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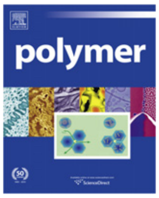

Vesicle formation of polystyrene-*block*-poly (ethylene oxide) block copolymers induced by supercritical CO_2 treatment

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ABSTRACT

A novel route for a preparation of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) block copolymer vesicles induced by supercritical carbon dioxide ($scCO_2$) is demonstrated. When PS-*b*-PEO block copolymer solutions in tetrahydrofuran (THF) are treated with $scCO_2$ at 70 °C for different times, PS-*b*-PEO copolymers first assemble into aggregated spheres; then aggregated spheres change into large compound micelles and finally evolve into vesicles. The possible formation mechanism of the vesicles is discussed.

1. Introduction

In recent years, block copolymer vesicles have been extensively investigated due to their chemical, thermal and mechanical stabilities and their potential applications in numerous fields ranging from cosmetics to anticancer agent [1–5]. In addition, the morphology of the vesicles can be tuned by changing copolymer composition, initial polymer concentration, nature of the solvent, temperature, and other additives. Block copolymer vesicles formed in aqueous media from various amphiphilic block copolymers and mixtures of block copolymers such as polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) and polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA), have been intensively studied [2,3,6] and reviewed by several authors [1,7,8].

The traditional preparation method is a solvent displacement or dialysis method, in which the block copolymer is first dissolved in a organic solvent (such as THF, *N*,*N*-dimethylformamide, or 1,4-dioxane) and then the block copolymer solution is either added dropwise to or dialyzed against water for vesicle formation and removal of the organic solvent. Many groups, such as Eisenberg's and Jiang's have done supereminent wok [2,8].

Supercritical fluids, such as supercritical carbon dioxide ($scCO_2$), have many unique properties, including a liquid-like density, low viscosity, and high diffusivity. $ScCO_2$ has been applied to polymer processing [9] and drug formulation [10] via the rapid expansion of supercritical solution (RESS) process and the supercritical anti-solvent (SAS) process [11]. However, CO_2 is a poor solvent for high molecular weight polymers. Only a few macromolecular species, such as fluoropolymers, polysiloxanes, polyacrylates, and polyethers, possess appreciable solubility in $scCO_2$ [12–14]. The self-assembly behaviors of block copolymers containing these species dissolved in $scCO_2$ have been investigated [12,15–17]. For example, it is found that polystyrene-*block*-poly (1, 1-dihydroperfluodihydroperfluorooctyl acrylate) (PS-*b*-PFOA) in $scCO_2$ form spherical micelles in all conditions [12d,12g]. The micellization behaviors of poly(vinyl acetate)-*block*-poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PVAc-*b*-PTAN) and PVAc-*b*-PFOA block copolymers in $scCO_2$ has also been investigated intensively [12h,16,18–21]. Recently, Lodge et al. reported that the formation of polylactide-*block*-poly(perfluoropropylene oxide) (PLA-*b*-PFPO) vesicles in liquid CO_2. This result partially extends the classic micelle morphology motif from conventional aqueous and organic solvents to potential solvent alternatives, such as condensed CO_2 [17]. Frankowski et al. reported that $scCO_2$ can have a profound impact on the phase behavior of poly(ferrocenyldimethylsilane-*block*-dimethylsiloxane) (PFS-*b*-PDMS) block copolymers [22]. In addition to $scCO_2$, block copolymer micelles have been observed in other supercritical fluids for several systems, including styrene-isoprene block copolymers in tetradecane [23], styrene-diene block copolymers in propane [24,25] and poly(ethylene glycol)-*block*-poly(caprolactone) (PEG-*b*-PCL) in supercritical trifluoromethane [26].

