Colloid Polym Sci (2006) 284: 556–561
DOI 10.1007/s00396-005-1412-4

SHORT COMMUNICATION

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Micelle-like particles based on self-assembly of rod-like FPEEK and coil-like PVA

Received: 6 May 2005
Accepted: 10 October 2005
Published online: 9 December 2005

This work was supported by the National Nature Science Foundation of China (50203004).

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Abstract The self-assembly of a rod-like polymer [hydroxyl-terminated trifluoromethylphenyl-substituted fluorinated poly(ether ether ketone) (FPEEK)] and a coil-like polymer (polyvinyl alcohol, PVA) in water has been studied. It was found that this polymer pair could form micelle-like particles. Hydrogen bonding between the hydroxy groups of rod-like FPEEK and coil-like PVA, and parallel packing of the rod-like FPEEK are the main factors affecting the formation of micelle-like particles. Over a broad range, when the FPEEK/PVA mass ratio or the tetrahydrofolate/H_2O volume ratio is decreased, the diameter of micelle-like particles is decreased. The diameters (around 250 nm) of micelle-like particles measured by scanning electron microscopy and dynamic light scattering are similar, but are different from that measured by transmission electron microscopy (around 150 nm). Thus, it can be concluded that micelle-like particles have a core–shell structure and the cores of micelles are composed of FPEEK, and that the shells of micelles are composed of PVA. When polyethylene glycol was used instead of PVA, micelle-like particles were also formed, but the average diameter was bigger than that of the particles formed by PVA and FPEEK.

Keywords Micelle-like particle · Self-assembly · Rod-like FPEEK · Coil-like PVA · Hydrogen bonding

Introduction

Micelle-like particles formed by polymers in solution have attracted great interest in both theoretical and applied research fields because of their potential applications in catalysis, controlled delivery, artificial cells, light fillers, low dielectric constant materials, acoustic insulation, and photonic crystals [1, 2]. There are many approaches used in forming micelle-like particles (e.g., layer-by-layer assisted template synthesis of core–shell and hollow spheres by Caruso et al. [3], and core–shell gel sphere template synthesis of core–shell composite and hollow spheres by Yang et al. [4]). Among others, it has been reported that block and graft copolymers both have the ability to form micelle-like particles in a selective solvent (which is a good solvent) for one of the blocks or grafts and in a nonsolvent for the other [5–11]. The core of micelle-like particles mainly consists of insoluble blocks (or grafts) in a selective solvent and is surrounded by a corona of soluble blocks (or grafts). In such systems, the driving force for forming micelle-like particles is mainly the repulsive interaction between one of the blocks (or grafts) and the selective solvent [12, 14]. Recently, efforts have been made to produce micelle-like particles via different methods, such as by changing pH values, altering temperature, and chemically modifying one of the blocks or grafts of a copolymer [15–20]. In addition, supramolecules, which are similar to "block copolymers" or "grafts copolymers," formed by two kinds of polymers via hydrogen-bonding interactions or electrostatic interactions have been reported to be able to form micelle-like

