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Micellar morphology of a semifluorinated diblock copolymer

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Summary

The diblock copolymer of methyl methacrylate and 1H,1H,2H,2H-perfluorooctyl methacrylate was shown to form micelles which could be deposited and imaged on a flat substrate upon casting from a solvent which is selective for the PMMA block, e.g. toluene and THF. The micelle formation was significantly affected by a small content of PMMA homopolymer. While the pure blockcopolymer formed cylindrical micelles, the presence of the PMMA shifted the association equilibrium to the side of spherical aggregates.

Introduction

Fluorine containing polymers posses low energy surfaces and combine oil and water repellency with an outstanding chemical stability. These properties make them feasible for a number of applications, including low friction and hydrophobic coatings, foaming agents, lubricants, etc. [1-3].

If a fluorine containing polymer is linked to a hydrocarbon polymer, typical surfactant properties can be expected, i.e. surface induced phase separation and micellar association [4-6]. Like in the case of any amphiphilic compound, the properties will depend on the type of the constituent blocks, the molecular weight and the composition. Recently, a number of block copolymers have been reported in literature where one of the blocks contains fluorinated side chains [7-16]. Several techniques were applied for the synthesis, including anionic [9], cationic [10-12], ring opening metathesis [13,14], living radical [7] and group transfer polymerization [8].

The amphiphilc copolymer discussed in this publication was prepared by sequential group transfer polymerization of methyl methacrylate and 1H,1H,2H,2H-perfluorooctyl methacrylate in THF [8]. Differential scanning calorimetry and transmission electron microscopy indicated a microphase separated bulk morphology. Cylindrical domains aligned in a parallel fashion could be observed (Fig. 1). According to the volume fraction and electron scattering density, the core of the cylinders consisted of the fluorinated block and the outer shell of the PMMA block. The diameter of the cylinders was determined to be ca. 25 nm.

The surface activity of this semifluorinated polymeric surfactant was demonstrated by surface tension measurements in toluene solution [8]. Although no sharp change in slope could be observed, the surface tension showed a large initial decrease followed by a

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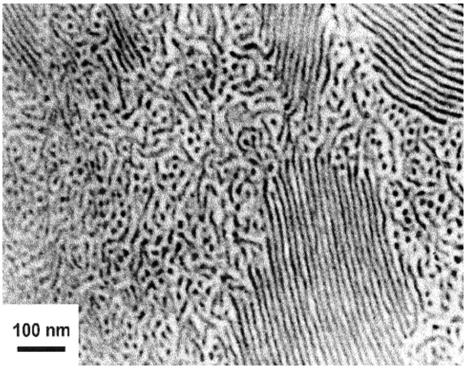

Figure 1. Transmission electron micrograph depicting a P(MMA-*b*-F6H2MA) bulk structure. The sample was used without any staining procedure. The dark regions correspond to the fluorinated block.

steady small decrease at higher concentrations. The absence of a clear break point in the surface tension-concentration curve was explained by the polydispersity of the block copolymer molecules [8]. The concentration dependent onset of the apparent critical micelle concentration (CMC) was estimated to be ca. 0.01 wt-%.

Herein we report a study on the association of P(MMA-*b*-F6H2MA). Spincasting of thin films from a selective solvent allowed to prepare specimen consisting of the dried micelles. By this, the micelles could be depicted by scanning force microscopy and also the film morphology could be correlated with results from surface tension measurements.

Experimental

Size exclusion chromatography (SEC) was conducted in chloroform at T=21°C. The set-up consisted of a Waters 590 HPLC pump, a hand injection system, a set of µ-styragel columns (10^5-10^4-10^3 Å) and a Waters 410 refractive index detector. The flow rate was 1.5 ml/min. Narrow polydispersity polystyrene standards were used for calibration. To remove PMMA homopolymer, small portions of a total amount of 125 mg contaminated copolymer were repeatedly injected into the SEC set-up and fractions were cut starting just before the PMMA peak and ending just after it. The collected fractions were subsequently precipitated in methanol and dried under vacuum at 60°C.

Scanning force microscopy (SFM) was performed at ambient conditions with a Nanoscope III (Digital Instruments) operating in the tapping mode. The probes were Si-tips with a resonant frequency of about 300 kHz. Samples were prepared by spin casting a polymer solution in either THF or toluene on a freshly cleaved mica substrate.