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Although block copolymer micelles, such as spheres, cylinders and vesicles, have been extensively investigated in aqueous or organic media, development of the method to prepare and stabilize vesicles formed from block copolymers is still very interesting and challenging. Similar to water, as a poor solvent for most polymers (except for fluoropolymers and silicones), $scCO_2$ is expected to be a potential solvent alternative to induce micellization of block copolymers in solution. The objective of this work is to study if $scCO_2$ can be used to prepare micelles of amphiphilic block copolymers (such as PS-*b*-PEO), which do not contain fluorine or siloxane components. Here we show that by using $scCO_2$ as a poor solvent, vesicles of amphiphilic block copolymers in solution can be generated. To this end, PS-*b*-PEO copolymers were chosen because the micellar morphologies of the samples have been investigated extensively [6] and the PEO domains have great potential for fabricating functional nanostructures, such as we used PS-*b*-PEO copolymers as templates to prepare various titania nanostructures [27]. PS-*b*-PEO is first dissolved in co-solvent THF, and then the solution is loaded into a high-pressure cell. The cell is charged with CO_2 and heated to setting temperature to bring CO_2 into the supercritical phase for the desired time. During this period, the $scCO_2$ mixes with the THF, changing its polarity and causing self-assembly of the block copolymer. After cooling the system and venting CO_2 from the cell slowly, the vesicle solution is obtained. The sample can be quenched by addition of a large amount of water for the morphology observation. Because many drugs are hydrophobic and have low aqueous solubility, they cannot be encapsulated in water alone. This method may be used to prepare hydrophobic drug-loaded vesicles in future.

2. Experimental section

2.1. Materials

PS-*b*-PEO was purchased from Polymer Source Inc., Dorval, Quebec, Canada. The molecular weight of the PS block was 19 000 and of the PEO block 6400, M_w/M_n was 1.13. The volume fraction of PEO block in the copolymer is 0.25. THF was purchased from Aldrich and used as received. CO_2 (99.99%) was purchased from the Gas Plant of Jinan, China.

2.2. Sample preparation

A known amount of PS-*b*-PEO was dissolved in THF and equilibrated for at least 24 h at room temperature. The copolymer solution (1.0 mL) was loaded into a fixed volume high-pressure cell (10 mL), which was subsequently sealed and pressurized with carbon dioxide. Then the high-pressure cell was heated to setting temperature (typically 70 °C) to bring CO_2 into the supercritical phase. The temperature was controlled to 0.1 °C by immersing the pressure cell into a water bath equipped with a temperature controller. After a treating period (varying from several hours to several days), the cell was cooled to room temperature and depressurized by venting

