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Morphological Changes Induced by Addition of Polystyrene to Dextran-Polystyrene Block Copolymer Solutions

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Summary: In this work we discuss the self-assembling behaviour in solution of a block copolymer, dextran-*block*-polystyrene, in the presence of homopolystyrene (PS) which allows to decrease the hydrophilic fraction *f* of the mixture. Dynamic and static light scattering experiments have been carried out in water-miscible solvents (DMSO and THF) to probe the formation of supramolecular structures. Results have been compared to those obtained with a block copolymer solution having the same hydrophilic fraction *f*. Interestingly, the morphology of the self-assembled structures was the same for a given value of *f*.

Keywords: blend; block copolymers; homopolymer; polysaccharide; self-assembly

Introduction

When dissolved in a selective solvent, block copolymers spontaneously self-assemble into a wide range of morphologies including spherical and wormlike micelles, vesicles and other nano- or microstructures. The morphologies resulting from this phenomenon are controlled by molecular parameters such as the volume fraction and chemical nature of the blocks, molar mass, and architecture of the copolymer,[1] as well as by solution parameters such as polymer concentration, temperature, solvent quality, pH and ionic strength.[2] The dissolution process is another key parameter that impacts morphological aspects of the nanoparticles formed.[3–6] The self-assembling phenomenon in solution is therefore extremely complex. Numerous theoretical[7–10] and experimental studies[4,5,11] have been devoted to the clarification of the micellisation process and to the generation of stable morphologies.

In the field of the self-assembling of block copolymers in solution it has been observed that a transition from spheres to cylinders and cylinders to vesicles occurs when the mass fraction of the hydrophilic (or soluble) block decreases.[12–15] A general empirical law based on experimental observations in the field of self-assembling of coil-coil block copolymer has been proposed by Discher and Eisenberg[11] to predict the morphology based on the hydrophilic or "soluble" mass fraction in the copolymer. The transition from spheres to cylinders and to vesicles is expected as the hydrophilic (or soluble) fraction decreases.[11]

If the hydrophilic mass fraction of the block copolymer can be controlled by chemistry, it can also be controlled through the addition of a homopolymer to a solution containing a block copolymer of defined composition. The solvent can be selective for the homopolymer[16,17] or nonselective.[14,18] In the former case, the depletion interactions are the key parameters which

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can either modify the aggregation number of the micelles[16] or even induce strong interactions between micelle-like structures, thereby leading to interesting rheological properties.[17] In the latter case the homopolymer is incorporated into the core of the micellar structure, which can induce morphological changes and/or size variations of the preformed micelle.[18] Opposite findings have been reported regarding the addition of an ''insoluble'' homopolymer to a solution of block copolymer: some authors noted a transition from spheres to cylinders[18] but others observed the contrary (transition from cylinders to spheres).[14] However, the micellisation process used by the authors was not the same.

The block copolymers we are interested in, namely synthetic polymer-*block*-polysaccharide, are hybrid materials consisting of an oligosaccharide as a naturally occurring block (e.g. dextran, Dex, as in the present study), the second block being a vinylic synthetic polymer grown by controlled polymerization (polystyrene, PS). Pioneering work in the development of polysaccharide-based block copolymers dates back to the early 1980s by Ziegast and Pfannemüller who coupled an oligosaccharide functionalized with an aldonolactone at its reducing end to an α,ω-diamino-poly(ethylene oxide) (PEO).[19] In recent years, a few other routes have been developed to obtain polysaccharide-based block copolymers.[20–27] It turns out, however, that the self-assembling of such hybrids in solution is far from being understood. In previous report,[28] we have demonstrated that dextran-polystyrene block copolymers self-assembled in solution (in organic or aqueous media) into miscellaneous morphologies (e.g. spherical micelles, vesicles, ovoids), depending on the overall copolymer composition as well as on the selective solvent used. The role of the dextran block in the self-assembling behaviour has been discussed.

