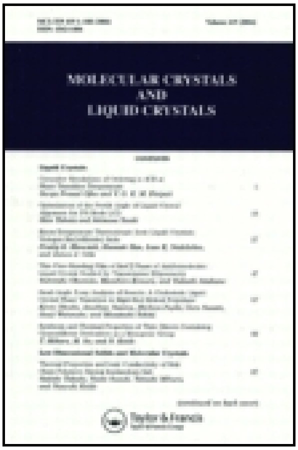

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Multiple Morphologies of Self-Assembled Amphiphilic Poly(FOMA-*b*-EO) Diblock Copolymers

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A series of well defined semifluorinated diblock copolymers of poly(1H,1H-dihydroperfluorooctyl methacrylate)-block-*polyethylene oxide (poly(FOMA-b-EO)) were used for the preparation of self-assembled structures. The morphologies of the poly(FOMA-b-EO) aggregates formed from solvent casting were investigated in terms of the copolymer composition, the concentrations of copolymer solutions, and the solvent type. From* $CHCl_3$*, the micellar film morphologies of poly(FOMA-*b*-*EO_{20k}*) were found to be well-ordered spherical and interconnected rods aggregates when PFOMA block sizes were 10 k (or 20 k) and 80 k. The aggregates were also found to depend strongly on the copolymer concentration. On the other hand, the morphological phase of block copolymeric micelles was inverted in trichlorofluoromethane (CFC-11) solution which is a good solvent for PFOMA, and aggregates were formed with PFOMA as a corona and PEO as a core. Morphological variations were also achieved by using different solvents such as N,N-dimethylformamide (DMF) and methanol, where the aggregates formed were vesicles and lamella with rods.*

Keywords: amphiphilic block copolymers; micelles; self-assembly

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1. INTRODUCTION

Block copolymers have received considerable attention due to their ability to self-assemble in solution forming a range of different morphologies and sizes [1–5]. When amphiphilic diblock copolymers were dissolved in a solvent which is good for only one of the blocks, they form nanosized aggregates as a result of the self-assembly of the less soluble segments [6–8]. In the pioneer work reported by Eisenberg *et al.*, multiple morphologies of micelles were made from block copolymers, such as spheres, rods, vesicles, lamellae, tubules, and large compound micelles (LCMs) etc [9–12]. The manipulation of the relative block length [10–12], concentration of block copolymer solution [13], solvent composition [14–16], presence of additives [17,18], and temperature [2,3] have known to produce a wide range of micelle morphologies.

Block copolymeric micelles, which can be either thermodynamically or kinetically stable under a given set of conditions, have many potential applications in various fields, such as cosmetics, drug delivery, electronics, pollution control, advanced materials formation, and separation [19–22]. It has been known that the equilibrium aggregate morphologies can be controlled by altering the influence exerted by the stretching of core-forming blocks, intercorona interactions, and the interfacial free energy between the solvent and the micellar core [5,23,24]. A change in any one of the above factors, disturbs the balance between forces governing aggregates, leading to the transformation of the one morphology into another.

It is well-known that fluorine-containing polymers exhibit unique properties such as low surface energy and high lipo- and hydrophobicity [26]. Moreover, they are promising materials in many photonic devices because of their good thermal stability and optical property [27]. While the synthesis and self-assembly of block copolymers were frequently observed in recent literatures, works of fluorine containing block copolymers were rarely studied. Recently, we reported the synthesis of well-defined fluorinated block copolymers and their self-assembled morphologies in micellar thin films [1–4]. Microphase-separated structures of semifluorinated block copolymers produced from solution cast were rearranged into thermodynamically stable morphologies upon aging above their glass transition temperature.