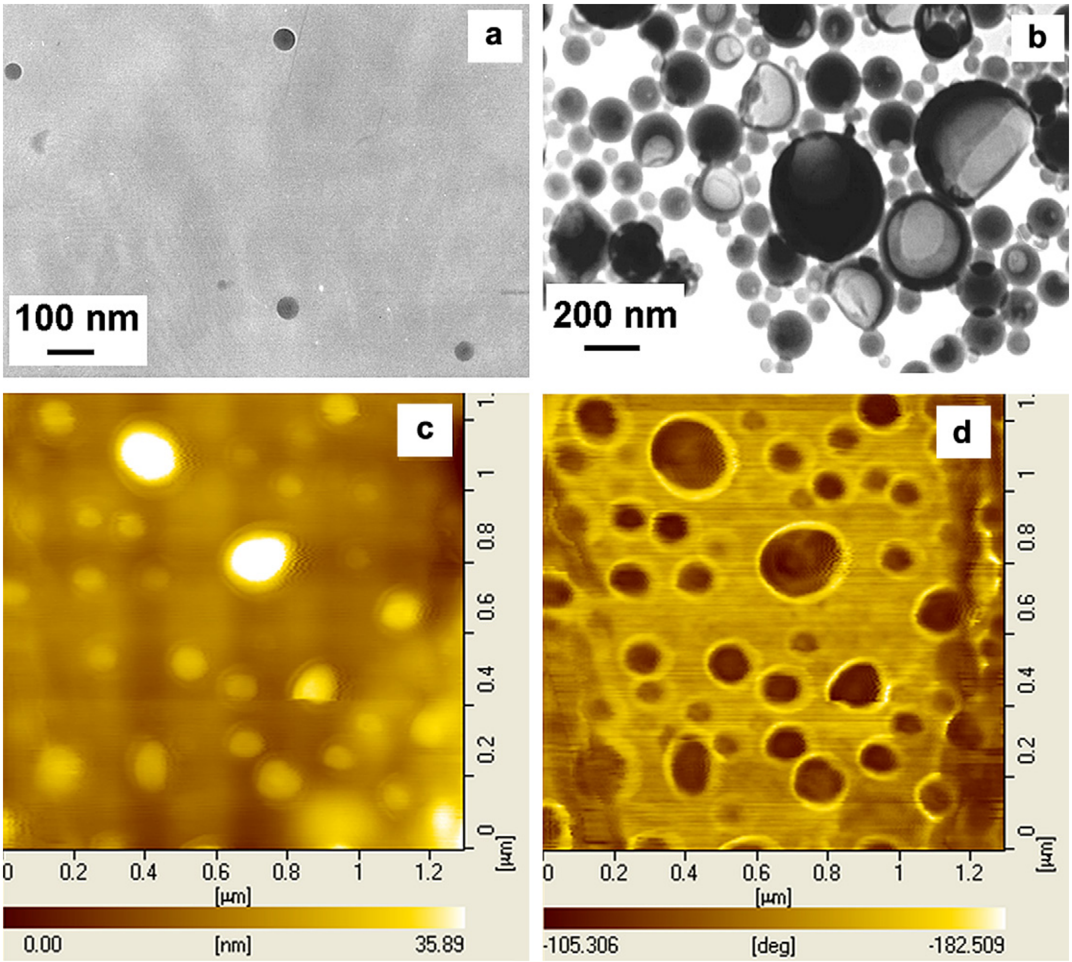

Fig. 1. (a) TEM image of PS-*b*-PEO aggregates obtained by quenching PS-*b*-PEO/THF solution with excess water. (b) TEM image of PS-*b*-PEO vesicles after PS-*b*-PEO/THF solution was treated with $scCO_2$ at 70 °C and 17 MPa for 48 h, depressurized and then quenched in excess water. (c) and (d) AFM height and phase images scanned from the sample (b).

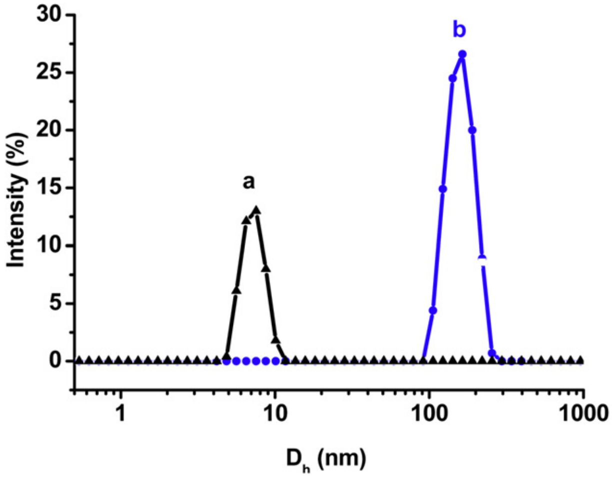

Fig. 2. (a) DLS result of 1.0 wt% PS-*b*-PEO solution in THF. (b) DLS result of 1.0 wt% PS-*b*-PEO solution after treatment in $scCO_2$ at 70 °C and 17 MPa for 48 h, depressurizing and then quenching in excess water.

$scCO_2$ as a vapor from the top. The sample could be quenched by addition of a large amount of water for the morphology observation.

2.3. Characterization

Transmission electron microscopy (TEM) was performed on an H-800 electron microscopy (Hitachi, Japan) operating at 100 kV. The atomic force microscopy (AFM) measurements of the aggregates were performed on SPA300HV with SPI3800 controller, Seiko Instruments Industry, Co., Ltd. The samples for TEM and AFM measurements were prepared by dropping a dilute micellar solution on a carbon-coated copper grid and dried in air. Dynamic light scattering (DLS) measurements were measured with a Zetasizer 3000 HS, Malvern Instruments, Ltd., UK. A He–Ne laser with a wavelength of 632.8 nm was used. The temperature was set to 25 °C and the angle measurement was 90°. Fourier transform infrared spectra (FTIR) measurements were taken on a Spectrum One FTIR spectrometer (Perkin–Elmer Co., USA).

3. Results and discussion

The solubility parameters of PS, PEO and THF are 18.6, 20.2 and 19.4 $(MPa)^{1/2}$, respectively [28]. The values demonstrate that THF is a common solvent for the PS and the PEO blocks. When PS-*b*-PEO is dissolved in THF, a clear and transparent solution is obtained, indicating that no large aggregates are formed. When 1.0 wt% PS-*b*-PEO copolymer solution is quenched in excess water, spherical micelles consisting of a PS core and a PEO corona are observed (Fig. 1a). If the PS-*b*-PEO copolymer solution at 1.0 wt% in THF was treated with $scCO_2$ at 70 °C and 17 MPa for 48 h, cooled to ambient temperature, depressurized and then quenched in excess water, unexpected results are obtained. One can see from the TEM image (Fig. 1b) that the morphologies of the PS-*b*-PEO copolymers are changed into vesicles upon $scCO_2$ treatment. The vesicular nature is evidenced from a high transmission in the center of the aggregates than around their periphery (Fig. 1b). The AFM height and phase images (Fig. 1c) show that vesicles can keep their integrity under the drying process for AFM measurements. A more detailed look at the differences between Fig. 1a–c, the vesicular morphology should be formed in solution due to the $scCO_2$ treatment and not formed during the TEM sample preparation process.