Due to a great potential of such materials, we focused on gaining insight into the control of their nanoscale morphologies. For that purpose we have evaluated the ability of the self-assembled microstructures of dextran-*block*-polystyrene to be modified by the addition of polystyrene in solution. The results are presented taking as a reference the previously described self-assembly of Dex$_{40}$-*b*-PS$_{270}$ where 40 and 270 stand for the degree of polymerization of dextran and PS. It has been compared to those obtained from the self-assembly Dex$_{40}$-*b*-PS$_{770}$ as previously reported.[28]

Materials

Molecular features of the Dex-PS diblock copolymers previously synthesized[27] are reported in Table 1. All organic solvents used (DMSO, THF) were of technical grade. The following nomenclature was used for the different block copolymers: Dex$_a$-*b*-PS$_b$, where a and b represent the degree of polymerization of dextran and polystyrene, respectively. Dextran T10 ($M_n = 6600$; PDI = 1.6 as determined by aqueous SEC using poly(ethylene oxide) standards) was purchased from Amersham Bioscience and polystyrene ($M_n = 25000$; PDI = 1.05) was purchased from Aldrich.

Methodology

As described in our previous work,[28] there is no common solvent for such hybrid systems. The Dex-PS diblock copolymers were dissolved in DMSO/THF mixtures containing 50–75% DMSO for Dex$_{40}$-*b*-PS$_{270}$ and 30–45% DMSO for Dex$_{40}$-*b*-PS$_{775}$

Table 1.
Molecular characteristics of the block copolymers used in this study.

Copolymer	M_n SEC[a]	DP$_n$ NMR[b]	PDI[a]	Φ_{PS} % (w/w)
Dex40-*b*-PS270	82200	270	1.7	81
Dex40-*b*-PS775	160000	775	1.9	92

[a] Determined by SEC in THF (calibration with PS standards).
[b] Overall composition determined by ^{1}H NMR spectroscopy knowing the molecular weight of commercial dextran ($M_n = 6600$).

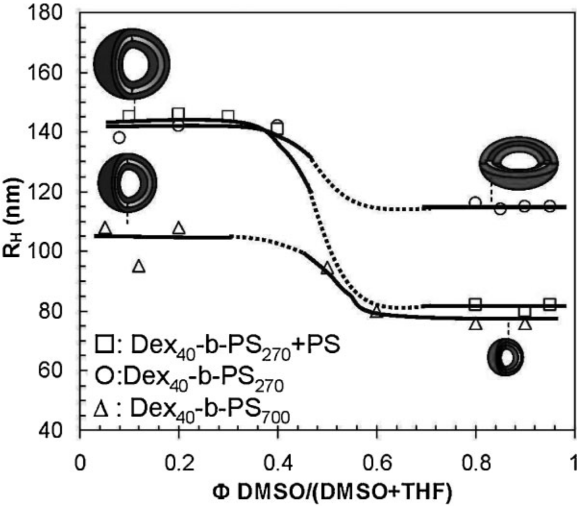

Figure 1.

Evolution of hydrodynamic radius versus DMSO volume fraction for different block copolymers and for blends (block copolymer - polystyrene). The lines are eye-guises. The dotted curves indicate the area where no scattered signal could be detected. Schematic morphologies are inserted in the graph. Light grey illustrates dextran, dark grey polystyrene.

(dotted lines in Fig. 1). In the subsequent step, the solvent composition was changed by addition of either DMSO or THF in order to induce self-assembling and create different morphologies. The block copolymers self-assemble into vesicular structure with characteristic hydrodynamic radii indicated in Fig. 1, regardless of the solvent mixture composition, with the exception of Dex_{40}-b-PS_{270} which self-assembles into an ovoidal structure in the DMSO-rich region. This was proven by dynamic and static light scattering, small-angle neutron scattering and AFM imaging.[28]

