

# Dispersion and incorporation of optical nanotracers

J. Samuel<sup>\*</sup>, O. Raccurt<sup>\*</sup>, O. Poncelet<sup>\*</sup>, F Tardif<sup>\*</sup> and O. Tillement<sup>\*\*</sup>

<sup>\*</sup>Commissariat à l'Energie Atomique, Laboratory of Tracer Technologies, 38054 Grenoble, France

<sup>\*\*</sup>Laboratory of Physico-Chemistry of Luminescent Materials, 69622 Villeurbanne, France

## ABSTRACT

Fluorescent silica nanoparticles are used as nanotracers to qualify the level of dispersion of nanoparticles into hydrophilic and hydrophobic polymers. In this context, a perfect control of their surface is researched. Reverse micelle is a well known sol-gel process to synthesize silica nanoparticles. But it is observed that using this method, there is an effect of the dye nature on the surface. This effect is erased by growing a thin silica layer on the surface of the nanoparticles. Then, two organosilane molecules have been successfully grafted, making the nanoparticles hydrophilic or hydrophobic and so well suited to fill homogeneously hydrophilic or hydrophobic polymers. Each adapted nanoparticle is indeed well dispersed into the corresponding polymer matrix. This dispersion is characterized thanks to the fluorescence properties of the nanoparticles.

**Keywords:** nanotracer, dispersion, polymer, nanoparticle, surface functionalization.

## 1 INTRODUCTION

The nanotechnologies offer new perspectives in numerous industrial and research domains today. New applications, thanks to the enhancement of the mechanical [1,2] or optical [3] properties of some polymers have been shown by the incorporation of nanoparticles into these polymers. Polysiloxane based nanoparticles encapsulating one or several dyes (organic or inorganic) offer several interesting properties : protection of the dyes against photo bleaching and chemical alterations; exaltation of the fluorescence; good dispersion in water and easy surface functionalization because of the reactive silanol groups. Thanks to these properties, the fluorescent silica nanoparticles can be used as nanotracers, to monitor the behavior of the nanoparticles into the polymer matrix

A control of the surface is thus being researched. To achieve a good dispersion in an aqueous medium, two parameters have to be considered: the hydrophilic/hydrophobic character of the surface and its Zeta Potential. It is well known that the highest the absolute value of the Zeta Potential is, the most stable the colloidal suspension is [4]. The Zeta Potential also gives an idea of the hydrophilic character of a surface. An hydrophobic surface has a Zeta Potential value close to zero [5]. Many studies have already been done especially on the grafting of an aminopropyl group onto the silica surface (APTES,

APMS, N-2-(aminoethyl)-3-APTES) [6,7]. It appears that the isoelectric point is shifted toward higher pH values, the Zeta Potential is higher at low pH and these particles are hydrophilic because they can form Hydrogen bounds with water molecules. [8] also studied the effect of another molecule (PhTES) which makes the particles hydrophobic and so well suited to fill hydrophobic polymers.

The dispersion of 40 nm colloidal nanoparticles encapsulating organic dyes synthesized by a reverse micro-emulsion sol-gel method and the quality of the dispersions obtained are studied here.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Triton X-100 is purchased from Sigma-Aldrich; Hexanol, Cyclohexane, Aqueous Ammonia (30%wt in water) were also purchased from Sigma Aldrich; TEOS (Tetraethylorthosilicate) was obtained from Sigma Aldrich; N-2-(amino ethyl)3-aminopropyltriethoxysilane 99% (Di-Apts) and Trichloro(1H,1H,2H,2H-perfluorooctyl)silane 97% (FDTS) were purchased from Sigma Aldrich. The dyes studied are Rhodamine B and Fluorescein. The polymer tested are PolyMethylMethAcrylate (PMMA) (average Mw=350) and Polyvinyl Alcohol (PVA) (average Mw = 31000) purchased from Sigma Aldrich.

### 2.2 Preparation of the silica nanoparticles

The Silica nanoparticles are synthesized by a reverse microemulsion process proposed by R. P. Bagwe[9]. The idea is to create a Water in Oil microemulsion by mixing Cyclohexane and Water. The microemulsion is stabilized by a non ionic surfactant (Triton X-100) and a co surfactant (Hexanol). The incorporation of the hydrophilic dye into the system is followed by the hydrolysis-condensation of the silica precursor (TEOS) catalyzed by aqueous Ammonia into the nanoreactors. The mixture is reacted for 24h under magnetic stirring. The nanoparticles are released from the microemulsion by the addition of Ethanol in excess. They are separated from the reaction mixture by centrifugation at 4000 rpm for 15-30 min and washed three times with anhydrous Ethanol or with Water. The nanoparticles redispersed into anhydrous Ethanol can be encapsulated by a next addition of silica precursor. The encapsulation is done in a basic medium during 6h at 70°C. The nanoparticles can also be functionalized by the addition of a coupling agent such as FDTS or Di-Apts. The mixture is

stirred overnight and then washed one time with anhydrous Ethanol and two times with Water or Acetone depending on the dispersion medium researched.

