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Intermacromolecular complexes due to specific interactions. 13. Formation of micelle-like structure from hydrogen-bonding graft-like complexes in selective solvents

Shiyong Liu[a], Ming Jiang[a,*], Haojun Liang[b], Chi Wu[b,c]

[a]*Institute of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China*

[b]*The Open Laboratory of Bond-Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, People's Republic of China*

[c]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong*

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Abstract

The complexation between poly(4-vinyl pyridine) (PVPy) and mono-carboxy terminated polystyrene (MCPS) in chloroform leads to the formation of a graft-like supramolecular architecture. LLS and fluorescence spectroscopy have been used to monitor the self-assembly process of the "graft" copolymers in a selective mixed solvent of chloroform/toluene which is a solvent for MCPS but a nonsolvent for PVPy. Adding toluene to PVPy/MCPS-1.8 blend solution in chloroform leads to a stable and clear solution indicating the formation of the micelle-like core-shell structure with the core and shell made of PVPy and MCPS, respectively. Here, the cores and shells are linked by hydrogen bonding. The final micelle-like particles are narrowly distributed and very stable on standing. Adding the blend solution of PVPy and MCPS in chloroform to an excess of toluene also produces micelles but these have a much smaller average hydrodynamic radius ($\langle R_h \rangle$) than those prepared by adding toluene to the blend solution. As the molar mass of MCPS is increased, the size of micelle-like structures increases dramatically.

Keywords: Micelle-like structure; Graft-like complexes; Hydrogen bonding

1. Introduction

It is well known that block or graft copolymers may form micelles in selective solvents, which are good for one of the blocks and a nonsolvent for the other [1–4]. Polymer micelles are of interest because of their structure variety on the dependence of the chemical structure [5] and their potential applications as solubilizers [6] and drugcarriers [7]. The core of a micelle basically consists of the compact insoluble blocks or backbone, stabilized by a corona of the solvated blocks. In a system without specific interaction between block or graft copolymer chains, the driving force for micellization is generally attributed to differences in solubility between the component blocks in selective solvents. Recently, specific interactions such as hydrogen bonding and electrostatic interactions have been used as additional agents to control the micelle formation. Zhao et. al. investigated the micelle formation of a monodisperse polystyrene-*b*-poly(vinyl phenol) (PS-*b*-PVPh) in toluene [8], a selective solvent for the PVPh block. The strong self-association due to hydrogen bonding between the phenol groups of PVPh in toluene provides additional force to induce the micelle formation. For ionic block copolymers consisting of an ionic block and a hydrocarbon chain, electrostatic interactions in the ionic block also contribute much to the micellization process [4]

Generally, the core and corona of the micelles reported in the literature are covalently linked. As far as we know, there are no reports in the literature dealing with the formation of a micelle-like structure where the core and shell are linked by specific interactions rather than by covalent bonds. Recently, we have obtained a new type of soluble graft-like complexes consisting of poly(4-vinyl pyridine) (PVPy) and mono-carboxy terminated polystyrene (MCPS) in common solvents such as chloroform [9,10]. It was found that MCPS chain can be "grafted" to PVPy backbone via hydrogen bonding between the pyridyl of PVPy and the carboxyl end of MCPS. This is evidenced by

* Corresponding author. Tel.: + 86-21-6564-3919; fax: + 86-21-6564-0293.

E-mail address: mjiang@fudan.edu.cn (M. Jiang).

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Table 1
Characteristics of the samples used in this study

Samples[a]	n[b]	$\frac{M_n}{10^3\ g/mol}$	M_w/M_n	f[c]	T_g(°C)
MCPS-1.8	17	1.8	1.28	0.95	86
MCPS-2.2	21	2.2	1.19	0.88	88
MCPS-3.9	38	3.9	1.16	0.91	93
MCPS-5.5	53	5.5	1.06	0.98	97
PS-2.3	22	2.3	1.14	–	63
PVPy	1330	140[d]	–	–	151
PVPy-a[e]	1190	125[d]	–	–	–
PVPy-c[e]	1140	120[d]	–	–	–

