Stable aqueous dispersions of C₆₀ fullerene by the use of a block copolymer

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Abstract. Stable aqueous solutions of C₆₀ fullerene have been prepared by the use of a well defined block copolymer, namely poly(styrene-b-ethyleneoxide) (PS-b-PEO). The protocol that has been followed involves, in a first step, the co-dissolution of C₆₀ fullerene and diblock copolymer in toluene, a solvent where formation of micelles with the PEO as the core block is favored. In the second step evaporation of toluene at room temperature takes place. Finally redissolution of the formed film in water, with simultaneous inversion of the micellar structure (PS containing C₆₀ as the core), is achieved. The aggregates prepared in this way have been characterized by dynamic light scattering as well as scanning electron microscopy. All the applied techniques have indicated the formation of at least two kinds of aggregates, of different sizes, that enclose fullerenes in their cores. This protocol allows the preparation of micellar aggregates, with biocompatible coronas, containing C₆₀ in 1-20% by weight in respect to the PS component.

1. Introduction
The use of fullerenes in the field of nanotechnology is currently of wide research interest because of their potential applications in medicine [1], superconductivity [2] and non-linear optics [3]. Unfortunately, the low solubility of fullerenes in most of the common organic solvents, and especially in water, for medical applications, imposes a limit in their use in the above fields. Many interesting approaches on the solubilization of C₆₀ by chemical modification of fullerene [4], by introduction of surfactants [5] or by encapsulation in polymer micelles [6] have been reported. Here we report on a novel and general method for the preparation of stable aqueous dispersions of C₆₀ fullerene in different concentrations by the use of an amphiphilic block copolymer, namely poly (styrene-b-ethyleneoxide) (PS-b-PEO).

2. Experimental Part

2.1. Synthesis of Block Copolymer
The synthesis of block copolymer has been achieved by anionic polymerization high vacuum techniques [7] employing sec-butyllithium as initiator and benzene as the solvent. Styrene was the first monomer to polymerize at 25 °C followed by ethylene oxide and phosphazine, and an elevation of temperature to 40°C. The polymer, denoted as SEO-1, was characterized by size exclusion chromatography, $^1$H-NMR and attenuated total reflectance FTIR (ATR-FTIR) in order to obtain the exact molecular characteristics and to confirm the uniformity of the sample. SEO-1 has an overall molecular weight, $M_w = 24,600$, polydispersity, $M_w/M_n = 1.06$ and the portion of polystyrene is 35wt%.

2.2. Dispersion Preparation Protocol
Distilled water and analytical grade toluene (from Aldrich) were used to prepare the micellar solutions. Polymer micelles solutions with the encapsulated C$_{60}$ (obtained from Aldrich) in the core were prepared by a three-step protocol (scheme 1). The first step was the co-dissolution of C$_{60}$ fullerene and diblock copolymer in toluene, a solvent where formation of micelles with the PEO as the core block is favored, at temperatures lower than 20°C. In the second step evaporation of toluene at room temperature took place leading to film formation. Finally re-dissolution of the formed film in water, with simultaneous inversion of the micellar structure was achieved (PS containing C$_{60}$ as the core). Four solutions of SEO-1 and C$_{60}$ in water were prepared, with the same concentration of the polymer, 1x10$^{-2}$ g/mL, and 1, 5, 10 and 20wt% C$_{60}$ to PS block. Dispersions had a brownish tint, with intensity varying with the amount of C$_{60}$. The solution with the higher C$_{60}$ content (20wt%), showed precipitation of the hybrid micelles after two weeks, probably due to their large size.

![Scheme 1. The three step preparation protocol of the SEO-C$_{60}$ micelles](image)

2.3. Measurements
The micelles formed by the block copolymer and C$_{60}$ molecules were studied in solution by dynamic light scattering and in solid films by scanning electron microscopy. Dynamic light scattering measurements (at 90°) were performed on a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS7 stepper motor controller, a Cyonics variable power Ar$^+$ laser, operating at 488 nm and with 10 mW power. A 192-channel correlator was used for accumulation of the data. Correlation functions were analyzed by the use of the CONTIN software. All the measurements were performed in diluted solutions. A Scanning Electron Microscope (Zeiss, Supra 35VP) having a 1.5 nm resolution at 20 kV, was used for surface morphology examination of C$_{60}$-SEO-1 in H$_2$O. Droplets of C$_{60}$-SEO 1%, 5% and 10% in H$_2$O were cast on metal slabs suitable for SEM observation and then dried in a furnace at 60°C. The specimens’ conductivity was improved by coating them with gold using a sputtering device.