To demonstrate the vesicular structures are induced during $scCO_2$ treatment process rather than during TEM sample preparation process, DLS experiments were performed. The DLS result reveals that PS-*b*-PEO block copolymers are molecularly dissolved in THF (Fig. 2a). The Z-average hydrodynamic diameter of the aggregates is about 7.0 nm. If the 1.0 wt% copolymer solution was treated with $scCO_2$ at 70 °C for 48 h, and quenched with an excess of water, the Z-average hydrodynamic diameter increases to 232 nm (mean peak at 160 nm) with a size distribution range from 122 nm to 468 nm, which is basically matched with that measured from TEM image (165 ± 86 nm, Fig. 1b). Therefore, it is reasonable to conclude that the formation of vesicles takes place upon the $scCO_2$ treatment.

To demonstrate the versatility of this method, copolymer concentration is changed to examine the possible effect on the morphologies of the PS-*b*-PEO aggregates. It is found that the similar morphologies are formed if the copolymer concentrations are varied from 1.0 wt% to 0.4 wt%. The TEM image (Fig. 3a) and the DLS result (Fig. 3b) of the 0.4 wt% copolymer solution upon the $scCO_2$ treatment and quenching with an excess of water illustrate that PS-b-PEO vesicles are also formed.

It is well known that block copolymers usually undergo phase transition starting from spheres via cylinders and then going to vesicles. The morphological changes of PS-*b*-PAA and PS-*b*-PEO micelles have been investigated extensively [6,29]. The morphological changes of PS-*b*-PEO and P4VP-*b*-PS-*b*-P4VP micelles from cylinders to vesicles are also via intermediate micelles (compound micelles or lamellae) [6,30]. Discher et al. recently reported the

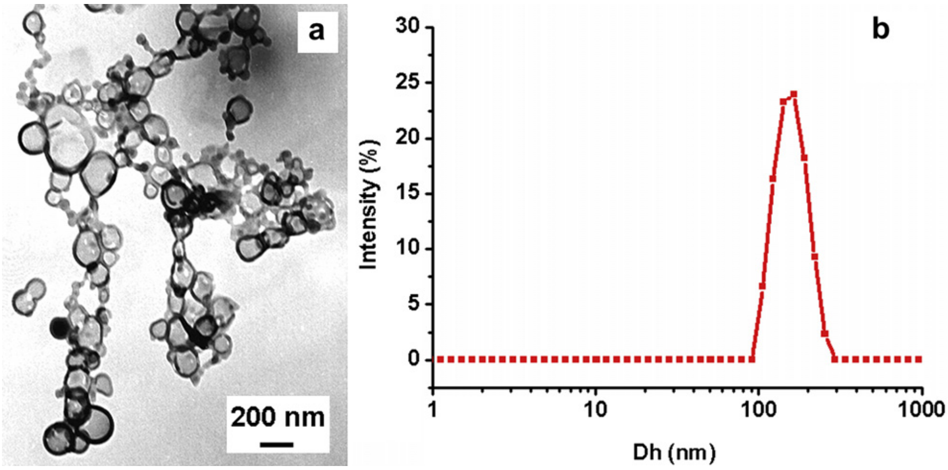

Fig. 3. The TEM image and DLS result of PS-*b*-PEO aggregates obtained by treating 0.4 wt% PS-*b*-PEO solution in $scCO_2$ at 70 °C and 17 MPa for 48 h, depressurized and then quenched with excess water.