[a] The numerals in sample code MCPS-*X* denote the molar mass of MCPS.
[b] n = average number of units per chain.
[c] f = functionality.
[d] Calculated from intrinsic viscosity data.
[e] a and c denote PVPy labeled with AMMA and vinyl carbazole units, respectively.

viscometry, laser light scattering (LLS) and fluorescence spectroscopy. The LLS results showed a dramatic increase of $\langle R_h \rangle$ of the mixed solution of PVPy and MCPS, compared to the pure components. Furthermore, when the MCPS/PVPy weight ratio increased to about 10/1, $\langle R_h \rangle$ reached its maximum indicating that the PVPy backbone was "saturated" by the grafted MCPS chains due to the repulsion of MCPS chains. Both LLS and nonradiative energy transfer (NRET) fluorescence have detected conformational extension of PVPy chains because of the steric repulsion of grafted MCPS chains.

Based on the discovery of the formation of the "graft copolymers" by hydrogen bonding, we report, in this paper, the micelle formation of the PVPy/MCPS blend solutions in a selective solvent, which dissolves MCPS but not PVPy. The motivation of the investigation is that the cores and coronas of this kind of micelles are linked by hydrogen bonding rather than by covalent bond and this may enable us to create some new morphologies of molecular assembly by further separation of the components in the core and corona.

2. Experimental section

2.1. Materials

THF, Benzene, Styrene and 4-vinyl pyridine were purified by general methods [11,12]. Vinylcarbazole, purchased from Aldrich, was used as received without further purification. The energy-acceptor monomer, 9-anthrylmethyl methacrylate was synthesized from 9-hydroxymethyl anthracene and methacroyl chloride in the presence of triethyl amine and anhydrous pyridine followed by column chromatography purification.

MCPS was prepared by terminating the living polystyryl using CO_2 free of oxygen and protonic impurities. The details have been reported previously [9,10]. MCPS samples are denoted as MCPS-*X*, where *X* represents the molar mass of MCPS in kg/mol.

PVPy was prepared by anionic polymerization in THF using naphthalene sodium as the initiator. Anthracene-labeled and carbozole labeled PVPy were produced through radical copolymerization of 4-vinyl pyridine and 9-anthrylmethyl methacrylate or vinyl carbazole. The chromophore contents in PVPy-a and PVPy-c (a and c denotes PVPy labeled with AMMA and vinyl carbazole units, respectively) determined by UV spectroscopy had 0.24 wt%.

2.2. Preparation of micelles

Micelle-like particle-containing solutions were prepared by adding toluene dropwise to a mildly stirred PVPy/MCPS chloroform solutions at a given blend ratio or by adding chloroform solution into toluene. Depending on the molar mass of MCPS, the blend solutions in the mixed solvent looked either clear or milky. The effect of solvent quality on the self-assembly process was investigated by changing the volume ratio of toluene to chloroform.

2.3. Fluorescence measurements

Emission spectra of the polymer solutions were recorded on a FZ-1 fluorescence spectrometer at room temperature (ca. 25°C). The component polymer solutions were prepared with oxygen-free solvents. The total concentration of PVPy-a, PVPy-c in $CHCl_3$ was kept at 1.0×10^{-3} g/ml. Blend solutions were prepared by mixing the corresponding polymer solutions at a weight ratio of PVPy-a/PVPy-c/MCPS 1/1/20 in a quartz cell with stirring and purged with nitrogen for at least 1 min prior to each recording. When toluene was added into the blend solution, stirring was kept for 10 min before the fluorescence measurements. The wavelength of the excitation light was set at 294 nm, and the direction of the excitation light was perpendicular to that of the emission detected. The energy transfer efficiency was characterized by I_c/I_a ratio between the emission intensity at 365 nm (I_c) and that at 416 nm (I_a), mainly contributed by the energy-donor carbazole and the energy-acceptor anthracene, respectively. The characteristic distance of the combination of fluorescent donor and acceptor in our case is 2.7 nm [13]