### 2.3 Preparation of the loaded polymers

The materials studied are all made by evaporation in an appropriate solvent : Chloroform for the PMMA and Water for the PVA.

PMMA: 2g of PMMA pallets are added to a 50 mL Chloroform solution and stirred for 3h. An adapted quantity of silica nanoparticles is added to the mixture when all the PMMA pallets have been dissolved. The colloidal suspension is then stirred 1h and deposited on a thin glass under controlled atmosphere. The evaporation of the Chloroform gives a thin PMMA loaded layer on a glass film.

PVA: 5g of PVA pallets are added to a 100 mL Water bath heated at 80°C. An aqueous solution containing di-Sodium Tetra Borate and a certain amount of silica nanoparticles is prepared and mixed with the first bath. The colloidal suspension is then deposited on a thin glass under controlled atmosphere. The evaporation of the Water gives a thin PVA loaded layer on a glass film.

### 2.4 Methods

The size and the dispersion of the silica nanoparticles are monitored by Transmission Electronic Microscopy. Zeta Potential measurements are carried out with a ZetaSizer Nano associated with an automatic Titrator MPT-2 supplied by Malvern Instruments to characterize surface charge and hydrophilicity. The hydrophilic/hydrophobic character is also measured by an adapted Dichloromethane method [5]. This method consists on mixing an aqueous phase containing the nanoparticles and a small amount of Hexadecane. The two solvents are stirred and let 30 min. Then 1mL of the aqueous phase is removed and the fluorescence intensity is measured by spectroscopic fluorescence. The hydrophilic/hydrophobic character is given by the ratio between the fluorescence intensity initially measured into the aqueous phase and the fluorescence intensity finally measured. The fluorescent properties of the nanoparticles are observed with a FS920 fluorimeter supplied by Edinburgh Instruments. The homogeneity of the incorporation into the polymer matrix is performed using confocal imaging.

## 3 RESULTS AND DISCUSSION

This section is divided into three main parts: the first part is the study of primary fluorescent silica nanoparticles; some characterizations are performed to see the effect of the fluorescent dye on the surface of the nanoparticles; the second part is an attempt to a perfect surface control; a control of the Zeta Potential and of the hydrophilic/hydrophobic character is thus researched; the

final part is the incorporation of the nanoparticles within the polymer matrix characterized by confocal microscopy.

### 3.1 Fluorescent silica nanoparticles

The Fluorescent silica nanoparticles synthesized are spherical, relatively monodispersed and of 40 nm diameter.

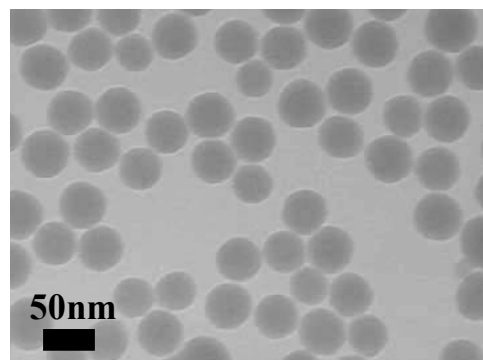


Figure 1: TEM image of the silica nanoparticles synthesized.

It is possible to control the particle size by modifying the ratio [surfactant]/[water] and by this way sizes of 12 nm can be obtained [10]. Other advantages of the reverse micellar synthesis are that nanoparticles are rather monodispersed and that several hydrophilic dye molecules can be incorporated into the silica matrix in contrast with the Stöber method which needs a modification of the dye to ensure its incorporation into the silica matrix.

The Zeta Potential is shown Fig.2 as a function of the pH value for two different dyes and for non fluorescent silica.

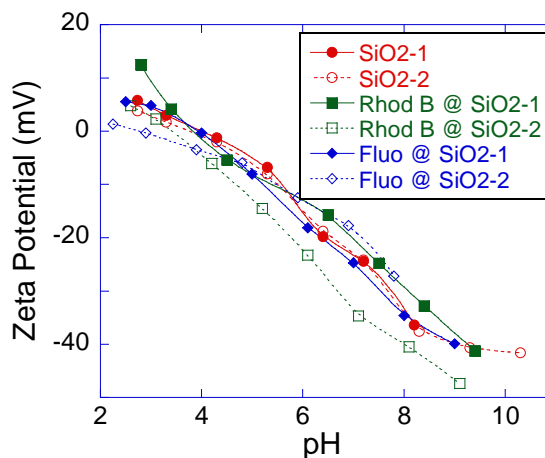


Figure 2: Zeta Potential as a function of the pH for silica nanoparticles without dye or with different dyes.

