Triblock copolymer micelles as templates for preparation of mesoporous niobia thin films

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Abstract. The micelle formation of commercially available Pluronic PE 6800 (PEO-PPO-PEO triblock copolymer) was studied by means of a dye solubilization method, and the solubility of 1,6-diphenyl-1,3,5-hexatriene in aqueous solutions of the copolymer with concentrations ranging from 0.05 to 20 % w/v was studied by recording the transmission and emission spectra of the solutions using UV-VIS and photoluminescense spectroscopy, respectively. Further, mesoporous Nb2O5 films using PE 6800 micelles templates were obtained through sol-gel using spin-coating; their morphology, structure and optical properties were studied by TEM, SAED and nonlinear fitting of reflectance measurements. The possible application of the films in optical sensing of vapors was demonstrated and discussed.

1. Introduction

The critical micelle concentration (CMC) is defined as the concentration at which thermodynamically stable polymolecular aggregates, the so-called micelles, start forming. The copolymer studied in this work was commercially available Pluronic PE 6800 (BASF), which consists of a central poly(propylene oxide) (PPO) block flanked by two poly(ethylene oxide) (PEO) blocks with formula PEO27PPO28PEO27. Pluronic are regarded as amphiphilic copolymers, where PEO is the hydrophilic part of the macromolecule and PPO, the hydrophobic segment. The micellization of amphiphilic block copolymers is more complex than that of low-molecular weight surfactants and is usually characterized by a lack of a sharp CMC or a critical micelle temperature (CMT) [1]. There are several techniques for CMC determination based on plotting a suitable physical property as a function of the polymer concentration, usually including measurements of absorption, emission, conductivity, size etc. [2, 3]. Among the most commonly used ones is the so-called dye solubilization method, whereby a hydrophobic dye is solubilized in the hydrophobic micelle interior, giving characteristic peaks, whose intensities are plotted versus the polymer concentration, the CMC being determined from the abrupt change in the curve [4].

In the work reported, we used a different approach. Instead of the intensity, we monitored the wavelength shift of the characteristic absorption and emission peaks of the hydrophobic dye 1,6-

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diphenyl-1,3,5-hexatriene (DPH) dissolved in aqueous solutions of the studied copolymer with different concentrations, thus determining the CMC from the abrupt change in the curve. The micelle solution was further used as a template for fabrication of mesoporous Nb$_2$O$_5$ films following the evaporation-induced self-assembly method [5]. The morphology, optical properties and sensing response to vapors of these films were compared with properties of porous Nb$_2$O$_5$ films templated with polymers whose concentration was below the CMC. Accordingly, we demonstrate and discuss the role of the micelles in the formation of porosity.

2. Experimental part

In order to study the micelles formation, Pluronic PE 6800 was dissolved in deionized water in concentrations from 0.05 to 20 % w/v and the hydrophobic fluorescence probe 1,6-diphenyl-1,3,5-hexatriene (DPH) dissolved in methanol in a concentration of 0.4 mM was added into copolymer solutions (25 µl DPH in 2.5 ml solution) and left for at least three hours in dark to equilibrate [3]. Transmission and emission spectra of the copolymer solutions containing DPH were measured using a Cary 5 UV-VIS-NIR spectrophotometer (Varian) and a Fluorolog 3-22 spectrofluorimeter (Horiba JobinYvon), respectively. The hydrodynamic diameter of micelles was studied by dynamic light scattering (DLS) using a Nano ZS Zetasizer (Malvern).

Porous Nb$_2$O$_5$ thin films were deposited by spin coating of niobium sol mixed with Pluronic PE 6800 solutions (5 and 20 % w/v) in a volume ratio of 5 to 1 and annealed at a temperature of 320 °C for 120 and 180 min in the cases of 5 and 20 % w/v, respectively. The Nb sol was synthesized using NbCl$_3$ and ethanol according to the recipe in [6]. The effective optical constants (refractive index, $n$, and extinction coefficient, $k$, along with the film thickness, $d$, were determined through non-linear curve fitting of reflectance spectra measured at normal light incidence by the UV-VIS-NIR spectrophotometer [6]. The porosity level in the films was evaluated using both the Bruggemann effective medium theory and the calculated effective refractive indices [7], and additionally visualized by TEM images of the films. The films for TEM analyses were prepared on soluble substrates of NaCl. After dissolution of the substrates in water, the films were transferred on Cu grids for direct observation by TEM (JEOL JEM 2100). The analyte adsorption was studied by measuring the reflectance spectra of the films prior to and after exposure to probe molecules (acetone in our case) in a homemade cell and saturator system [8]. The reflectance spectra measured were further used to determine the refractive index change due to acetone vapor adsorption [7].