2.4. Laser light scattering measurements

A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-ι digital time correlator (ALV-5000e) and a solid-state laser (ADLAS DPY425 II, output *power* ≅ 50 mw, at $\lambda_0 = 532$ nm) was used. The incident beam was vertically polarized with respect to the scattering plane. The detail of LLS instrumentation and theory can be found elsewhere. All measurements were measured at 25.0 ± 0.01°C. All the samples used in the LLS measurements were clarified by a 0.5 μm Anotop filter. The measured time correlation functions were analyzed by both the Cumulants and

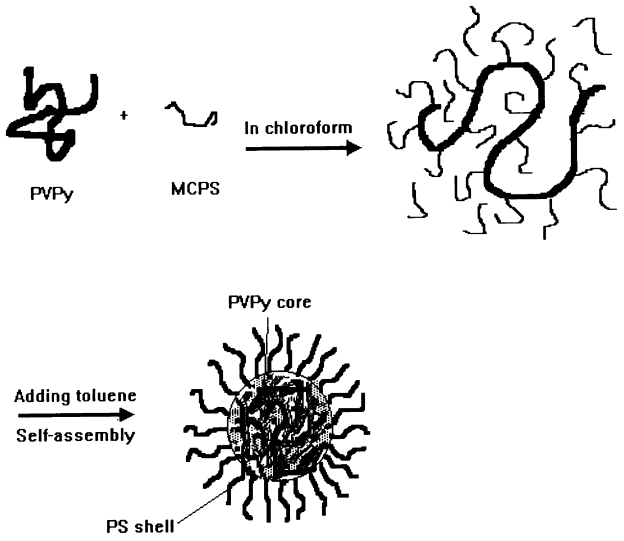

Fig. 1. A schematic illustration of the self-assembly process. The PVPy chain undergoes the partially collapsed coil—extended coil—collapsed coil transition.

Laplace inversion (CONTIN) programs equipped with the correlator.

3. Results and discussion

The characteristic data and the glass transition temperatures of MCPS, PVPy, PVPy-a, PVPy-c are given in Table 1 of our previous paper [10].

For PVPy/MCPS blend solutions in $CHCl_3$, the conformation of PVPy chains undergoes extension resulting from excluded volume effect due to the grafting of MCPS chains. Toluene is a nonsolvent for PVPy, as it was observed that PVPy precipitated out when the volume fraction of toluene added into chloroform solutions of either pure PVPy or PVPy/PS blends reached about 0.15. However, when toluene was added dropwise to a blend solution of PVPy-a/PVPy-c/MCPS-1.8 (weight ratio 1/1/20) in chloroform, the solution kept clear and showed a bluish tinge characteristic of micelle formation over the volume fraction range of toluene from 0.3 to 0.9. Considering the substantial difference in solubility between PVPy and MCPS in toluene/chloroform mixed solvents, it is reasonable to think that micelle-like structures consisting of insoluble PVPy core and soluble MCPS coronas are formed in the solutions. The PVPy core is stabilized by the soluble, grafted MCPS chains. It is worth noting that unlike the micelles of block or graft copolymers in which the core and shell are linked by covalent bond, in the present case, the polymer chains in the core and shell are bonded by secondary interactions, i.e. hydrogen bonding. A schematic illustration of both the grafting complexation of MCPS onto PVPy and the subsequent micellization process is shown in Fig. 1.

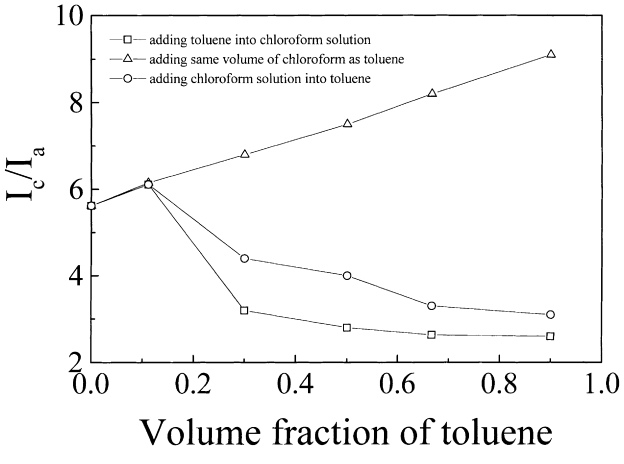

Fig. 2. The variation of I_c/I_a of blend solutions of PVPy-a/PVPy-c//MCPS-1.8K (weight ratio, 1/1/20) in chloroform/toluene blend solutions with volume fraction of toluene. The control solution was prepared by adding the same volume of chloroform as the toluene added. The blend solutions were prepared by adding toluene into chloroform solutions.