Transmission electron microscopy (TEM) was performed on a Philips 302 transmission electron microscope at 80 keV. Samples were prepared by putting a drop of polymer solution on a carbon coated copper grid, which was in direct contact with a soaking tissue to remove the solution immediately.

Contact angles against hexadecane (γ=27.8 mN/m) were measured at 20°C with a G40 sessile drop technique (Krüss GmbH). Sample preparation was done by spin casting polymer solutions in THF with different concentrations on cleaned microscopic glass slides (22 x 22 mm^2).

Results and discussion

The poly(methyl methacrylate-*block*-1H,1H,2H,2H-perfluorooctyl methacrylate) block copolymer was synthesized by group transfer polymerization as it was described before elsewhere [8]. The PMMA block had a number average molecular weight of 8.9 kg/mol and a polydispersity of 1.10. The weight of the perfluoroctyl metacrylate block was estimated to be 5.1 kg/mol from MMA/F6H2MA ratios determined by ^{1}H NMR.

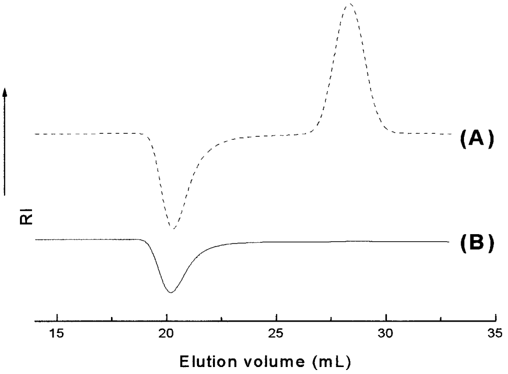

Figure 2. Size exclusion elugram showing contaminated (A) and purified P(MMA-*b*-F6H2MA) (B). Chloroform was used as solvent.

Due to partial initiation of the polymerization of 1H,1H,2H,2H-perfluorooctyl methacrylate by the PMMA macroninitiator, the blockcopolymer was contaminated by a certain amount of homo-PMMA which is demonstrated by the size exclusion elugram in Fig. 2A. The negative peak at higher elution rates can be ascribed to block copolymer associates. Absolute molar mass can be only estimated to be in a range from $2*10^7$ to $6*10^7$ g/mol based on SEC on line light scattering. The large variation has to be considered because of the evaluation is based on an average dn/dc for the blocks, large scattering of the LS-data and the eventual variation of polymer association during the elution process. The value corresponds to a degree of association between 1000 and 4000 which is consistent with the SFM results shown below.

Semipreparative SEC was performed to obtain a sample of the pure diblock copolymer. Complete separation of the homopolymer fraction is demonstrated by the absence of the peak at high elution volume in the SEC elugram in Fig. 2B.

The purified copolymer showed different solubility properties in comparison to the sample contaminated by PMMA. While the latter dissolved readily in toluene, the purified sample could not be dissolved even when it was heated for one day in toluene to 100°C. THF and chloroform dissolved both the purified and the contaminated diblock copolymer.

Spin casted films were prepared from both samples and studied by SFM and TEM in order to visualize the association to micelles. Fig. 3 shows a scanning force micrograph of a thin film of the purified blockcopolymer cast from a toluene solution. Wormlike features are depicted which we consider to represent cylindrical micelles formed by coagulation of spherical micelles [17].

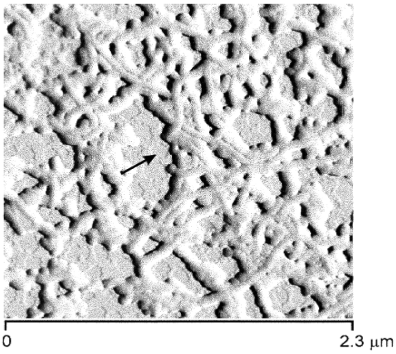

Figure 3. Scanning force micrographs of cylindrical micelles of a purified a P(MMA-*b*-F6H2MA) film cast from a 10 g/l solution in THF on freshly cleaved mica.