In this study, the self-assembly behavior of poly(1H,1H-dihydroperfluorooctyl methacrylate)-*block*-polyethylene oxide (poly(FOMA-*b*-EO)) with different block compositions was investigated in solution at various conditions, such as the copolymer concentration and the solvent type.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Block Copolymer

Poly(FOMA-*b*-EO) was synthesized according to the procedure as reported previously [1]. In brief description, methoxy polyethylene oxide (MPEO-Br) was prepared by reacting MPEO-OH ($M_n =$ 20 000 g/mol, from Polymer source) with 2-bromoisobutyryl bromide (BBB, from Sigma-Aldrich). The MPEO-Br was used as a macroinitiator in atom transfer radical polymerization (ATRP) of FOMA. Well-defined diblock copolymers of poly(FOMA-*b*-EO) could be synthesized using the mixed halogen initiation system of R-Br/CuCl in the mixed solvent of trifluorotoluene and benzene. The molecular weight of poly(FOMA) blocks was precisely controlled by varying the ratio of monomer to macroinitiator concentration, and block copolymers of poly($FOMA_m$-*b*-EO_{20K}) with 10, 20, and 80 K of PFOMA were prepared. Table 1 summarizes the results of the polymerizations.

2.2. Preparation of Micellar Solutions

The micellar solutions of block copolymers were prepared in $CHCl_3$, trichlorofluoromethane (CFC-11), N,N-dimethylformamide (DMF) and methanol. The micellar thin films were made by spin-casting of micellar solutions (0.5 and 2 wt%) onto a copper grid coated with carbon. Solvents were allowed to evaporate from the grids at atmospheric pressure and room temperature. The morphologies of the thin films were investigated by transmission electron microscope (TEM) using a Hitachi H-7500 instrument operated at 80 kV.

TABLE 1 The Preparation of poly(FOMA-*b*-EO) by ATRP[a]

Block copolymer[b]	[M]/[I]/[CuBr]/ [bpy]	Monomer conv.[c] (%)	m(PFOMA)/ n(PEO)[d]
Poly($FOMA_{10k}$-*b*-EO_{20k})	25/1/1/3	75	0.5
Poly($FOMA_{20k}$-*b*-EO_{20k})	38/1/1/3	90	1
Poly($FOMA_{80k}$-*b*-EO_{20k})	128/1/1/3	96	4

[a] 110°C, solvent : mixed solvent of trifluorotoluene and benzene (50:50 by weight).

[b] Composition of poly(FOMA-*b*-EO) was determined by ^1H NMR.

[c] Conversions were measured by gravimetric method.

[d] m/n = weight ratio of PFOMA and PEO in the block copolymer.

3. RESULTS AND DISCUSSION

Due to the different nature as well as solubility difference between the amorphous PFOMA and the crystalline PEO block, these copolymers undergo self-assembly into nanosized micelles with various shapes and dimensions, induced by selective solvent systems [28]. In order to compare the morphologies of the self-assembled structures, the concentration of the block copolymer solution was kept constant (0.5 wt%). When the copolymers were dissolved in $CHCl_3$, which is a precipitant for PFOMA but a good solvent for PEO, poly(FOMA-*b*-EO) formed micelles of PEO corona and PFOMA core.

The TEM micrographs of the micelles formed in $CHCl_3$ are shown in Figure 1. The dark core regions correspond to the PFOMA in accordance with the higher electron density of the fluorinated blocks. Poly($FOMA_{10k}$-*b*-EO_{20k}) formed spherical micelles with a diameter of 15 nm, as shown in Figure 1A. When the length of PEO corona is long enough compared with PFOMA core, the repulsive interactions among intercoronal chains exceed the interfacial energies and these interactions dominate the equilibrium structure [5]. The block copolymer hence favors the formation of star-like spherical micelles with extended PEO corona. In the case of poly($FOMA_{20k}$-*b*-EO_{20k}) where the molecular weight of PFOMA core was 20 000 g/mol, the average diameter of the aggregates increased to 26 nm (see Fig. 1B), indicating that the micellar size majorly depends on the block length of PFOMA core. However, as the molecular weight of PFOMA increased further as it was poly($FOMA_{80k}$-*b*-EO_{20k}), the micellar morphology became