3.1. Fluorescence studies on the self-assembly of PVPy/MCPS blend solutions

It is well-known that block or graft copolymers may form micelles consisting of either a large number of chains or only a single chain, which are called multimolecular micelles unimolecular micelles, respectively. The "graft copolymer" of PVPy/MCPS is some kind of "multi-block copolymers", one of the unique properties of multi-block copolymers is their ability to form unimolecular micelles with intramolecular associations, which are not seen in low-molecular-weight surfactants. Halperin [14] theoretically predicts that a copolymer of multiblocks connecting alternately forms a unimolecular micelle of the flower type or a flexible string of the flowers in a selective solvent. Kikuchi and Nose [15] have reported the unimolecular micelle formation of poly(methyl methacrylate)-*graft*-polystyrene copolymers with low grafted chain densities in dilute solutions of selective solvents to the backbone. No doubt, it is interesting to know whether the predominant micelle-like structure resulting from our graft copolymers is unimolecular or multimolecular, and NRET fluorescence is quite helpful with answering this question.

The principle of NRET fluorescence is that the efficiency of energy transfer between a fluorescence energy donor and acceptor depends strongly on their proximity over a scale of ~2–4 nm [16]. Conventionally, the ratio of I_c/I_a, which is reversely proportional to the energy transfer efficiency, is used to measure the degree of molecular interpenetrating of polymer components carrying fluorescence donor and acceptor, respectively [13,16]. In the process of micellization of PVPy/MCPS graft copolymers, where the chromophore-labeled PVPy chains form the cores, a substantial change of I_c/I_a is expected. In a unimolecular micellization process, the energy transfer efficiency will decrease due to the collapse and isolation of the individual PVPy coils, while for a multimolecular micellization process, the energy

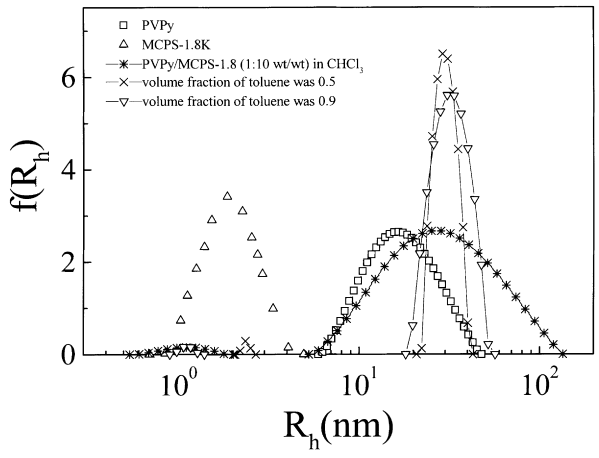

Fig. 3. The hydrodynamic radius distributions of PVPy/MCPS-1.8 (1/10 wt/wt), pure PVPy, MCPS-1.8 and the blend solutions in chloroform/toluene mixed solvent with different toluene volume fractions. The initial concentration of PVPy was 1×10^{-3} g/ml, the micellar solution was prepared by adding toluene dropwise into chloroform solutions.

transfer efficiency will increase as many PVPy-a and PVPy-c chains aggregate to form the cores.

