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Stability and dynamics of silicate/organic hybrid micelles

Stabilité et dynamique de micelles hybrides silicates/organiques

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ABSTRACT

The formation of silicate/organic hybrid micelles is an important milestone in the two-step synthesis of mesoporous silica with polyethyleneoxide (PEO) nonionic structure directing agents (C.R. Chimie 8 (2005) 579). Unlike many inorganic/organic hybrid micelles, these objects have the inorganic component as a diffuse layer positioned at the periphery of the initial micelles and interacting with the hydrophilic polyoxyethylene palisade. We studied how this additional inorganic layer can modify the structure and dynamics of micelles prepared with different types of nonionic surfactants using steady-state and time-resolved fluorescence and dynamic light scattering. Our results show that these hybrid micelles still possess a versatile behavior, which allows them to adapt reversibly to temperature changes. This silicate layer tends to stabilize and consolidate the micelle structure, especially close to the cloud point of critical micelle temperature for polypropyleneoxide (PPO)-based triblock copolymers. Their internal structure is only slightly disturbed by the silicate layer, which reduces the molecular exchanges a little bit. Among other results, we managed to elucidate why mesoporous silica prepared with Pluronic P123, according to our synthesis, stands a dramatic structural change from wormhole to hexagonal structure at 40 °C. Our dynamic light scattering study shows that 40 °C is a critical temperature corresponding to a sphere-to-rodlike structural transition of hybrid micelles, which is not observed with pure micelles.

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RESUME

La formation de micelles hybrides organiques/inorganiques est une étape importante dans la synthèse en deux étapes des silices mésoporeuses obtenues avec des agents structurants de type copolymère diblock polyéthylène glycol (PEG) (C. R. Chimie 8 (2005) 579). Contrairement à la plupart des objets décrits comme micelles hybrides organique/inorganique, ces objets micellaires présentent leur composant inorganique positionné comme une couche diffuse à la périphérie de la micelle initiale, et en interaction avec la couronne hydrophile formée des chaînes PEG. Nous avons étudié par fluorescence en mode statique et résolu en temps, ainsi que par spectroscopie de photocorrélation, comment l'ajout d'une telle couche inorganique peut modifier la structure et la dynamique de micelles préparées avec différents types de tensioactifs non ioniques. Nos résultats démontrent que ces micelles hybrides possèdent un comportement très versatile, leur permettant de s'adapter réversiblement aux variations de température. Ces couches de silicate tendent à stabiliser et renforcer la structure micellaire, en particulier lorsqu'on s'approche du point de trouble (CP) et de la température micellaire critique (CMT) pour les copolymères triblock à base de polypropylène

Mots-clés:

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oxyde. Leur structure interne est déstabilisée légèrement par la couche de silicate, avec pour conséquence une faible réduction des échanges moléculaires. Entre autres résultats, nous sommes parvenus à trouver la raison pour laquelle les silices mésoporeuses préparées avec du Pluronic™ P123, selon notre mode de synthèse, sont affectées par un changement structural majeur à 40 °C, avec la formation d'une structure hexagonale en nid d'abeille. Notre étude par spectroscopie de photocorrélation montre que 40 °C correspond à une température critique avec une transition de micelle sphérique en micelle allongée, une telle transition n'étant pas observée pour les solutions micellaires pures.

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1. Introduction

There is an increasing demand of integration of functionalities in nanomanufacturing of advanced materials. This leads to a growing trend in creating nanobuilding blocks with integrated components at the molecular scale. In this domain, which belongs to integrative chemistry or syntheses [1–3], the need of intimate interactions between building blocks becomes more and more expected.

