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Core microstructure, morphology and chain arrangement of block copolymer self-assemblies as investigated by thermal field-flow fractionation

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ABSTRACT

The self-assembly of block copolymers (BCPs), as a result of solvent selectivity for one block, has recently received significant attention due to novel applications of BCPs in pharmaceuticals, biomedicine, cosmetics, electronics and nanotechnology. The correlation of BCP microstructure and the structure of the resulting self-assemblies requires advanced analytical methods. However, traditional bulk characterization techniques are limited in the quest of providing detailed information regarding molar mass (M_w), hydrodynamic size (D_h), chemical composition, and morphology for these self-assemblies. In the present study, thermal field-flow fractionation (ThFFF) is utilised to investigate the impact of core microstructure on the resultant solution properties of vesicles prepared from polystyrene-polybutadiene block copolymers (PS-b-PBd) with 1.2- and 1.4-polybutadiene blocks, respectively. As compared to investigations on the impact of the corona microstructure, the impact of core microstructure on micellar properties has largely been neglected in previous work. In *N,N*-dimethylacetamide (DMAc) these BCPs form vesicles having PS shells and PBd cores. D_h, M_w, aggregation number, and critical micelle concentration of these micelles are shown to be sensitive to the core microstructure, therefore, demonstrating the potential of microstructural differences to be used for providing tuneable pathways to specific self-assemblies. It is shown that micelles prepared from BCPs of similar PS and PBd block sizes are successfully separated by ThFFF. It is further demonstrated in this study that PS-b-PBd vesicles and PS homopolymers of identical surface chemistry (PS) and comparable D_h in DMAc, can be separated by ThFFF.

1. Introduction

The evolution of self-assembled structures from block copolymers (BCPs) in solution, being primarily a result of solvent selectivity for one block, has received much attention due to novel applications of self-assembled structures in pharmaceuticals, biomedicine, cosmetics, electronics and oil recovery [1–3]. These self-assembled structures can be spheres, cylinders or vesicles depending on various molecular factors such as the hydrophobic-hydrophilic (or more generally solvophobic-solvophilic) block ratio, chemical composition and molar mass. On the other hand, solution factors such as solvent type and thermodynamic quality, temperature, pH, ionic strength and concentration also determine what type of self-assembled structure is formed. In addition to these effects, microstructural differences in BCPs are also known to influence physical and chemical properties. This was shown by Schmelz et al. and Du et al. who demonstrated that when the BCPs in solution are heated above the crystallization temperature of the core forming block, the resultant micelle morphologies can be manipulated via controlling the temperature at which crystallization occurs [4,5]. Furthermore, investigations on polyethylene glycol (PEO)-based BCP micelles with either ε-caprolactone (ε-CPL) or ε-decalactone (ε-DCL) as the hydrophobic blocks in aqueous solvents illustrated the influence of M_w and chemical composition (CC) of the core [6]. It was shown that the resultant amorphous or crystalline core, as induced by varying the M_w and CC of the micelle core, had an influence on properties such as the critical micelle concentration (CMC) and morphology [6].

The correlation of BCP microstructure to the structure of the resulting self-assemblies requires advanced analytical methods. Traditional bulk characterization techniques like electron microscopy, light scattering and spectroscopy are limited in the

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quest of providing detailed information regarding molar mass (M_w), hydrodynamic size (D_h), chemical composition, and morphology for self-assemblies. Moreover, column-based techniques like size exclusion chromatography (SEC) can provide information on M_w, D_h and the associated distributions, however, fragile self-assemblies can be shear-degraded by interactions with the SEC column [7,8]. Thus, in order to fully comprehend and understand the behaviour of self-assemblies in solution, there is a need to establish robust characterization techniques capable of defining micelles at molecular level with regard to M_w, D_h, CC, and morphology.

Most recently, thermal field-flow fractionation (ThFFF) has been shown to be a versatile tool capable to separate and characterize micelles according to CC and size, microstructure and morphology [9–11]. ThFFF is a sub-technique of field-flow fractionation (FFF) that makes use of a thermal gradient as the driving force to separate analytes across a narrow channel clamped between two metallic plates [12]. In ThFFF, the temperature gradient is achieved by heating the one plate (hot wall) and cooling the other (the cold accumulation wall). The aspect ratio of the plates is such that a parabolic flow profile of the carrier solvent is established along the channel. Moreover, the thermal gradient drives analyte molecules away from the hot wall towards the cold/accumulation wall by the process of thermal diffusion. This in turn creates a concentration build-up of the analyte molecules at the accumulation wall, thereby triggering a counteracting concentration diffusion motion [13,14]. The thermal and concentration diffusion processes eventually balance out and the analyte molecules are differentially distributed across the channel. Thus, depending on the analytes position in the concentration gradient, they will reside in different velocity flow streams and elute at different times from the channel. Thermal diffusion, as described by the thermal diffusion coefficient (D_T), is sensitive to surface chemistry, while on the other hand, concentration diffusion, as described by the diffusion coefficient (D), is sensitive to size (D_h) [13,15]. As a result, separations according to D_h and CC are possible by ThFFF in one measurement [16,17].