Fig. 2 shows the variation of I_c/I_a of the blend solution of PVPy-a/PVPy-c/MCPS-1.8 (1/1/20) in chloroform as a function of the volume fraction of toluene added. The control solutions were prepared by adding the same amount of $CHCl_3$ as that of toluene. For the control, I_c/I_a increases with the addition of $CHCl_3$ showing a "dilution effect", i.e. energy transfer between donor and acceptor groups attached to different PVPy chains decreases as the polymer solution was diluted. For the blend solution of PVPy-a/PVPy-c/MCPS-1.8, I_c/I_a increases initially, which is in accordance with the control. It seems that the dilution effect makes main contribution to the I_c/I_a increase, besides, the PVPy chain contraction due to worsening solvent quality will also lead to fluorescene donor and acceptor groups being partly buried in the coils and then lower energy transfer efficiency between them. A further increase of the toluene fraction causes a drop in I_c/I_a, and then it flattens out to a plateau when the toluene volume fraction exceeds 0.3. This pronounced increase of the energy transfer efficiency between the PVPy-a and PVPy-c chains clearly indicates the close packing of PVPy chains in the self-assembly process. In other words, the micellization is found to be a multi-molecular process. During the micellization, two processes occurred simultaneously, i.e. intrachain collapse of PVPy and interchain aggregation of different PVPy coils. The final state of the self-assembly depends on the relative rate of these two processes.

The preparation procedure also has a considerable effect on the micellization process. The I_c/I_a data of micellar solutions prepared by adding chloroform solution into toluene is also shown in Fig. 2. The I_c/I_a values are considerably higher than in the micelle solutions prepared by adding toluene into chloroform solution. This indicates that in the former case, fewer PVPy chains are involved in the micelle core. This difference in energy-transfer efficiency can be attributed to a competition between intrachain collapse and interchain aggregation. When adding chloroform solution into toluene, the diffusion of chloroform into an excess of toluene is so fast that intrachain collapse dominates over interchain aggregation, so that some of chromophores are buried in the collapsed PVPy chain, leading to a lesser increase of the energy transfer efficiency. In the opposite case, the solvent quality for PVPy chains worsens gradually as toluene is added dropwise, and this provides sufficient time not only for the intrachain collapse but also for the interchain aggregation. If we increase the relative rate of the intrachain collapse to the interchain aggregation by decreasing the initial concentration, under extreme conditions, we maybe able to prepare the unimolecular micelles.

For the blend solutions of PVPy, PVPy-c and MCPS-2.2, with a higher molecular weight, a similar result was obtained in the I_c/I_a as a function of the toluene fraction as that for PVPy-a/PVPy-c/MCPS-1.8. The data are not shown, for the sake of simplicity.

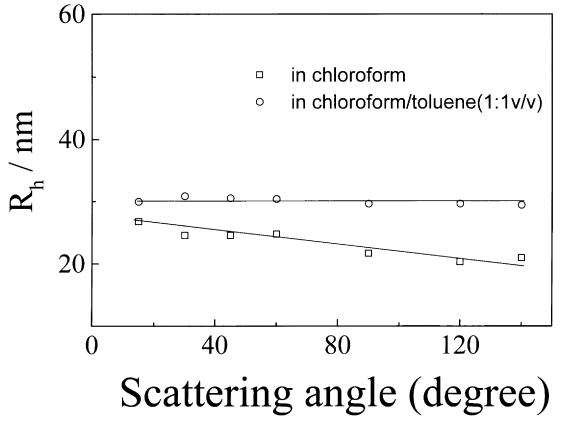

Fig. 4. Variation of $\langle R_h \rangle$ of PVPy/MCPS-1.8K (1/10 wt/wt) blend solutions in chloroform (□) and in chloroform/toluene mixed solvents (toluene volume fraction was 0.5) (○).

3.2. Laser light scattering studies on the self-assembly process of PVPy/MCPS

LLS has been successfully applied in studying interpolymer complexation and aggregation in both aqueous and nonaqueous solution, especially in very dilute solutions [17–20]. Fig. 3 shows the hydrodynamic radius (R_h) distributions of the PVPy/MCPS-1.8 blend solution in chloroform and blend solutions added with different amounts of toluene. Fig. 3 also shows the R_h distributions of pure MCPS and PVPy, the respective peaks of which are located at 1–2 nm and 17 nm. The peak of PVPy/MCPS-1.8 (1/10 wt/wt) moves to 27 nm with a relatively wide distribution as a result of the formation of graft-like complexes. It is interesting to see that the R_h peak moves to 30 nm and its distribution substantially narrows (20–40 nm) when the volume fraction of toluene added reaches 0.5. At this point, the