3. Results and discussion

To study the micelles formation in a PE 6800 aqueous solution, we used three methods: UV-VIS spectroscopy, photoluminescence and DLS measurements. The idea was to find the concentration at which some property of the copolymer solution (absorbance, emission or particle size) undergoes a sharp change.

In the first two methods, a hydrophobic fluorescence probe (DPH) is used, which has different absorbance and fluorescence in hydrophilic and hydrophobic environments, thus providing a sensitive indicator of micelle formation. The fact that micelles can solubilize relatively large amounts of compounds of poor solubility in water has been used to determine the onset of micelle formation [9]. Figure 1(a) shows typical absorbance of DPH in water and methanol. The influence of the environment is obvious – a distinctive change in the spectra is seen – from one weak peak in water centered at 310 nm to three distinctive peaks in methanol. As Pluronic concentration is increased, solubilization of the dye takes place: the peak at 310 nm shifts toward the longer wavelengths and the characteristics peaks of DPH in methanol become more pronounced (figure 1 (b)). Instead of monitoring the absorption values at 357 nm, as generally accepted, we plotted the wavelength position of the characteristic absorption peak of DPH in water as a function of the copolymer concentration (figure 1(c)). We believe that we thus improved the sensitivity of micelles formation detection, because no substantial amount of DPH needs to be solubilized in order for the characteristics peaks to
appear. As seen, the dependence exhibits an abrupt change at PE 6800 concentration of 13.1 %, which we defined as the CMC value.

![Figure 1](image1.png)

**Figure 1.** (a) DPH absorbance in water and methanol (25 µl of 0.4 mM stock solution of DPH in methanol is added in 2.5 ml water or methanol); (b) PE 6800 aqueous solutions absorbance with concentrations as denoted mixed with DPH (25 µl DPH stock solution in 2.5 ml aqueous copolymer solution); (c) wavelength position of the DPH characteristic absorption peak in a PE 6800 aqueous solution as a function of the copolymer concentration.

To confirm the CMC values obtained from UV-VIS spectroscopy, we used photoluminescence measurements of DPH in aqueous PE 6800 solutions with different concentrations (figure 2(a)). Instead of tracking the emission intensity with the copolymer concentration, we monitored the shift of the emission peak at 441 nm that is characteristic for DPH in water.

![Figure 2](image2.png)

**Figure 2.** (a) Photoluminescence (PL) intensity of DPH in aqueous solution of PE 6800 with concentrations as denoted in % w/v; (b) peak position of the maximum PL intensity as a function of the PE 6800 concentration.

As the copolymer concentration is raised, the peak shifts toward the shorter wavelengths; at 20 % w/v it matches the characteristics peak of DPH in methanol (428 nm). The plot of peak position as a function of the PE 6800 concentration is presented in figure 2(b). The CMC can be determined from the inflection point of the curve. The value obtained is 12.6 %, which is very close to the value of CMC as determined by UV-VIS spectroscopy (13.1 %).

The DLS measurements conducted (figure 3) confirmed the presence of particles with a hydrodynamic diameter from 4 to 25 nm. The micelles size in PE 6800 (20 % w/v) gradually increased with the temperature, starting from 3 nm and reaching a size of 12 nm. For PE 6800 (5 % w/v) a sharp increase of the size was observed at temperatures above 40 °C, reaching the highest value of 27 nm at 50 °C, where the size began decreasing. At all studied temperatures, a mono-modal distribution of
micelle size was observed, except for the temperature range around 40 °C, where micelles with a bi-modal distribution existed.

The next step in our investigation included preparation of mesoporous Nb2O5 films using a PE 6800 micelle solution as a template. To check the role of the micelles in the pore formation, we prepared films templated with copolymer aqueous solutions with concentrations 5 and 20 % w/v – one below and another one above the CMC, respectively.

![Figure 3](image_url)

**Figure 3.** (a) Dynamic light scattering curves (DLS) of 5 % w/v aqueous solution of PE 6800 measured at different temperatures denoted by the numbers on the graph; (b) calculated hydrodynamic diameter versus the temperature for 5 and 20 % w/v aqueous solutions of PE 6800.