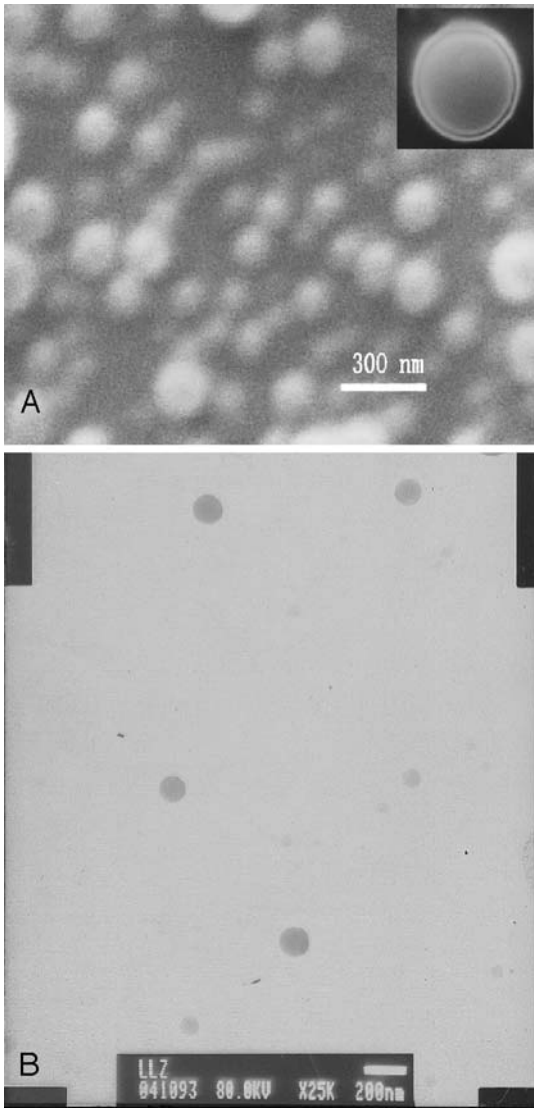


Fig. 1 **a** SEM micrograph of micelles of FPEEK/PVA (1:5, wt/wt). **b** TEM micrograph of micelles of FPEEK/PVA (1:5, wt/wt)

particles in selective solvents, too [21–24]. In most cases, polymers used to form supramolecules always contain coil-like chains. However, supramolecules formed by rigid polymers, instead of coil-like polymers such as polymer polyimide (PI), with coil-like polymer poly(4-vinyl pyridine) (PVPy) have also been reported. PI and PVPy can be mixed in their common solvent $CHCl_3$, which can lead to the formation of submicron hollow spheres, with PI as the inner shell material and PVPy as the outer shell material. The rigid character of PI and its "grafting" to the PVPy chains, and the propensity of rod-like blocks to parallel packing are believed to play important roles in such assembly behavior [25–27]. Our study is about the self-assembly of a rod-like polymer fluorinated poly(ether ether ketone) (FPEEK) and a coil-like polymer PVA. When we used rigid hydroxyl-terminated FPEEK and coil-like PVA as building blocks to fabricate micelle-like particles, we found that they formed micelle-like particles, too. Because of the advantages of FPEEK, we hope that the micelle-like particles formed by FPEEK and PVA would have some more advantages. In this work, the supramolecules formed by hydroxyl-terminated rod-like FPEEK and coil-like PVA via hydrogen-bonding interactions were used as building blocks to form noncovalently connected micelles; the characterization and structural study of resulting micelle-like particles were carried out; and the factors affecting the formation of micelle-like particles were also examined.

Experimental

Materials

3-Trifluoromethyl phenyl hydroquinone was synthesized according to a procedure reported by our group [28]; hydroxyl-terminated trifluoromethylphenyl-substituted FPEEK was prepared by the condensation polymerization of 3-trifluoromethyl phenyl hydroquinone and 4,4′-difluorobenzophenone, which was catalyzed by K_2CO_3 in tetramethylenesulfone, with a 14% excess of (3-trifluoromethyl) phenyl hydroquinone. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 8.3×10^3 and 1.3×10^4, respectively, and the polydispersity was 1.53 according to gel permeation chromatography. The glass transition temperature

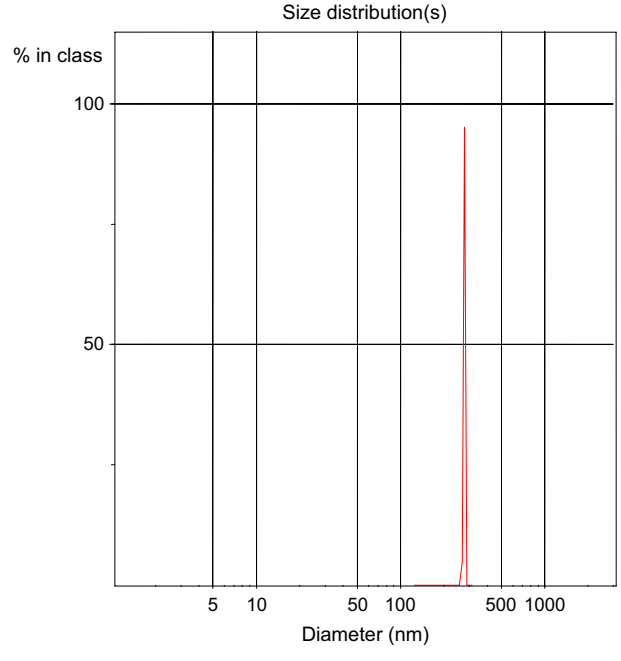
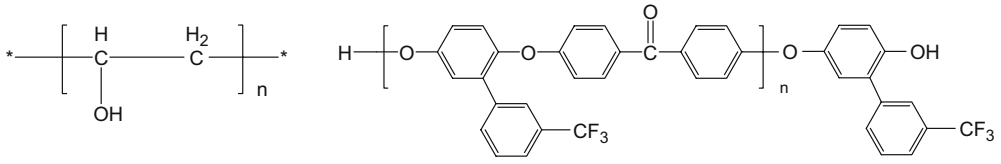


Fig. 2 Hydrodynamic diameter distribution of FPEEK/PVA (1:5, wt/wt) aggregates

Scheme 1 Chemical structure of FPEEK and PVA



(T_g) was 118°C, showing the stiffness of the chains. Polyvinyl alcohol (PVA) was used as received.

