

## EFFECT OF SYNTHESIS VARIABLES ON THE FLUORESCENCE OF CDSE QUANTUM DOTS - POLYSTYRENE LATEXES

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### Abstract

The process of miniemulsion polymerization permits the encapsulation of quantum particles into a polymer matrix providing them of chemical stability without affecting their luminescent properties. In this work, the synthesis process was conducted varying levels of surfactant, initiator and CdSe QDs. A microscopy study on the composite latexes and later a statistical analysis indicated that the increment in surfactant concentration produced a decrease in the polymer particle size, which increased in turn the rate of polymerization and percentage conversion. The obtained latexes were stable and showed fluorescence by excitation with UV light. The spectrofluorometry studies indicated that in composite latexes the fluorescence was a function of polymer particle size and the amount of encapsulated dots per polymer particle.

### Introduction

Cadmium selenide quantum dots (CdSe QDs) are semiconductor nanocrystals from II-VI group. Due to their zero-dimensional quantum confinement and their size (1-10nm), they own extensive absorption spectra with narrow and symmetric emission bands when they are excited by a single light source [1,2]. The incorporation of semiconducting nanocrystals into a polymer matrix increase QDs photostability and improves optical characteristics [3-5], producing a solid material with specific optical properties and offering new perspectives to studies and applications [6-8].

The miniemulsion polymerization process implicates the formation of monomer droplets uniformly dispersed and stable within a continuous phase, which become the reactors to generate latex polymer with characteristics determined by variables in their kinetics and synthesis [8-9]. This synthetic technique allows the dispersion of the QDs in the polymer particles due to phase affinity between the monomer and them, which protects QDs structure and emission characteristics [3,5]. By changing the synthesis variables it is possible to modifying the polymer particle size, which in turn, produces changes in both the QDs/polymer particle ratio and the fluorescent emission intensity.

The purpose of this study was to determine the effect of miniemulsion variables on the fluorescence of CdSe QDs/ polystyrene latexes. It was considered that variations in the surfactant and initiator concentrations reflect changes in the polymer particle size and rate of polymerization. It is expected that by controlling these changes it could be possible the design of fluorescent polymer composites with tailored functionality.

## Experimental

### Miniemulsion polymerization

Miniemulsion polymerization process was achieved using cetyltrimethylammonium bromide (CTAB) as the surfactant, at concentration levels of  $1.3 \times 10^{-3} \text{M}$ ,  $3.2 \times 10^{-3} \text{M}$  and  $5.4 \times 10^{-3} \text{M}$ . The initiator 2,2-azobisisobutyronitrile (AIBN) and CdSe QDs were used at 0.50 and 0.75% and 0.075, 0.15 and 0.225%, both with respect to monomer content, respectively. Table 1 shows the different treatments implemented. First, a surfactant solution of CTAB and water (20 g) was prepared into the reactor. To obtain the miniemulsion a hydrophobe mixture containing the CdSe QDs, styrene monomer, hexadecylamine, hexadecane and the initiator was charged into the reactor. The mixture was sonicated for 2 min at 40% amplitude (Sonic dismembrator FB-505). The polymerization process was achieved at  $70^\circ\text{C}$  with continuous magnetic stirring in nitrogen atmosphere.

### Characterization

The average particle size, particle size distribution and polydispersity index of polymer particle was determinate by statistic method considering the measurement of at least 500 particles. Latexes micrographs were obtained by a transmission electron microscope Jeol JSM-7401F. Photoluminescence (PL) spectra of CdSe/polystyrene latexes were acquired using a Varian Eclipse spectrofluorometer at 360 nm excitation.

**Table 1.** Conditions of the synthesis process by miniemulsion polymerization for the different treatments.

Treatment	Surfactant CTAB (M)	Initiator AIBN (%)	CdSe QDs (wt%)	Treatment	Surfactant CTAB (M)	Initiator AIBN (%)	CdSe QDs (wt%)
1	0.0016	0.50	0.075	10	0.0016	0.75	0.075
2	0.0016	0.50	0.150	11	0.0016	0.75	0.150
3	0.0016	0.50	0.225	12	0.0016	0.75	0.225
4	0.0032	0.50	0.075	13	0.0032	0.75	0.075
5	0.0032	0.50	0.150	14	0.0032	0.75	0.150
6	0.0032	0.50	0.225	15	0.0032	0.75	0.225
7	0.0054	0.50	0.075	16	0.0054	0.75	0.075
8	0.0054	0.50	0.150	17	0.0054	0.75	0.150
9	0.0054	0.50	0.225	18	0.0054	0.75	0.225

## Results and Discussions

The latexes obtained were stable and showed fluorescence by excitation with UV light, indicating that the method used prevented QDs deactivation also known as quenching. It was observed that as effect of the different treatments, the latexes displayed fluorescent emission with different intensity. The variations in the surfactant concentration influenced the polymer particle size in the latex; these variations affected the positioning of the QDs in the matrix and consequently the compound fluorescent emission.

In order to quantify the effect of the different treatments on the fluorescence emission, photoluminescence spectra of the latexes were obtained. It was observed a stable emission at 580nm at 360nm excitation wavelength for all treatments. The fluorescence intensity was in correlation with the synthesis parameters. Figure 1 shows the photoluminescence emission spectra of the latexes with the different treatments. Emission intensity presented changes with respect to synthesis parameters. The higher QDs concentration presented higher emission intensity, this behavior was already reported by Joumaa et al. [3], specifying that emission intensity increased with the concentration of QDs.