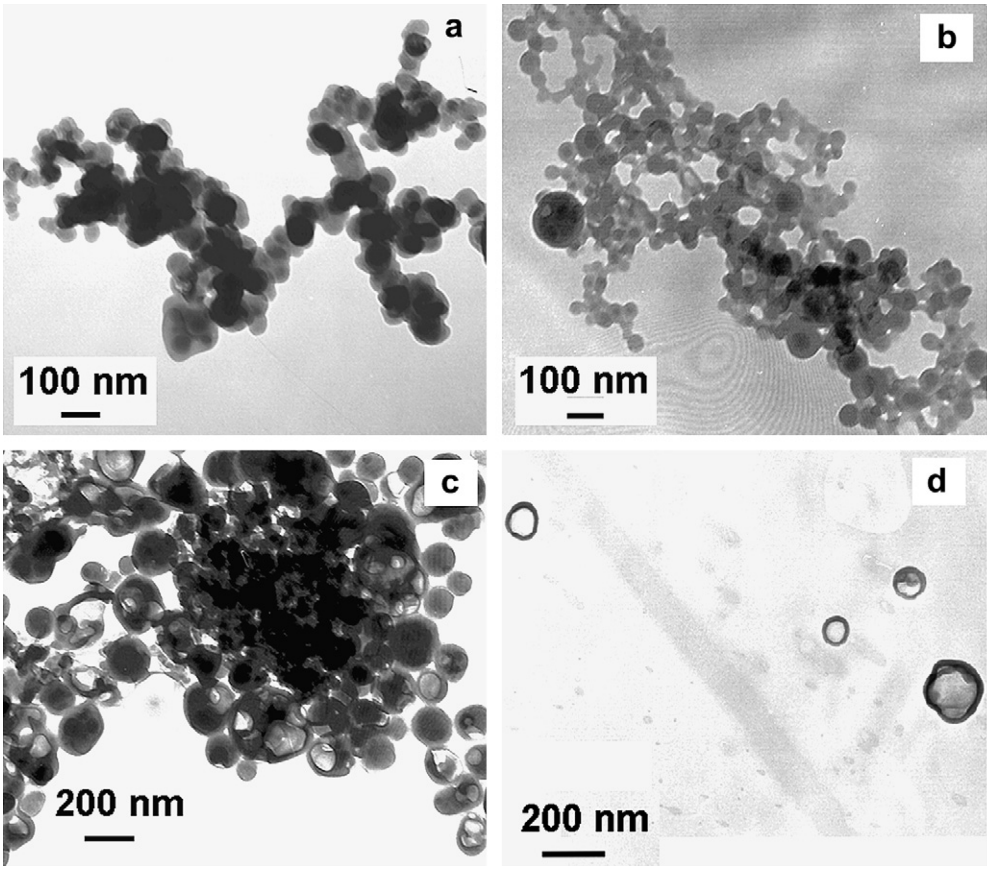

Fig. 4. The TEM images of PS-*b*-PEO aggregates obtained by treating 1.0 wt% PS-*b*-PEO solution in $scCO_2$ at 70 °C and 17 MPa for different times, depressurized and then quenched with excess water. (a) 3 h, (b) 6 h, (c) 12 h, and (d) 24 h.

vesicles form via a network-like structure [31]. Recently, the Müller group investigated the self-assembly of polybutadiene-*block*-poly (2-vinylpyridine) (PB-*b*-P2VP) diblock copolymers in aqueous media. It is proposed that the cylinders assemble into large network-like structures and hollow globules and then release smaller vesicles upon completion of the phase transition [32].

To analyze the formation process of vesicles, the effect of the treating time on the morphologies of the PS-*b*-PEO aggregates was investigated. Fig. 4 shows the TEM images of PS-*b*-PEO aggregates obtained from the copolymer solutions after treatment with $scCO_2$ at 70 °C for different times and then quenched with an excess of water. For relatively short treating time (3 h), aggregated spheres are detected (Fig. 4a). As the treating time increases, the shape of the aggregates changes slowly. However, large spherical aggregates or compound micelles appear (Fig. 4b). When the treating time is further increased to 12 h, in addition to spherical micelles, vesicles are observed (Fig. 4c). Further increase treating time leads to the formation of vesicles. It is also noted that interconnected aggregates (Fig. 4) are mostly observed, which are attributed to the quality of water for PEO is not good enough and PEO chains might be less effective in providing colloidal stabilization to the aggregates upon quenching the $scCO_2$ treated sample in water [6b].