Preparation of micelle-like particles

A dispersal system containing micelle-like particles was obtained by mixing the solutions of FPEEK/tetrahydrofolate (THF) and PVA/H_2O at different ratios and by adding a suitable volume of water (which is a good solvent for PVA) and a nonsolvent for FPEEK. The solution turned to slightly bluish, indicating the formation of the micelle-like particles of FPEEK/PVA.

Scanning electron microscopy

Scanning electron microscopy (SEM) observations were made on an SSX-550 electron microscope at an accelerating voltage of 15 kV. For sample preparation, a drop of the aggregate solution was placed on a piece of aluminum foil and then was dried in vacuum at 50°C. All samples for SEM observations were prepared accordingly. The specimens were coated with gold before the SEM observations.

Transmission electron microscopy

Transmission electron microscopy (TEM) observations were made on a JEM-1200EX electron microscope. To prepare the samples, a drop of the aggregate solution was placed on a carbon-coated copper grid followed by solvent evaporation at room temperature.

Dynamic light scattering

Diameter data were obtained on Malvern Zatasizer PCS 3000HSA (λ=633 nm, n=1.40) using the solution containing micelle-like particles.

Results and discussion

Self-assembly of FPEEK and PVA into micelle-like particles

Although FPEEK is a rigid polymer and there are no chemical bonds between FPEEK and PVA, the micelle-like particles with PVA as the outer shell material and with FPEEK as the inner core material could also be formed over a broad composition of w(FPEEK)/w(PVA). They displayed a narrow range of distributions, as indicated by the small value of the polydispersity index (PDI). Fig. 1 shows the SEM and TEM micrographs of micelle-like particles, and Fig. 2 shows the size distribution of micelle-like particles, which was obtained using the same samples for the SEM and TEM measurements. We can see that the average diameters (around 250 nm) of the particles examined by SEM and dynamic light scattering (DLS) methods ($\langle D_h \rangle$=277 nm) are similar, but they are different from the result obtained by TEM (around 150 nm). The reason for the difference is probably because both the cores and the shells of micelle-like particles can be observed by scanning electron and DLS microscopes, but only the inner cores of the micelle-like particles formed by FPEEK can be observed by a transmission electron microscope and the outer shells of the micelle-like particles formed by PVA are

Scheme 2 Formation of micelle-like particle

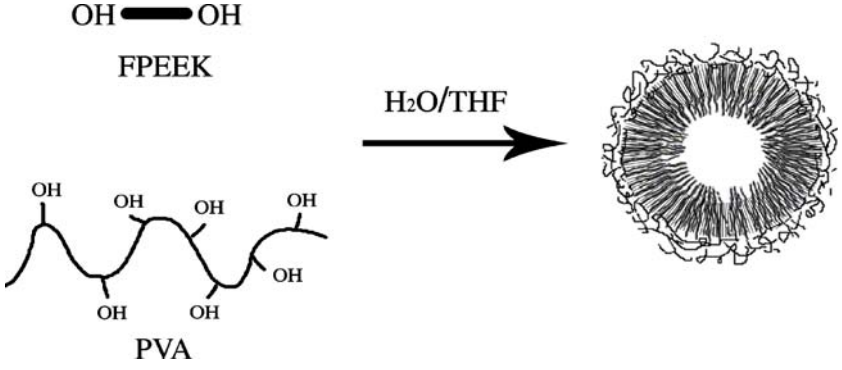


Table 1 Diameters of micelle-like particles vs the FPEEK/PVA weight ratio

FPEEK/PVA (wt/wt)	$\langle D_h \rangle$ (nm)	PDI
4:1	380.2	0.03
1:1	371.3	0.05
1:5	272.3	0.09
1:10	266.5	0.13
1:20	258.4	0.10

too rare to be observed by a transmission electron microscope . According to the above analysis, we can conclude that the micelle-like particles composed of FPEEK and PVA have a core–shell structure, that the cores of the micelles are formed by FPEEK, and that the shells of the micelles are formed by PVA. In addition, the average diameter of the inner FPEEK cores is around 150 nm, and the thickness of the outer shells formed by PVA is around 100 nm. Scheme 1 shows the chemical structures of FPEEK and PVA, and Scheme 2 illustrates the formation and the structure of micelle-like particles.