3. Results and Discussion
The key goal of this project was the preparation of stable aqueous dispersions of C$_{60}$ in water. The solutions that had been prepared as described above were very stable and no precipitation has been observed within 9 months after their preparation. Photographs of the three stable original solutions and
their diluted forms, where the homogeneity of the samples is more obvious, are shown in figure 1. It is well known that the amphiphilic block copolymers, with a long enough soluble block, can form very stable star-like micelles in selective solvents [8]. Moreover, the core forming PS block, is a very friendly matrix for C60. From the known solubility parameters of C60 [9] and PS [10] (equal to 10 and 9.1 (cal/cm^3)^1/2 at 25°C respectively), the Flory-Huggins interaction parameter $\chi$ [11], could be calculated. The resulting parameter, $\chi=0.015$ indicates a strong interaction between C60 and PS.

The preparation protocol (scheme 1) ensures the encapsulation of all C60 molecules. A film of strongly separated PS and PEO phases is formed after evaporation of the solvent [12]. The C60 fullerenes are selectively distributed in the PS phase. The re-dissolution of the film involves phase inversion and leads to the formation of micelles with the PS, and everything contained in this matrix, acting as the core. No free C60 as precipitate was observed even in the case of 20wt% solution.

Dynamic light scattering measurements gave the aggregate populations in solutions and their average diameter. The results are summarized in Table 1. In all cases at least two populations were observed, even in solutions of pure SEO-1, prepared by the same protocol. The above results suggest that the formed micelles are kinetically frozen and not in thermodynamic equilibrium [8]. It is noted that SEO-1 forms one type of micelles when it is dissolved directly in water. This observation can be attributed to the phase inversion of the matrix that takes place during the second step.

| Sample      | 1st population diameter (nm) | 2nd population diameter (nm) | 3rd population diameter (nm) |
|-------------|------------------------------|------------------------------|------------------------------|
| SEO-1       | 95                           | 380                          | -                            |
| SEO-1/1 wt% C60 | 85                           | 400                          | -                            |
| SEO-1/5 wt% C60 | 100                          | 470                          | 1300                         |
| SEO-1/10 wt% C60 | 100                          | 790                          | 2800                         |
| SEO-1/20 wt% C60 | 160                          | 2000                         | Non-resolved                 |

The observation that the SEO-1/1 wt% C60 solution has an identical dynamic light scattering profile with pure SEO-1, reveals that it is possible to enclose fullerene in the core without appreciable change in the overall dimensions of the micelles. The formation of a third population, with even greater diameter, was observed upon increasing the C60 content. Furthermore, the larger the amount of C60 the larger the micelles that are formed. At the same time the size of the smallest micelles remains constant at 100 nm, whereas the size of the second population shifts to larger diameters (400 to 2000 nm) was observed as the C60 content increased, leading eventually to partial precipitation at 20wt% fullerene.

The micelles have been studied also in solid state by SEM. The SEM image of a film resulted from the solution with 10wt% C60 is shown in figure 2A. In this image the well-shaped spherical structure of the formed micelles is evident, as well as the presence of more than one population of aggregates. In figure 2B the image from a 1:20 diluted 10wt% C60 solution is given, where the spherical structures...
and the heterogeneity of the diameter among the micelles can be seen more clearly. SEM images of solutions with 1wt% and 5wt% C_{60} (not shown) lead to the same observations.

**Figure 2:** SEM images of films resulted from a 10wt%C_{60} solution (A) and from a diluted (1:20) 10wt% C_{60} solution (B)

The results from DLS and SEM agree well, leading to the conclusion of a multi-population micellar solution, where the micelle diameter varies with C_{60} content.

4. Conclusions

Stable aqueous solutions of C_{60} have been prepared by the use of an amphiphilic diblock copolymer. A preparation protocol was developed and involved the co-dissolution of C_{60} and polymer in toluene, evaporation of the solvent, so that a two-phase film was formed with the C_{60} residing in the hydrophobic phase, and finally the re-dissolution of the film in water with simultaneous formation of micelles (with the core forming block encapsulating C_{60}). Studies of the solutions, by DLS and SEM, led to two conclusions: a) more than one micellar populations exist in solutions and b) the diameters of the formed micelles are strongly dependent on the C_{60} content.

5. Acknowledgements

Financial support through the project “Excellence in the Research Institutes” (project No 64769) supervised by the Greek General Secretariat for Research and Technology is gratefully acknowledged. Partial support by the IST project NANOPHOS is also acknowledged.

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