Dynamic Light Scattering Measurements

The detailed methodology can be found in ref.[28] Briefly, the measurements were performed at 25 °C, using an ALV laser goniometer, which consists of a 22 mW HeNe linear polarized laser (632.8 nm) and an ALV-5000/EPP multiple τ digital correlator with initial sampling time125 ns. All the scattering measurements were carried out at 40°–120° by steps of 10°. Fitting of the measured normalized time autocorrelation function was performed with the constrained regularization algorithm (CONTIN). Apparent diffusion coefficients D were obtained by plotting the relaxation frequency, Γ ($\Gamma = \tau^{-1}$), versus q^2. Hydrodynamic radii were calculated from the Stokes-Einstein relation. The polydispersity of the particles was obtained by cumulant analysis of the first-order correlation function.

The reduced elastic scattering was measured in steps from 40° to 120° of scattering angle, Elastic (static) intensity was calculated using standard procedures with toluene as the standard of the known absolute scattering intensity. Because of the large characteristic size of the nanoparticles obtained, a curvature of the angular dependence in a Zimm plot was often observed; Berry modification was employed to linearize this curvature.[29] The radius of gyration (R_g) was obtained from the Berry plot.

Results and Discussion

Copolymer Dex_{40}-b-PS_{270} was dissolved in the composition range of solvents leading to full solubility, (see Methodology), block copolymer chains behaving as unimers. To this solution, a certain volume of solution of the PS standard was added. The concentration and volume of the polystyrene solution were selected to reach a PS mass fraction of 0.9 for the comparison purpose with the block copolymer Dex$_{40}$-*b*-PS$_{775}$ having the same overall composition. The solution was then diluted with various volume fractions of DMSO (0.8–0.95) to bring about self-assembling before analysis by dynamic and static light scattering. The results are illustrated in Fig. 1. In the DMSO-rich region (>80%), one can notice that the hydrodynamic radius decreases from 115 nm to 80 nm upon adding the PS standard while the polydispersity index given by cumulant analysis is close to 0.1. Cumulant analysis of the decay of the autocorrelation function was performed at various detection angles to plot the decay rate Γ as a function of q^2 where q is the scattering vector (Fig. 2). The linear variation of Γ versus q^2 passing through the origin is characteristic of a translational diffusive process typical of spherical objects (Fig. 2). The hydrodynamic radius has been obtained from the mean diffusion coefficient D ($\Gamma = Dq^2$) determined from the slope of the function $\Gamma(q^2)$. The value of the hydrodynamic radius as obtained by this method ($R_H = 80$ nm) is very close to that obtained for Dex$_{40}$-*b*-PS$_{775}$ ($R_H = 75$ nm). In other words, it can be hypothesized that morphologies obtained from blending Dex$_{40}$-*b*-PS$_{270}$ with the PS additive are the same. In order to get a better insight into the micellar structure obtained we have measured the radius of gyration by static light scattering.

The corresponding Berry plot is shown in Fig. 3. We obtained a value of $R_g = 90$ nm in this way. The ratio $R_g/R_H = 1.08$ can thus be deduced, which is very close to the value expected for vesicular structure.[29,30] It is important to note that no reliable results could be obtained by imaging techniques (AFM, TEM) in the DMSO-rich region. Indeed, DMSO must be evaporated in dynamic vacuum and this led to disruption of the morphologies. In THF region, the added polystyrene led to the formation of a film which rendered the observation of the morphologies difficult.

One can thus conclude that incorporation of linear PS in a solution of Dex$_{40}$-*b*-PS$_{270}$ causes a morphological change from an ovoidal structure ($R_g/R_H = 2.2$), as previously reported,[28] to a vesicular morphology in the DMSO-rich region, with hydrodynamic radius of 80 nm. In addition,