According to the formation mechanism of micelle-like particles, we can see that the main factors affecting the self-assembly of FPEEK and PVA are the hydrogen bonding between hydroxyl ends of FPEEK and hydroxyl groups of PVA and the packing of the rigid "grafts" (FPEEK). Although hydrogen-bonding interactions between -OH and -OH are not very strong, they are strong enough to be the driving force in forming micelle-like particles. Table 1 and Fig. 3 show the average diameter of micelle-like particles formed with different FPEEK/PVA mass ratios. It can be seen from the data that the average diameter decreases with the decrease of the FPEEK/PVA mass ratio. When the proportion of PVA is increased but the amount of FPEEK that connects PVA with hydrogen-bonding interactions is not increased, contacting areas will definitely increase in order to meet the demand of increasing PVA (i.e., there must be more FPEEK molecules exposed to the surface of FPEEK micelles in order to form more hydrogen bonds with PVA). Therefore, the average diameter of micelle-like particles decreases, and the number of micelle-like particles increases. Table 2 and Fig. 4 show the diameters of the micelle-like particles formed with different THF/H_2O volume ratios. It can be seen from the data that the diameter decreases with decreasing THF/H_2O volume ratios. One reason might be that the increase in the amount of water can promote the dispersal of FPEEK in the THF solution. The other reason might be that, when the volume ratio of water is increased, the concentration of PVA in water is decreased; thus, the possibility of hydrogen bonding between FPEEK and PVA is reduced. Therefore, there must be more FPEEK molecules exposed to the surface of inner FPEEK micelles in order to make the best connection with FPEEK via hydrogen-bonding interactions. Thus, the diameter decreases and the number of micelle-like particles increases. On the other hand, when the amount of water achieves a certain value, the average diameter of micelle-like particles does not increase much because, at this point, increasing amounts of water no longer play an important role in disposing the THF solution and in decreasing the concentration of PVA in water.

Self-assembly of FPEEK and polyethylene glycol

When we used polyethylene glycol (PEG) instead of PVA, micelle-like particles were also formed. But the diameter of

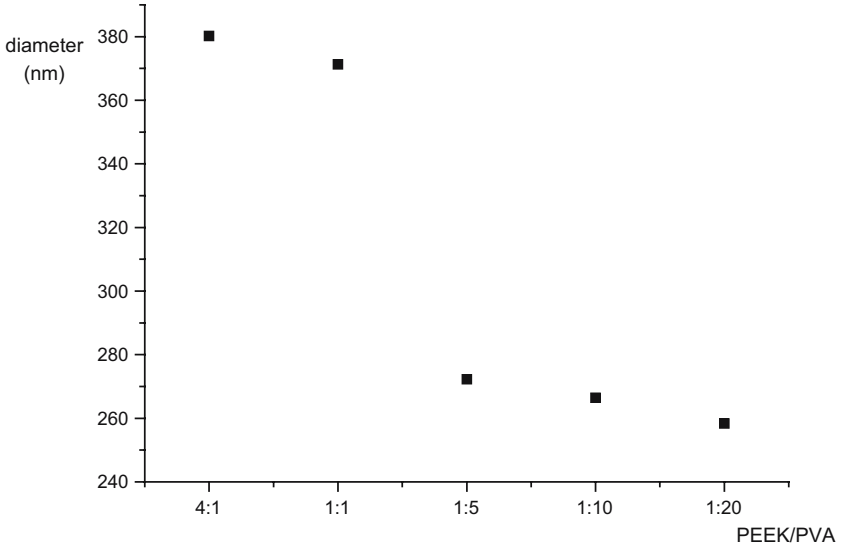


Fig. 3 Dependence of the diameter of micelle-like particles in water on the proportion of FPEEK/PVA (wt/wt)

Table 2 Diameters of micelle-like particles vs the THF/H_2O volume ratio

THF/H_2O	$\langle D_h \rangle$ (nm)	PDI
1:5	399.5	0.04
1:10	316.8	0.07
1:20	304.2	0.11
1:40	281.9	0.09
1:80	276.1	0.13

the micelle-like particles formed by FPEEK and PEG was bigger than that formed by FPEEK and PVA, and the micelles were not homogeneous. Fig. 5 shows the micrograph of a micelle-like particle formed by FPEEK and PEG. The reason for the difference between their diameters is that PVA is soluble in water but is insoluble in THF, while PEG is soluble in both water and THF. Thus, when much water is added into the system, PEG cannot transfer into the water completely, and a great amount of PEG remains in THF. We will continue the study on the factors affecting the formation and structure of this kind of micelle-like particles.