ThFFF has previously been applied to separate and characterize poly(methyl methacrylate)-b-polystyrene (PMMA-b-PS) micelles with isotactic and syndiotactic coronas as a function of corona composition [18]. The CMC was found to be dependent on the tacticity of the PMMA corona. Micelles with the syndiotactic PMMA (sPMMA) corona exhibited lower CMC values than the isotactic equivalent owing to the better capability of the more flexible sPMMA blocks to pack together in the corona. Polystyrene-b-polybutadiene (PS-b-PBd) micelles of different PBd corona microstructures (1.2- and 1.4-PBd) have been shown via ThFFF to exhibit similar micelle-vesicle transition trends as a function of temperature gradients [9]. The corona microstructure was thus shown to have no significant impact on the resultant morphology.

Notably, in all previous ThFFF studies, emphasis has been on investigating the impact of the corona microstructure on the micelle properties [9,11,18]. It is against this background that the present study aims to utilise ThFFF to evaluate the impact of core microstructure on properties such as the degree of crystallinity, elasticity, chain flexibility and topology on the retention behaviour of PS-b-PBd self-assemblies. Since the stereoregular 1.2-PBd isomer is more crystalline and rigid than the 1.4(cis)-isomer, it is expected that self-assemblies with PBd cores having 1.2- and 1.4-isomeric structures should have different degrees of core crystallinity, elasticity and flexibility which would have an impact on morphology. This study describes the application of ThFFF coupled online to multiangle laser light scattering (MALLS), differential refractive index (dRI) and dynamic light scattering (DLS) detectors to determine the influence of microstructure, morphology and chain arrangement of the PBd core on retention behaviour of PS-b-PBd self-assemblies in ThFFF.

Table 1
Sample code names and isomeric contents of the PS-PBd block copolymers and PS homopolymers. PS-polystyrene, PBd-polybutadiene.

Sample[1]	Code name	PBd content	Dispersity[2]
1.2-PS_{66}-PBd_{75}	1.2-PS66-PBd75	1.2 > 90%	1.09
1.4-PS_{65}-PBd_{80}	1.4-PS65-PBd80	1.4 > 90%	1.14
1.2-PS_{66}-PBd_{75}	1.2-PS64-PBd33	1.2 > 90%	1.08
PS_{1400}	PS 1.4Mil	0	1.10
PS_{2400}	PS 2.4Mil	0	1.10

[1] subscript numbers indicate molar masses in kg/mol.
[2] as M_w/M_n.

2. Materials and methods

2.1. Materials

All standards were purchased from Polymer Source (Montreal, Canada) and were used as received. The subscripts represent the molar masses for the respective blocks in kg/mol (Table 1).

HPLC grade *N*,*N*-dimethylacetamide (DMAc) (Sigma Aldrich, South Africa) was used as received for preparing the self-assemblies and as the carrier solvent. ^{1}H NMR spectra (see Section 2.4.) was recorded using deuterated DMAc (DMAc-d_9), deuterated cyclohexane (cycloxane-d_{12}) and HPLC grade heptane. All solvents were purchased from Sigma Aldrich, South Africa.

2.2. ThFFF conditions

Measurements were performed using the TF2000 (Postnova Analytics, Landsberg, Germany) coupled in series to the following detectors, MALLS (7 angles over a range of 35–145° using Zimm plot) (PN3070, Postnova Analytics), dRI (PN 3140, Postnova Analytics) and a zetasizer nano-series (Malvern Instruments, Worcestershire, UK) with built-in data processing software was used for dynamic light scattering (DLS) detection at an angle 175° (back scattering detection). In excess of 100 μL of 1 mg/mL of the sample was manually injected into a 100 μL capillary sample loop to insure capillary flooding, and each analysis was performed in triplicate. A temperature drop (ΔT) of 25 °C was applied for all fractionations and an external chiller (Unichiller, Monitoring and Control Laboratories, South Africa) maintained a stable cold wall temperature at about ≈25 °C. The carrier solvent for all measurements, (DMAc), was pumped by an isocratic pump (PN 1130, Postnova Analytics) at a flow rate of 0.2 mL/min. Values for D_T were calculated according to:

$$D_T = \frac{6Dt_R}{\Delta T t_0}$$

where D is the diffusion coefficient as determined by DLS, t_R and t_0 are the respective retention and void times of the sample and ΔT is the temperature difference between the hot and cold wall [12].

2.3. Micelle preparation

1.2- and 1.4-isomeric PS-PBd block copolymers of similar PS and PBd block molar masses are separately and directly dissolved in DMAc at a temperature of 70 °C for 30 min. Complete dissolution was confirmed by dynamic light scattering (DLS) experiments, whereby, stable and reproducible unimodal peaks are observed. The expected result is two different types of micelles, both having PS coronas, but one type having a 1.2-PBd core and the other having 1.4-PBd core.