It appears that the nature of the dye has an effect on the Zeta Potential. Since the synthesis process is the same regardless of the dye molecule incorporated, the surfaces should be identical. Moreover two different measurements with the same dye (Rhodamine B) or with different dyes

(Rhodamine B and Fluorescein) give two different Zeta Potential behaviors. The only values constant are the values obtained for the silica nanoparticles without dye. This difference could therefore be explained by the presence of dye molecules at the surface of the nanoparticles.

### 3.2 Attempts to control the surface

An attempt to erase the effect of the dye on the surface has consisted on the growth of a non fluorescent silica shell around the primary nanoparticles. The Fig.3 shows that this encapsulation has been done without agglomeration of several primary nanoparticles into a same silica shell.

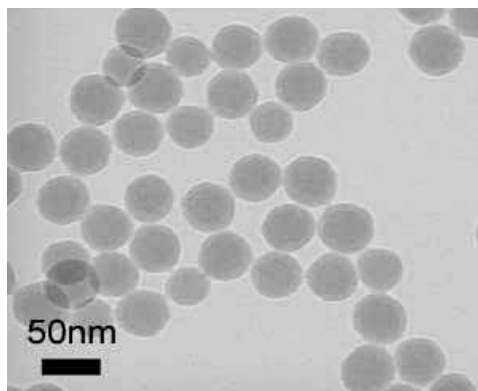


Figure 3: TEM image of the silica nanoparticles encapsulated.

A silica shell of 5 nm in diameter has been grown around the primary nanoparticles. This silica shell has an effect on the Zeta Potential behavior of the fluorescent silica nanoparticles. The Fig.4 shows that encapsulated silica nanoparticles containing Rhodamine B have now the same surface, so there might be no more dye at the surface.

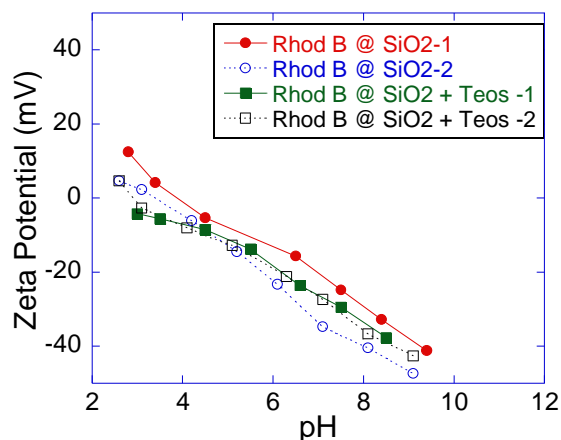


Figure 4: : Zeta Potential as a function of the pH for the silica nanoparticles with and without shell.

This method is therefore an efficient way to control the surface of fluorescent nanoparticles synthesized by reverse microemulsion and so to make efficient nanotracers.

In order to fill homogeneously these nanoparticles into hydrophilic or hydrophobic polymers, it is now essential to modify their surface with adapted chemical molecules. Two molecules have been tested: Di-Apts and FDTS. The first characterization performed is the behavior of the zeta potential of the chemically modified nanoparticles as a function of the pH.

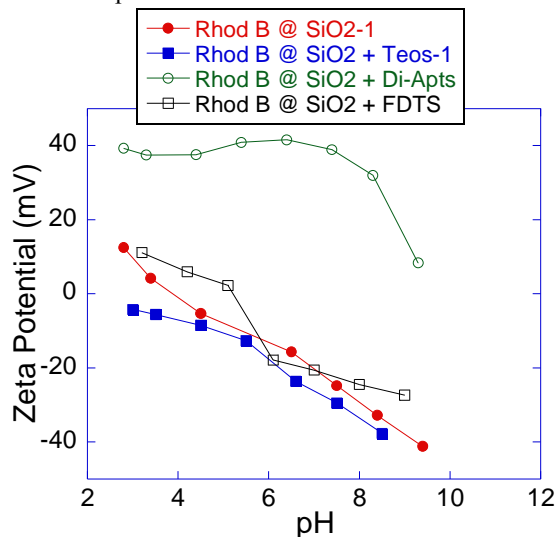


Figure 5: Zeta Potential as a function of the pH for the functionalized silica nanoparticles.

The Zeta Potential becomes highly positive with the Diamino group at acidic pH values and the isoelectric point is shifted toward higher pH values. As a consequence, amino modified nanoparticles will be highly dispersed at low pH values. The fluoric function also modified the surface of the nanoparticles because the Zeta Potential becomes relatively lower in absolute value and the isoelectric point is shifted. Therefore the nanoparticles have been successfully modified. The most hydrophobic seems to be the fluoric functionalized ones.