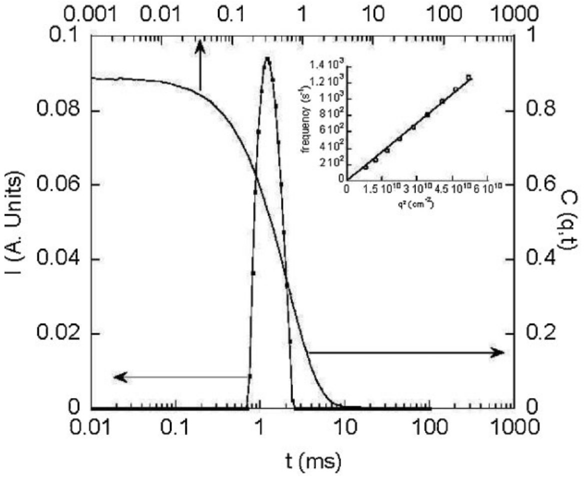

Figure 2.
Autocorrelation function at 90° and time distribution function after CONTIN analysis for Dex$_{40}$-*b*-PS$_{270}$ with added polystyrene in the DMSO region (80% DMSO). Frequency relaxation versus q^2 is presented in the inset.

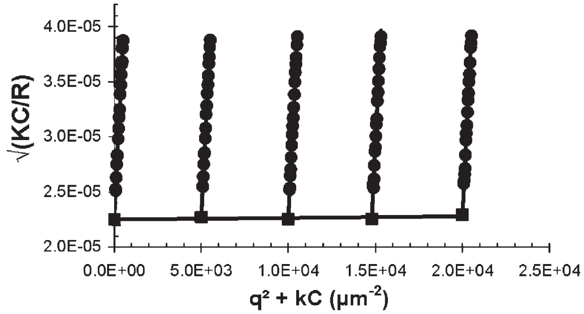

Figure 3.
Berry plot for Dex_{40}-*b*-PS_{270} with added polystyrene. Concentration range of polymer 0.25 - 0.0625 mg/ml in the DMSO region (80% DMSO).

the morphology of the resulting blend is similar to that observed for Dex_{40}-*b*-PS_{775} with the same overall composition.

Next, we investigated the self-assembling behaviour of blends in the THF-rich region. For that purpose, an appropriate amount of THF was added to the DMSO-rich solution, upon increasing the THF content until no scattered signal was observed (50–75% v/v of DMSO). This indicated that the morphologies disassemble, releasing the PS additive entrapped in the micellar structure. Upon diluting the solution further with THF, Dex_{40}-*b*-PS_{270} self-assembled again, forming the same morphology obtained with Dex_{40}-*b*-PS_{270} alone, i.e., without any added PS standard. Indeed, the measured values of the hydrodynamic radius and the ratio $R_g/R_H = 1.4$ using static light scattering were very close, in the absence or presence of the PS additive. This ratio is above the characteristic value of unity expected for vesicles. This could be a consequence of a rather large size dispersity of the nanoparticles, as already visualized by AFM imaging.[28] The slight increase in the hydrodynamic radius (from ~140 to 145 nm) might be explained by interactions of the added PS chains with the PS-based corona of the vesicles in THF.

Conclusion

We demonstrate the modulation of morphologies obtained by self-assembling a new class of polysaccharide-based block copolymers through simple addition of a homopolymer in blending experiments. Though this method has already been reported,[14,18] conflicting tendencies have been observed with regard to the morphology modification due perhaps to the different micellisation processes chosen. In our case there is a direct analogy between the chemical block copolymer composition and the composition produced by addition of a homopolymer to that block copolymer. The morphologies obtained by the addition of polystyrene to a solution of Dex_{40}-*b*-PS_{270} in order to reach a polystyrene mass fraction of 0.9 are similar to those obtained from self-assembling Dex_{40}-*b*-PS_{775} in which the PS mass fraction is 0.9. A transition from ovoids with a hydrodynamic radius of 115 nm to vesicles with a hydrodynamic radius of 80 nm is observed. It has been shown in the previous study that morphologies obtained in DMSO could be transferred to water, thus paving the way for potential applications of these structures as carriers or vehicles. With the knowledge of the phase diagram of a particular block copolymer in a DMSO/THF mixture, one could therefore anticipate the morphologies obtained from a simple addition of a homopolymer to that particular block copolymer.

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