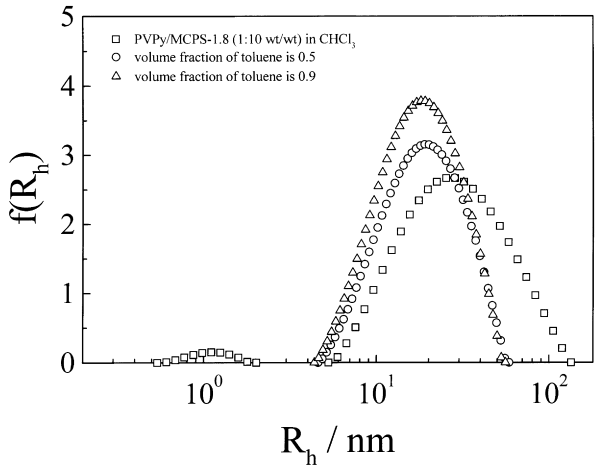

Fig. 5. Hydrodynamic radius distributions of PVPy/MCPS-1.8 (1/10 wt/wt) in chloroform and chloroform/toluene mixed solvents with different volume fraction of toluene. The initial concentration of PVPy was 1×10^{-3} g/ml, the micellar solutions were prepared by adding chloroform solution into toluene.

worsening of the solvent quality should lead to the collapse of PVPy chain but PVPy does not precipitate out and the blend solution keeps clear and transparent. This fact is obviously attributed to the chain aggregation and rearrangement into the formation of the micelle-like structure. When the volume fraction of toluene increases further to 0.9, the peak corresponding to the self-assembled micelles shifts to about at 31 nm, namely, only a very small size and distribution variation was observed when the solvent quality for PVPy was considerably changed. It may mean that the chain exchange between the micelles is difficult at toluene volume fraction being 0.5 although the micelle core and shell are linked by hydrogen bonding only instead of covalent bond in conventional micelles between which chain exchange is possible when the solvent quality (composition) is suitable [21].

The final micelle-like particles are narrowly distributed

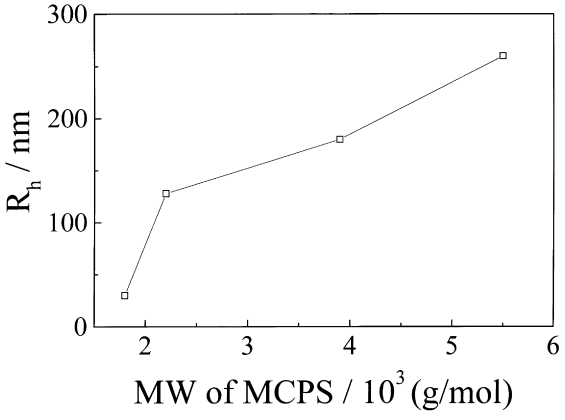

Fig. 6. The variation of $\langle R_h \rangle$ of the blend solution of PVPy/MCPS (weight ratio 1/10) in chloroform/toluene (1/1, volume ratio) with the molar mass of MCPS. The blend solution was prepared by adding toluene into chloroform solution. The initial concentration of PVPy is 1×10^{-3} g/ml.

($\mu_2/\Gamma^2 < 0.1$). Fig. 4 shows the angular dependence of R_h of blend solutions of PVPy/MCPS-1.8 "graft-like complexes" in chloroform and in chloroform/toluene (1/1, vol. ratio), respectively. Apparently, compared to the "graft" complexes in chloroform, the micelles in chloroform/toluene (1/1) shows much lesser angular dependence. This indicates that the micelles take a shape much closer to spheres. This observation is in accordance with the core-shell micelle-like structure shown in Fig. 1.