To control the hydrophobicity of the nanoparticles a Dichloromethane test is done (Fig.6).

	Di-Apts	FDTS	Teos
<b>Ratio</b>	<b>0,967</b>	<b>0,509</b>	<b>0,915</b>

Figure 6: Ratio Hydrophilic/Hydrophobic character for chemically modified silica nanoparticles.

This test confirms that the fluoric compound confers an hydrophobic character to the fluorescent silica nanoparticles and that the diamino molecule gives the most hydrophilic nanoparticles. These two kinds of modified nanoparticles seem to be well suited to fill hydrophilic and hydrophobic polymers.

It is now important to verify the effect of the encapsulation and the different graftings on the intrinsic fluorescence properties of the silica nanoparticles. Indeed the idea is to provide fluorescent nanoparticles whose

properties are not dependant on the surface, especially for the emission wavelength. The spectroscopic measures performed Fig.7 show that there is no difference between the dye fluorescence, the fluorescent silica nanoparticles and the functionalized silica nanoparticles.

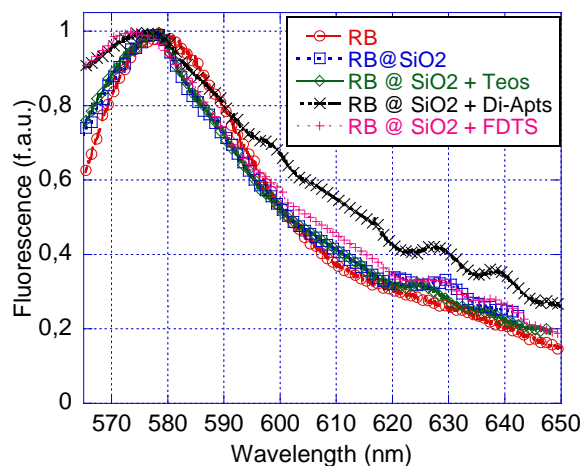


Figure 7: Fluorescence spectroscopy of fluorescent silica nanoparticles doped with Rhodamine B with different surfaces and compared to free Rhodamine B for an excitation at 545 nm.

### 3.3 Incorporation into a polymer matrix

The nanoparticles being characterized, the aim of the study is now to qualify the level of dispersion obtained into an hydrophobic polymer (PMMA) and an hydrophilic one (PVA). The Fig.8 shows that hydrophobic nanoparticles are more adapted than hydrophilic ones to be homogeneously incorporated into a PMMA matrix. Identically, hydrophilic nanoparticles are more suited for an hydrophilic PVA matrix. So the surface functionalization previously described is essential to achieve a better dispersion of the nanoparticles into a polymer matrix.

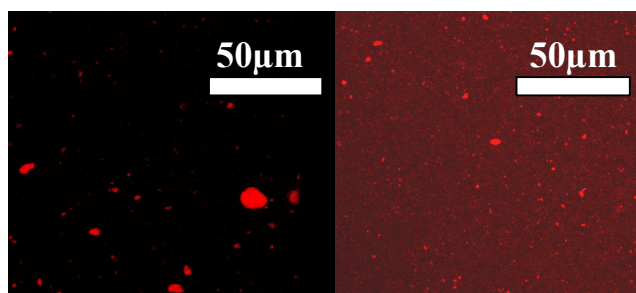


Figure 8: Confocal imaging of fluorescent silica nanoparticles doped with Rhodamine B with different surfaces (left: hydrophilic; right: hydrophobic) into a PMMA matrix.

The use of fluorescent silica nanoparticles is therefore an interesting way to characterize the homogeneity of the incorporation of nanoparticles into polymers.

The Fig.9 shows moreover that homogeneous dispersions can easily be obtained, combining cavitation forces provided by ultrasonication and an adapted surface functionalization.

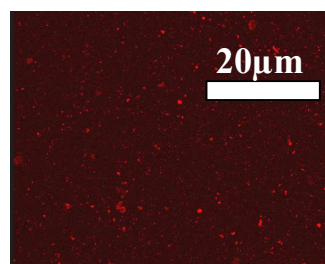


Figure 9: Confocal imaging of hydrophilic fluorescent silica nanoparticles doped with Rhodamine B into a PVA matrix.

## 4 CONCLUSION

Fluorescent silica nanoparticles are efficient nanotracers to monitor the incorporation of nanoparticles into polymers. Their fluorescence and surface properties are versatile and can be easily tailored. The homogeneous incorporation of hydrophobic nanoparticles into an hydrophobic polymer has been shown, so as the heterogeneous incorporation of hydrophilic nanotracers into an hydrophobic polymer.

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