The diameter of the cylinders was measured parallel and perpendicular to the surface plane. The values of 50 and 45 nm respectively, corresponded well to the periodicity of the cylindrical bulk structure in Fig. 1. The black stripes in Fig. 1 are about a factor of two smaller due to the selective visualization of the fluorinated core of the cylinders. In addition, the SFM image shows a flat layer which covers the areas between the cylindrical micelles partly. This may be assigned to a layer of polymer chains which formed on top of the substrate. As marked by the arrow in Fig. 3, this film has a broken up top layer indicating that it has a lamellar structure. The thickness of this top layer was determined to be ca. 2.5 nm corresponding to layer ordering of the side chains.

When a toluene solution containing both diblock copolymer and a certain amount of PMMA homopolymer was used to prepare polymeric films, SFM yielded completely different pictures. When the films were cast from low concentrations the substrate got covered by a thin featureless layer with a uniform thickness of 1 nm. Upon increasing concentration, small globuli were observed (Fig. 4a) whose number increased upon increasing polymer concentration. Deposition at high concentration yielded densely agglomerated spherical particles which covered the entire substrate (Fig. 4b). The particles measured 14 ± 1 nm in height and 60 ± 2 nm in diameter. The discrepancy between the height and diameter is only partly an imaging artifact caused by the convolution of the curvature of the scanning probe and the contour of the particles and can be regarded as an indication for strongly prolate shape of the particles [18]. At high concentration the SFM micrograph gave a first indication for the coagulation to cylindrical structures (indicated by the arrows in Fig. 4b).

Films cast at low concentration contained particles which varied by a factor of two in diameter (Fig. 4a). The enforced association during casting of a dilute solution with C<CMC followed by rapid evaporation of the solvent might account for this observation. Only, at concentrations which are larger then the CMC, formation of uniformly sized micelles can take place under equilibrium conditions in the original solution (Fig. 4b).

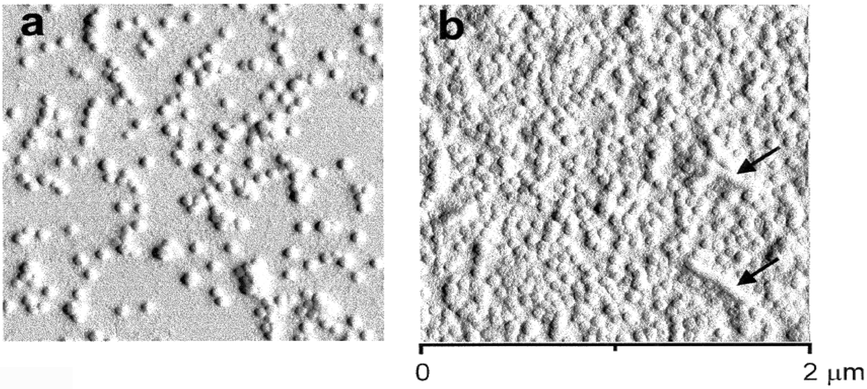

Figure 4. Scanning force micrographs (2 x 2 µm^2) of a PMMA contaminated P(MMA-*b*-F6H2MA) film. The surface coverage was varied by changing the concentration of the toluene solution from which the film was cast. a: 0.05 g/l, b: 1 g/l.

Formation of a particulate layer was also confirmed by TEM. Figure 5 depicts a TEM image of a spin cast block copolymer film consisting of small spherical particles, with an average diameter of ca. 35 nm. The average distance between the center of two neighboring particles was ca. 55 nm. This value corresponded well to the approximate average diameter of the spheres as determined by SFM.

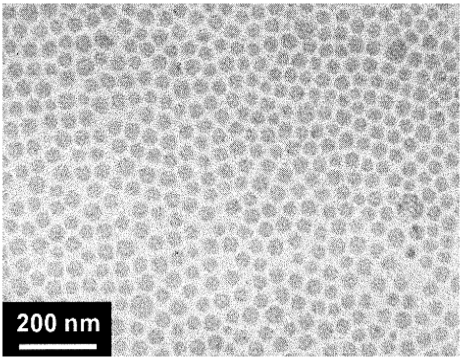

Figure 5. Transmission electron micrograph of spherical particles of contaminated P(MMA-*b*-F6H2MA) prepared from a 0.1 wt-% solution in toluene. The picture shows the core of the particles which most likely consists of the fluorinated block.