The effect of CO_2 pressure was also studied with different pressures of 15 and 18 MPa at 70 °C. For 15 MPa, the formation of

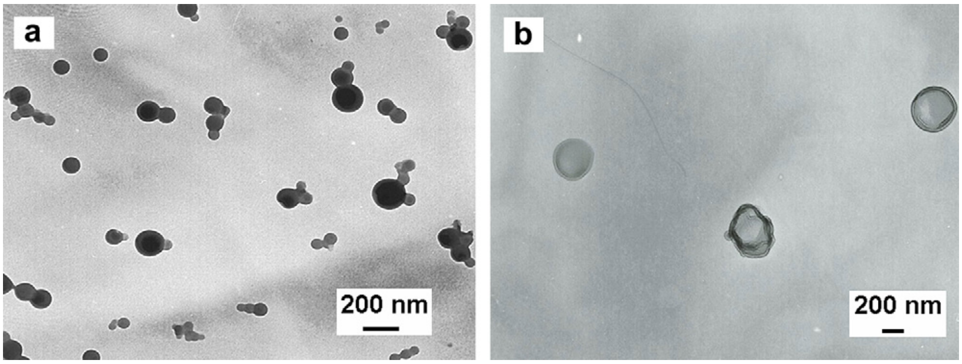

Fig. 5. The TEM images of PS-*b*-PEO aggregates obtained by treating 1.0 wt% PS-*b*-PEO solutions in $scCO_2$ with pressures of 15 MPa (a) and 18 MPa (b) at 70 °C for 48 h, and then quenched in excess water.

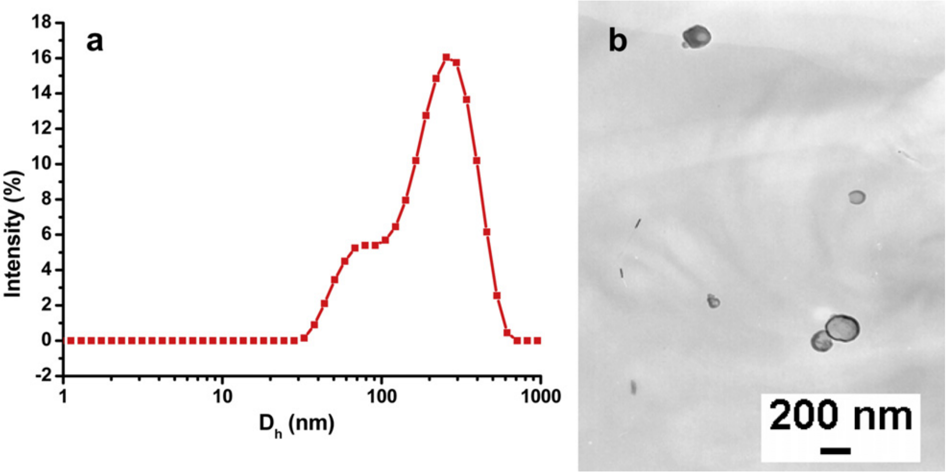

Fig. 6. DLS result and TEM image of the PS-*b*-PEO aggregates prepared by treating PS-*b*-PEO solution in $scCO_2$ at 70 °C and 17 MPa for 48 h, and then the solution was cooled to room temperature and released directly into an excess of water.

spherical aggregates is observed (Fig. 5a). For 18 MPa, vesicles are observed (Fig. 5b). In this work, vesicles can be obtained in the pressure range 16 ∼ 20 MPa at 70 °C, indicating that pressure has an influence on the morphologies of the PS-*b*-PEO aggregates.

Understanding the formation mechanism of vesicles induced by CO_2 is very challenging. At present it is very difficult for us to give an exact mechanism on this. To understand the vesicle formation mechanism, two control experiments were carried out. First, the PS-*b*-PEO solution in THF was treated at 70 °C for 48 h and cooled to room temperature and then quenched in excess water, similar to Fig. 1a, small spherical aggregates were observed (not shown). Second, the PS-*b*-PEO solution in THF was pressured through addition of CO_2 gas to form an expanded copolymer solution, and then kept at 70 °C for 48 h. The expanded copolymer solution was cooled to room temperature and released directly into a large amount of water (a poor solvent for PS and a good solvent for PEO) to freeze the morphology of the copolymer aggregates formed during $scCO_2$ treatment process. The DLS result and TEM image of such PS-*b*-PEO aggregates are shown in Fig. 6. The z-average hydrodynamic diameter of the aggregates obtained from Fig. 6a is 200 nm (the main peak at 265 nm). Compared with Fig. 2b, a peak at 75 nm was observed, which might be attributed to the PS-*b*-PEO micelles. However, the peak corresponding to PS-*b*-PEO unimers was not detected in Fig. 6. TEM image shows that vesicular structures are also formed (Fig. 6b). Therefore, it is reasonable to deduce that the vesicular structures have been formed in the THF/$scCO_2$ mixture and retained upon release in water.