As seen in figure 4, adding PE 6800 generated porosity in the thin films, which more pronounced at a copolymer concentration of 20 % w/v. The approximate size of the pores was 3-4 nm in the case of 5 % w/v and 7-8 nm in the case of 20 % w/v. In both cases, the porosity was non-periodic. Selected area electron diffraction (SAED) (inset in figure 4(a)) confirmed that all samples were amorphous. This is in line with our previous results showing amorphous status at 320 °C and crystalline at 450 °C [10]. The refractive index and extinction coefficient of the films, along with their thickness, are presented in table 1.

Adding Pluronic PE 6800, resulted in a decrease in the effective refractive index, while the thickness increased, most pronounced for the films obtained with a copolymer concentration of 20 % w/v. This can be expected, because after annealing the polymer degrades and leaves empty spaces (pores) in the film. The growth in thickness is due to the copolymer addition and is an indication for the lack of contraction in the films after annealing. The extinction coefficient values were

![Figure 4](image_url)

**Figure 4.** TEM and SAED (inset) images of Nb2O5 thin films prepared using PE 6800 aqueous solution as template with concentration of (a) 0, (b) 5 % w/v and (c) 20 % w/v (the bar is 100 nm).
Table 1. Refractive index (n) and extinction coefficient (k) at wavelength of 600 nm, thickness (d), volume fraction of pores (f_{air}), change in n after exposure to acetone (Δn_{ac}) and volume fraction of acetone (f_{ac}) in the Nb_2O_5 films deposited using different concentration of Pluronic PE 6800 as a template.

| PE conc.(% w/v) | n_{600} | k_{600} | d (nm) | f_{air} (%) | Δn_{ac} | f_{ac} (%) |
|----------------|---------|---------|--------|-------------|---------|-----------|
| 0              | 2.18    | 0.020   | 64     | 0           | 0       | 0         |
| 5              | 1.87    | 0.018   | 80     | 24          | 0.0015  | 0.4       |
| 20             | 1.49    | 0.019   | 146    | 54          | 0.028   | 6.7       |

the same for all samples. The refractive index dispersion curves calculated were further used to determine the volume fraction of air in the films [7]. In the calculations we assumed the film without template as being the dense phase. The data in Table 1 shows that f_{air} increased from 24 % to 54 % when a copolymer with concentration of 5 or 20 % w/v was used for template, respectively. The refractive index change due to adsorption of acetone vapor in the pores was 0.028 in the case of the film templated with micelles, and only 0.0015 for the one consisting of 5 % w/v polymer. The difference in the acetone volume fraction adsorbed (more details on the calculation can be found in [7]) was also significant: 6.7 % when using micelles templates, and 0.4 % when using a polymer with concentration below the CMC. A possible reason may be the different organization of the pores system in the two films, with the more opened porosity in the first case favoring a higher adsorption of analytic vapor. Another possibility is the different degree of hydrophilicity/hydrophobicity of the samples responsible for different states of the pores: empty or partially filled with water from the ambient. Whatever the reason, more experiments are needed to confirm these assumptions. However, the change obtained in the refractive index of about 0.03 after exposure to acetone vapor is significant and guarantees a successful implementation of the samples studied as sensitive media for chemooptical sensors.

4. Conclusions
A dye solubilization method, along with UV-VIS transmittance and photoluminescence (PL) measurements, were used to determine the critical micelle concentration (CMC) of the triblock copolymer PEO-PPO-PEO (Pluronic PE 6800). A new approach was adopted for CMC determination, consisting in monitoring the wavelength shift of characteristic absorption and emission peaks of the DPH (1,6-diphenyl-1,3,5-hexatriene) in hydrophilic and hydrophobic environments as a function of the polymer concentration, instead of commonly-accepted observation of the peaks intensities. A very good agreement was achieved between the CMC values obtained by the two methods: 13.1 % determined by UV-VIS spectroscopy, and 12.6 % by PL measurements. The positive role of polymer micelles for pore formation in Nb_2O_5 films was demonstrated by using PE 6800 with concentration bellow and above CMC as templates. The micelle solution led to the formation of 54 % porosity, while in other case the film porosity was 24 %. Moreover, the change in the refractive indices of the porous films obtained using micelles after acetone vapor exposure was about 0.03, while the films deposited with polymer templates below CMC exhibited a very low response, namely, 0.0015.

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