Average particle diameter ( $D_n$ ), particle size distribution (PSD) and polydispersity index (I) were calculated from a statistical study performed on at least 500 polymer particles. Table 2 shows the results of the different response variables obtained from the different treatments. The values of I were found to be narrow for all the treatments, presuming the stability of the miniemulsion systems during the polymerization. This can be corroborated by the STEM images obtained from the latexes (Figure 2).

The increment in surfactant concentration produced the decrement in  $D_n$ . However, the effect of varying the initiator concentration did not affect significantly  $D_n$ . The fluorescent emission of the latexes varied as a consequence of variations on both surfactant and initiator concentration. These values also affected directly the final number of polymer particles ( $N_p$ ) per unit volume. Considering that, the number of QDs per polymer particle also was affected. The relationship of QDs-polymer particle was theoretically calculate taking into account the number of CdSe per cubic centimeter determined by polymer average particle size and the amount of dots incorporated in the synthesis process.

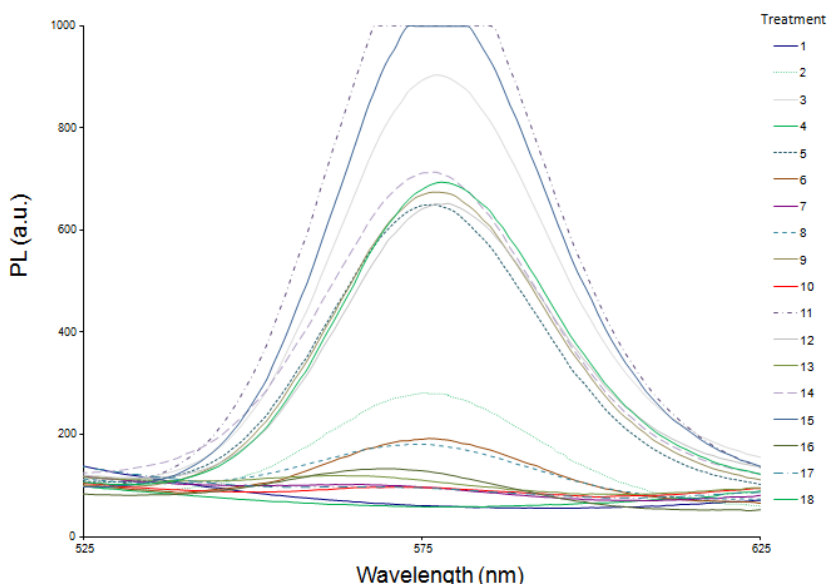


Figure 1. Photoluminescence emission spectra of CdSe-polystyrene latexes.

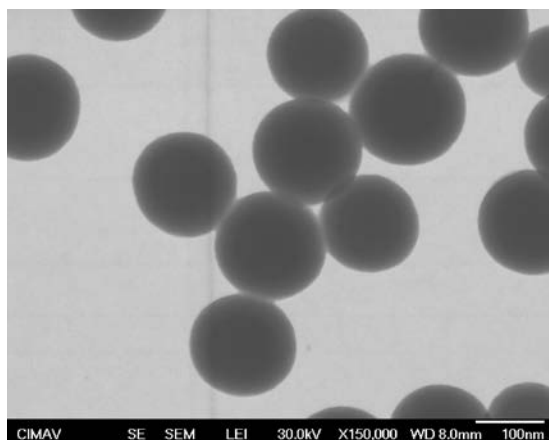


Figure 2. Micrograph scanning electron microscopy in transmission mode of CdSe-PS latex

Table 2. Characteristics of CdSe-polystyrene latexes obtained by miniemulsion polymerization.

Treatment	Dn (nm)	I	Np (cm <sup>3</sup> )x10 <sup>-16</sup>	QDs/ polymer particle
1	139	1.01	0.821	0.2161
2	134	1.02	0.896	0.3949
3	138	1.01	0.840	0.6350
4	124	1.01	1.42	0.1249
5	131	1.01	1.22	0.2900
6	129	1.01	1.27	0.4200
7	101	1.02	3.89	0.0456
8	97	1.04	4.10	0.0863
9	102	1.04	3.76	0.1418
10	141	1.01	0.982	0.1806
11	144	1.01	0.917	0.3859
12	144	1.02	0.907	0.5881
13	110	1.02	3.06	0.0579
14	109	1.03	3.07	0.1152
15	109	1.03	3.06	0.1743
16	110	1.03	3.00	0.0591
17	106	1.02	3.65	0.0960
18	96	1.03	4.87	0.1095

The results obtained indicate that the QDs were not uniformly distributed among the latex particles, since the number of dots per polymer particle was not directly proportional to the fluorescence emission intensity. These facts let us to consider that there was no homogeneous encapsulation of dots by polymer particles and that there were dots which were not encapsulated and they could be degraded during the process.

### Conclusions

The emission results obtained revealed a successful encapsulation of nanoparticles in the polymer matrix. The emission intensity of the CdSe-polystyrene latexes underwent changes due mostly to the changes in the polymer particle size, induced by variations in the levels of surfactant and initiator used, and the number of QDs encapsulated per polymer particle.

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