It is known that CO_2 is nonpolar and it is soluble in alkanes and other organic liquids such as toluene and benzene, at elevated pressures [33,34]. THF is natural solvent for PS and PEO blocks, and no micellization behavior takes place with the block copolymer in THF. When the $scCO_2$ is introduced into the copolymer solution containing both THF and PS-*b*-PEO molecules, due to the volume expansion in the presence of $scCO_2$, the THF/$scCO_2$ mixture become poorer for PEO and PS blocks, that is the solvation power decreases, the copolymer chains will change their conformations, and as a consequence, aggregation or micellization of PS-*b*-PEO copolymers takes place. The micelles (including their cores) or aggregates contain solvent THF and CO_2 molecules. It has been reported that amorphous PEO can be clearly swollen by $scCO_2$, that is, CO_2 can be localized within the amorphous PEO regions [35]. It has also been reported that the $scCO_2$ can insert into surfactant tail region of Triton X-100/cyclohexane reverse micelles, or the regions of micelles to swell the micelles [36]. Due to specific interactions between the ether oxygens and CO_2, it can be deduced that PEO is relatively more CO_2-philic than PS [21]. It is found that the vesicular structure remain when the block copolymer solution treated with $scCO_2$ is equilibrated for 20 days at ambient temperature and pressure (not shown). To prove that CO_2 molecules inserted in the copolymer solution exist after depressurization, IR spectra of the PS-*b*-PEO/THF solution before and after treatment with $scCO_2$ were measured (Fig. 7). Comparison of Fig. 7a and b, it is found that a band at 2335 cm^{-1} appears after THF was treated with $scCO_2$, indicating that CO_2 can solubilize in THF even if after depressurization. Compared with the characteristic absorption band of CO_2 (2350 cm^{-1}), the shift of the band positions to low wave number reveals the existence of some interactions between the THF or PEO and CO_2 molecules. Therefore, it can be concluded that the property of the solvent has been changed after introduction of $scCO_2$. The number of CO_2 molecules inserted into PEO domains is larger than that into PS domains. The small aggregates are formed first in THF/$scCO_2$ mixtures. With the increase of treating time, the large aggregates or compound micelles are formed, and then the large aggregates or compound micelles change into vesicles. That is, upon depressurization of the expanded copolymer solution, the aggregates of vesicular morphology are obtained.

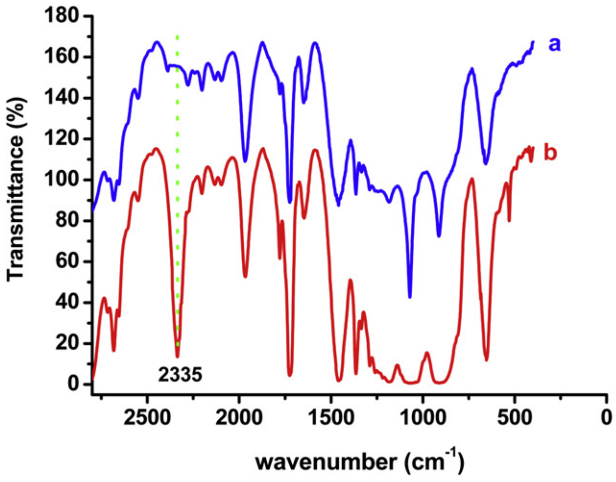

Fig. 7. IR spectra of the PS-*b*-PEO/THF solution before (a) and after (b) treatment with $scCO_2$ at 70 °C and 17 MPa for 48 h, cooling to room temperature and depressurization.

4. Conclusions

It is demonstrated a novel route for a preparation of block copolymer vesicles induced by $scCO_2$ treatment. When PS-*b*-PEO diblock copolymer solutions are swollen with $scCO_2$, aggregation or micellization of PS-*b*-PEO copolymers takes place and aggregated spheres form. With the increase of the treating time, spheres assemble into large compound micelles and then into vesicles upon completion of the phase transition. The approach might be used to prepare hydrophobic drug-loaded polymeric nanoparticles.

Acknowledgements

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