Conclusions

We have prepared micelle-like particles formed by rod-like hydroxyl-terminated FPEEK and coil-like PVA with hydrogen-bonding interactions between them. The products were characterized by means of SEM, TEM, and DLS.

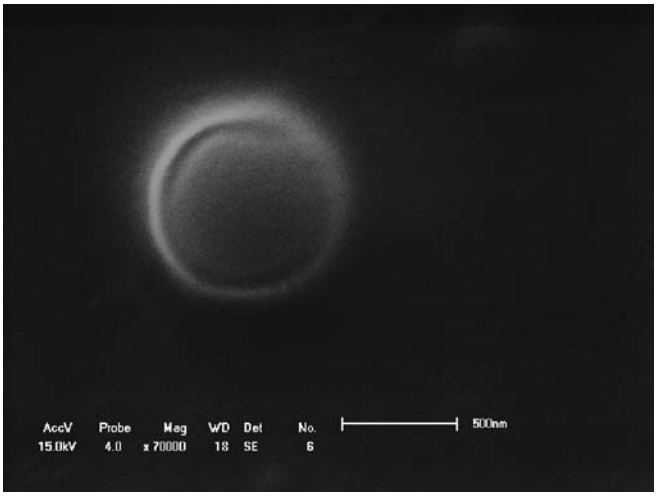


Fig. 5 SEM micrograph of FPEEK/PEG micelles

We have proven that the polymer pair of FPEEK and PVA can form micelle-like particles. The phenomenon does not appear during this process, and the diameters of micelle-like particles are very homogeneous. The diameters of the micelle-like particles examined by SEM and DLS are between 200 and 300 nm, and those examined by TEM are between 100 and 200 nm. The difference in diameters illuminates that micelle-like particles have a core–shell structure. The cores of micelle-like particles are made of FPEEK, and the shells of micelle-like particles are formed by PVA. The average diameter of micelle-like particles is around 200–300 nm, while the average diameter

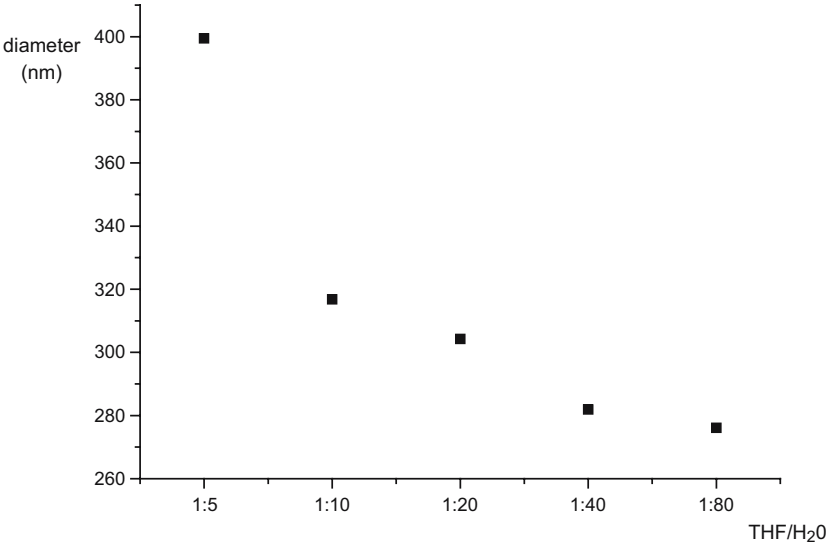


Fig. 4 Dependence of the diameter of micelle-like particles in water on the proportion of THF /H_2O (vol/vol)

of the inner cores formed by FPEEK is around 150 nm. The thickness of the outer shells formed by PVA is about 100 nm. The average diameter of micelle-like particles increases with increasing FPEEK/PVA mass ratios and THF/H_2O volume ratios.

FPEEK and PEG can also form micelle-like particles in water, but the average diameter is bigger than that formed by FPEEK and PVA, and the diameters of micelle-like particles are not homogeneous. The reason why a difference between diameters exists cannot be explained very clearly. This is one of the problems that we will study more in the future.

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