Among the list of potential nanobuilding blocks, hybrid micelles offer this type of intimate combination of composite nanostructures and specific interactions at the mesoscale. Organic hybrid micelles combine amphiphiles and polymers [4,5], whereas inorganic/organic hybrid micelles are usually made of nanoparticles embedded in the core of the micelle and wrapped with amphiphiles [6–10]. We have reported how mesoporous silica can be synthesized with a fine-tuning of pore size, when nonionic amphiphilic copolymers are used in combination of a fine adjustment of the synthesis temperature [11]. This fine-tuning of the silica mesostructure is allowed by the intermediary formation of stable silicate/surfactant hybrid micelles [12]. Unlike most of the hybrid organic/inorganic micelles reported so far, these hybrid micelles have their inorganic component as a diffuse shell of weakly reticulated silicate oligomers around the organic core. This diffuse layer of silicates should confer a higher dynamics to the hybrid micelles than when nanoparticles are involved. Unlike ionic surfactants, polyethyleneoxide (PEO)-based diblock copolymer micelles possess specific properties, because of the nature of the hydrophilic interactions, with by example, the cloud point (CP) temperature corresponding to the temperature beyond which the hydrophilic behavior is lost as a result of the breakage of H-bonds. As the temperature rises, the PEO chains progressively dehydrate, resulting in chain stretching, and leading to a reversible micelle size increasing. Another property of PEO-polypropyleneoxide (PPO)-based triblock copolymers is the critical micelle temperature (CMT), the minimum temperature below which the PPO chains are not hydrophobic enough.

These hybrid micelles are the fundamental intermediates of our two-step synthesis pathway, where small changes in synthesis parameters, especially temperature, can lead to drastic modifications of the final material [13]. Therefore, the full description of the structure of these hybrid micelles and their temperature-dependent dynamics is an important requirement for the complete understanding of the material

mesostructuring, and a way to explore how different nonionic templates can direct the formation of different mesoporous structures. In the present study, we used temperature-dependent dynamic light scattering (DLS) to follow the micelle size evolution. Steady-state and time-resolved fluorescence studies were used to probe the internal structure and dynamics of these hybrid micelles and explore how the presence of the outer silicate shell modifies these characteristics, compared with pure micelles.

2. Experimental section

2.1. Materials

Except when specified, all chemicals were purchased from Sigma Aldrich and used as received. The chemicals used for the preparation of the hybrid micelles combined a nonionic surfactant selected among several are as follows: Tergitol 15S12 (polyoxyethylene (12) pentadecyl ether $\text{CH}_3(\text{CH}_2)_{14}(\text{EO})_{12}$; $d = 0.993$; $M_w = 740$ g; CP = 89), Tergitol 15-S-30 (polyoxyethylene (30) pentadecyl ether $\text{CH}_3(\text{CH}_2)_{14}(\text{EO})_{30}$; $d = 1.055$; $M_w = 1520$ g; CP > 100 °C), Tergitol NP-10 (nonylphenol ethoxylate; $d = 1.060$, $M_w = 645$ g; CP ≈ 63 °C), Tween 20 (polyoxyethylene (20) sorbitan monolaurate; $d = 1.095$; $M_w = 1230$ g; CP = 76 °C), Brij 98 (polyoxyethylene (20) oleyl ether; $d = 1.070$; $M_w = 1150$ g; CP > 100 °C), Brij 35 (polyoxyethylene (24) dodecyl ether; $d = 1.060$; $M_w = 1198$ g; CP > 100 °C), Pluronic P123 (triblock copolymer $(\text{PEO})_{20}-(\text{PPO})_{70}-(\text{PEO})_{20}$; $d = 1.040$; $M_w = 5800$ g; CP = 90 °C), and tetraethylorthosilicate (TEOS: $\text{Si}(\text{CH}_2\text{CH}_3)_4$; $M_w = 208$ g). The pH of water (deionized water, PALL Cascada IX with 18 M Ω quality) was adjusted with hydrochloric acid (Fisher Scientific) at pH 2. Fluorescence studies used tetrahydrofuran (Caledon) and pyrene.

2.2. Sample preparation

Silica hybrid micelles were prepared by first dissolving the surfactant into a solution of hydrochloric acid diluted to pH 2 under magnetic stirring. After full dissolution of the surfactant, TEOS was added at room temperature to the solution dropwise under stirring at 500 rpm. The solution turned cloudy upon immediate addition of the TEOS. The solution remained under stirring until it turned clear within 10 min, as a result of TEOS hydrolysis [12]. The concentration of surfactant was kept constant at 20 mM.

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