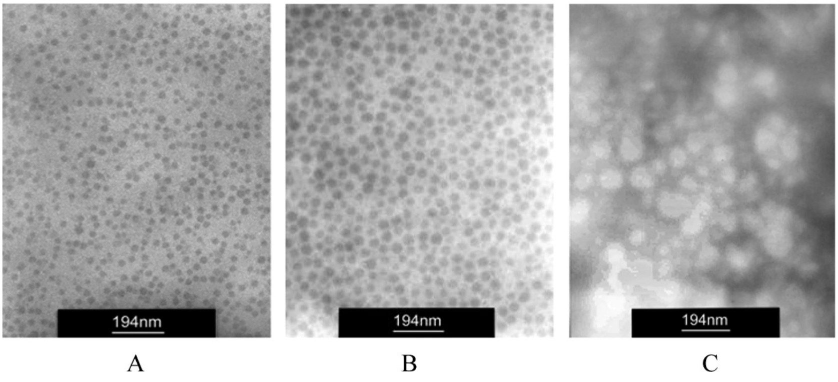

FIGURE 1 TEM images of micelles of poly($FOMA_{10k}$-*b*-EO_{20k}) (A), poly($FOMA_{20k}$-*b*-EO_{20k}) (B), and poly($FOMA_{80k}$-*b*-EO_{20k}) (C) spin cast from $CHCl_3$ solutions of 0.5 wt%.

interconnected rods with a diameter of 25 nm (see Fig. 1C). At a constant PEO block length, therefore, the morphology of aggregates changed from spherical to interconnected rods with an increase in the PFOMA block length. This morphological change can be explained by the fact that the morphological transition takes place due to changes in the degree of stretching of the PFOMA blocks in the core region like crew-cut aggregates where soluble blocks are shorter than insoluble blocks [29]. The three kinds of micellar solutions, two of the core-shell spheres (Fig. 1A and 1B) and the other one of interconnected rods (Fig. 1C) were further characterized by DLS. The results obtained for each system by the cumulant method are summarized in Table 2. The micellar size of block copolymers were 60, 100 and 300 nm for poly($FOMA_{10k}$-*b*-EO_{20k}), poly($FOMA_{20k}$-*b*-EO_{20k}) and poly($FOMA_{80k}$-*b*-EO_{20k}), respectively.

The morphology was also found to depend strongly on the solution concentration. At the low concentration (polymer solutions of 0.5 wt% in $CHCl_3$), spherical morphologies with fairly long-range order were observed (Fig. 1B). The unfavorable interaction between PFOMA and PEO limits the amount of PFOMA/PEO interfacial area and determines the minimum spherical micelle size and micelle-micelle distance [30]. With an increase in concentration (the polymer solution of 2 wt% in $CHCl_3$), the micelles were transformed from spherical to sphere necklace due to the increased interaction between micelles (Fig. 2). Similarly, Lam *et al.* [13] reported aggregates of poly(S-*b*-4VP), depending on the solution concentration (0.2, 0.8 and 1.3 wt%). With an increase in concentration, the micelles become bigger such that their diameter might exceed the thickness of the film. In this case, the second layer of spherical micelles lies above the first layer in the film and the micelles transform to sphere necklace that extends from one side of the film to the other.

The copolymers were insoluble in pure CFC-11 which is a good solvent for PFOMA but a precipitant for PEO, probably due to

TABLE 2 Hydrodynamic Radius (R_h) and Polydispersity Index (PDI) of the Micelles Formed by Block Copolymers in Chloroform Solvent

	Concentration of 1 mg/mL	
Micelles	R_h (nm)	PDI
poly($FOMA_{10k}$-*b*-EO_{20k})	60	0.2
poly($FOMA_{20k}$-*b*-EO_{20k})	100	0.21
poly($FOMA_{80k}$-*b*-EO_{20k})	300	0.26