Apparently, the different morphology of purified and contaminated diblock copolymer originated from the low molecular weight fraction of the PMMA homopolymer. While, the core of the particles is formed by the fluorinated block, the PMMA block as well as the unreacted PMMA initiator are present in the corona. The particular structure of the block copolymer favors formation of cylindrical micelles, i.e. ratios of the block length and the location of the perfluorinated segments in the side chains. Addition of a homopolymer fraction can be expected to impede the formation of cylindrical structures, because effectively it increases the volume fraction of the PMMA block and hence enforces an enlarged interface between the fluorinated block and the PMMA block.

Contact angle measurements against hexadecane were carried out to characterise the surface energy of the copolymer films. Open circles represent the data obtained for films as spincast at room temperature while open squares denote the values measured on films which had been annealed at 110°C for 20 hours. For both cases, a steep increase of the contact angle was observed at low polymer concentration indicating increasing coverage of the substrate by the copolymer film. At higher concentrations, a constant value of the contact angle was approached asymptotically.

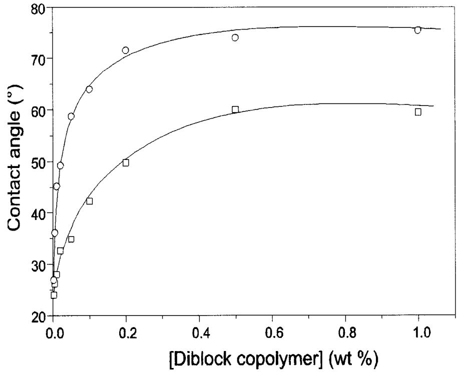

Figure 6. Contact angle of *n*-hexadecane on P(MMA-*b*-F6H2MA) films cast from toluene solutions of different concentrations. (□) as prepared, (○) after annealing at 110°C.

Samples prepared at room temperature yielded maximum contact angles of ca. 60°, a value which is indicative for a fluorine containing top layer. Annealing resulted in even larger contact angles of ca. 76°C demonstrating a high degree of lipophobicity of the coatings which is typical for a surface formed by densely packed CF_3 groups. The structure reorganization during the temperature treatment was confirmed by SFM indicating disappearance of the micelles and film smoothening.

Conclusions

Increasing block copolymer concentrations resulted in an increased surface coverage by either cylindrical or globular particles depending on the content of the unreacted PMMA homopolymer. While pure block copolymer samples formed cylindrical micelles, increasing the PMMA fraction resulted in globular aggregates. The uniformity of the globuli improved with increasing concentration probably due to the fact that a larger fraction was formed by association under equilibrium conditions in solution, rather than during solvent evaporation.

The contact angle experiments demonstrate that the surface of the films are always formed mostly from CF_3-groups, irrespectively whether it had a morphology like in Fig. 3 or in Fig. 4. Clearly annealing resulted in some improvement of the surface structure but apparently the fluorinated side chains got adsorbed at the surface already during the evaporation process. As the micelles were formed in toluene they must posses a corona of PMMA. A PMMA surface can however not explain the high contact angles found against hexadecane also for thick films whose surface is closely covered by micelles as depicted in Fig. 5b.

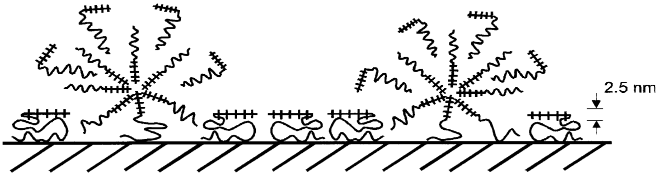

Figure 7. Schematic representation of semifluorinated diblock copolymeric films prepared by casting of micellar solutions.

So far, the picture shown schematically in Figure 7 emerges: non associated P(MMA-*b*-F6H2MA) molecules are primarily adsorbed via the PMMA block on the mica substrate with the fluorinated block being exposed to the air. Preferential adsorption of the PMMA block was also found by others for P(St-*b*-MMA) block copolymers [19]. According to the contact angles, micelles must be covered by a thin brush layer of copolymer chains to yield a surface which is maximally constituted of fluorocarbon moieties resulting in large contact angles against hexadecane.

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