would increase upon J-aggregation, where A_1 and A_2 donates the proportion of $S_0 \rightarrow S_1$ transition and $S_0 \rightarrow S_2$ transition. This feature could be found in figure 8b, as the peaks at 327 nm and 340 nm in the absorption spectra represent $S_0 \rightarrow S_1$ transition while the peak at 292 nm represents $S_0 \rightarrow S_2$ transition. As stated by Spano[36] in the strong coupling regime oscillator strength is mainly concentrated in a single lower energy peak, which coincides with the results in figure 9b. Thus all the excitation and absorption spectral features suggest that J-aggregates were formed by carbazole unites.

Unfortunately the observed aggregation induced quenching in the carbazole aggregates is contrary to that of J-aggregates, which is more likely to H-aggregates. Meanwhile the 0-0 transition would vanish upon H-aggregation which is opposite to J-aggregation. From the decrease in I_{346}/I_{363} (peak at 346 nm represents 0-0 transition and peak at 363 nm represents 0-1 transition) in figure 7a and vanish of emission peak at 346 nm in figure 9a, the spectral signatures of emission imply the vanish of 0-0 transition upon aggregation. Thus it seems H-aggregates were formed by carbazole unites according to the emission spectra. However the same vanish of

0-0 emission might also be observed in J-aggregates with increasing disorder according to Spano's work.[36] Thus the spectral signatures of excitation and emission could be well understood within the scope of Spano's simulation results,[36] a possible explanation might be that J-aggregates were formed by carbazole unites and the disorder in the aggregates increases upon the open association process from unimers to slight aggregates in regime (Ⅱ) to intensive aggregates in regime (Ⅲ).

The speculation of disorder in the J-aggregates could also be supported by the absence of excimer formation from the emission spectra. Excimer[41-42] denotes molecular configurations which absorb as monomers but in the excited state one excited molecule and one un-excited monomer physically associate to form dimers and fluoresce as such. It is a very common to observe excimer formation in aromatic chromophores[7, 42] such as pyrene and carbazole at high local concentration. The excimer formed by carbazole containing polymers has been investigated in dilute solution and thin film for a long time.[12, 23-28, 43] Different excimer species have been observed which was assigned as the partially overlapped (lower energy $\lambda_{emission}$=380 nm) and sandwich excimers (higher energy $\lambda_{emission}$=430 nm). It is reasonable that there is only monomer emission in regime (Ⅰ) because of the extremely low mole fraction of NVC in the copolymer which is the same as the situation in literature. Unexpectedly there is no obvious signatures of excimer emission upon aggregation in regime (Ⅱ) and (Ⅲ). The most possible reason might be the disorder of carbazole unites in the aggregates. Only at the condition of that the molecules in the crystal must be ordered pairwise in parallel planes, with a small distance between neighboring planes, excimer might form in the aggregates.[35] However for carbazole unites in the aggregates， they the lost their mobility to adjust to the right conformation for excimer formation. Therefore the dominating head-to-tail orientation and the disorder in the aggregates caused the absence of the excimer formation in our system.

Conclusions

In summary, a novel carbazole-labelled HMWSP was synthesized by dispersion copolymerization of NVC and AM in ethanol and a concentration dependent open association process of this labeled polymer has been studied by DLS and fluorescence spectroscopy in water. The spectral features of excitation and emission spectra were summarized in three different regimes upon association process. All these spectral signatures are tried to be understood within the scope of Spano's simulation and carbazole unites are ascribed to formation of J-aggregates with high disorder. However these explanations need to be further investigated since the inner filter effect could be hardly excluded experimentally especially the signatures in excitation spectra. Nevertheless these fluorescence features in association process of carbazole unites were of significance to develop carbazole based fluorescence analytical method and fluorescent materials.

Acknowledgements

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