The effect of the order of solvent mixing on the self-assembly process and the size of the final micelle-like structures is also reflected by the LLS results. Fig. 5 shows the R_h distributions of the micellar solutions prepared by adding PVPy/MCPS-1.8 chloroform, solutions into toluene. It was found that the peak R_h value decreases from 27 nm in chloroform to about 18 nm in the solvent mixture. Meanwhile, along with this change from graft-like complexes to the corresponding micelles, the size distribution becomes much narrower as evidenced by the change of μ_2/Γ^2 from 0.29 to 0.10. This means that the formed micellar structure is characteristic of a narrow size distribution just as that found in block copolymer micelles. A further increase of the volume fraction of toluene to 0.9 leads to little changes in the peak position and the R_h distribution. The micelles formed are conspicuously smaller when the chloroform solution is added into toluene than the other way round. In the latter case (adding toluene into chloroform solution), the solvent quality changes gradually, PVPy coils have enough time to rearrange and interchain fusion between different collapsed PVPy chains may dominate over intrachain collapse, while in the former case (adding chloroform solution into toluene), the solvent quality changes suddenly and intrachain collapse is the main process leading to smaller micelles. This is in good agreement with the result found by the NRET fluorescence studies shown in Fig. 2. The difference between the micelles prepared from different adding sequences indicates that the micelle formation process is a kinetically controlled process. The micelles formed did not reach the thermodynamic equilibrium and chain exchanges between different micelles at toluene volume fraction being 0.5 and 0.9 are limited.

Fig. 6 shows the variation of $\langle R_h \rangle$ of PVPy/MCPS micelle solution in chloroform/toluene (1/1 volume ratio) with the molar mass of MCPS. The solutions were prepared by adding toluene to blend solutions in chloroform. Generally, $\langle R_h \rangle$ increases markedly with increase in the molar mass of MCPS. This actually reflects the effect of the carboxyl density of the graft chains on the self-assembly, i.e. the higher the molar mass of MCPS, the weaker the stabilization ability and consequently, the larger micelles formed.

It is worth noting another pathway to realize the self-assembly from PVPy/MCPS blend solutions in chloroform, namely, by changing the temperature. It was observed that PVPy precipitated out in PVPy/PS blend solution at -10°C and this was expected as PVPy in chloroform had its cloud point at about -5 to 0°C. The blend solutions of

PVPy/MCPS (M_n ranges from 1800 to 5500) still remained clear and stable even at −20°C. It obviously implies the formation of the micelle-like structure. Qiu and Wu [22] have reported thermally induced core-shell nanoparticle formation of poly(*N*-isopropylacrylamide)-*g*-poly(ethylene oxide) (PNIPAM-*g*-PEO). When the temperature is increased above ~32°C, the PNIPAM-*g*-PEO chain backbone undergoes the "coil-to-globule" transition, forming a hydrophobic PNIPAM core and a soluble hydrophilic PEO shell. In the present case of PVPy/MCPS, the temperature-induced marcophase separation of PVPy must have been prevented, instead, the PVPy aggregates are stabilized by the grafted MCPS chains, which are still well solvated in $CHCl_3$.

4. Conclusions

The complexation between PVPy and MCPS in chloroform leads to the formation of a graft-like supramolecular architecture. LLS and fluorescence spectroscopy have been used to monitor the toluene-induced self-assembly process for the PVPy/MCPS "graft-like" complexes. It was found that, differing from PVPy/PS blend solution in chloroform, where the addition of toluene leads to macroscopic precipitate since toluene is a nonsolvent for PVPy, adding toluene to the blend solution of PVPy and MCPS-1.8 leads to a stable and clear dispersion. This indicates the formation of a micelle-like core-shell structure with the core and shell made of the PVPy and MCPS, respectively. The cores and shells are linked by hydrogen bonding. The final micelle-like particles are narrowly distributed ($\mu_2/\Gamma^2 < 0.1$) and very stable on standing. Adding blend solutions of PVPy and MCPS in chloroform to an excess of toluene also produced micelles but with $\langle R_h \rangle$ much smaller than those prepared by adding toluene into chloroform solution. This indicates that the self-assembly process is controlled by a competition between interchain aggregation and intrachain contraction of PVPy chains. Compared with PVPy/MCPS-1.8 graft-like complexes in chloroform, R_h of the micelles show a much smaller angular dependence indicating that the micelles may be taking a spherical shape. When the molar mass of MCPS increases, the size of micelle-like structure increases dramatically. Besides, NRET fluorescence studies show that the micellization is a multi-molecular process rather than an unimolecular one.

Acknowledgements

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