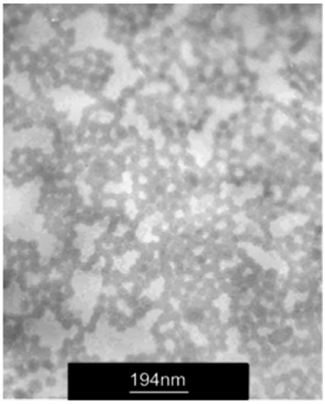

FIGURE 2 TEM image of micelles of poly(FOMA$_{20k}$-*b*-EO$_{20k}$) spin-cast from the CHCl$_3$ solution of 2 wt%.

crystalline PEO chains. However, a couple of drops of CHCl$_3$ made the block copolymer solution clear with bluish tinge. The TEM analysis indicated that inverted micelles were formed in the solution. CHCl$_3$ swells PEO chains and the block copolymer self-assembles to micelles in the solution. When the selective solvent changes from CHCl$_3$ to CFC-11, the PFOMA blocks become the outer part of the aggregates. Figure 3 shows various morphologies formed by poly(FOMA-*b*-EO) copolymers in CFC-11 (with a couple of drops of CHCl$_3$). Figure 3A shows that poly(FOMA$_{10k}$-*b*-EO$_{20k}$) forms micellar aggregates where

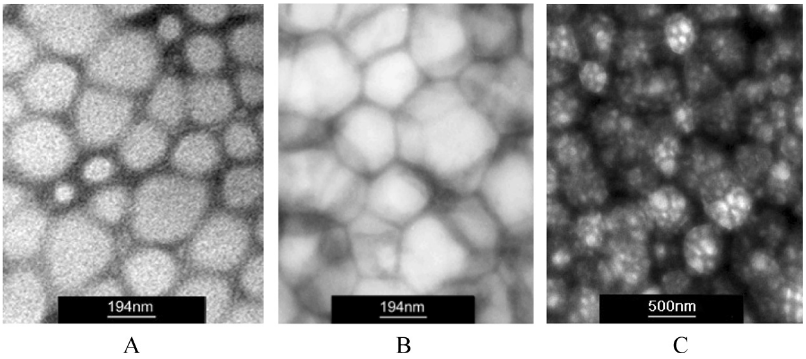

FIGURE 3 TEM images of micelles of poly(FOMA$_{10k}$-*b*-EO$_{20k}$) (A), poly(FOMA$_{20k}$-*b*-EO$_{20k}$) (B), and poly(FOMA$_{80k}$-*b*-EO$_{20k}$) (C) spin-cast from CFC-11 solutions of 0.5 wt%.

more extensive interconnection of the minor phase is delineated, so that the major component PEO forms discrete domains in a continuous matrix of the minor component PFOMA. As the PFOMA content increased in the case of poly($FOMA_{20k}$-*b*-EO_{20k}), the block copolymer produced regions consisting of a highly interconnected polygonal network with hexagonal domains (Fig. 3B). The domain size of poly ($FOMA_{10k}$-*b*-EO_{20k}) (ca. 200 nm) is about the same as that of poly($FOMA_{20k}$-*b*-EO_{20k}) (ca. 200 nm) although both diblock copolymers have different molar ratios (0.5 vs. 1, Table 1). In contrast, the poly($FOMA_{80k}$-*b*-EO_{20k}) possessing the higher molar ratio of 4 has a significantly smaller hole size at 50 nm in diameter (Fig. 3C).

To investigate the effect of solvent type on the micellar morphologies, two other solvents (methanol and DMF) were used for poly($FOMA_{10k}$-*b*-EO_{20k}) micelles. The copolymer was expected to undergo self-assembly into nanosized micelles with various morphologies caused by the selective solvent system. Depending on the organic solvent employed, aggregates from spheres to rods, vesicles, and compound micelles have been reported by others [11]. There are mainly two factors which might be considered for the effect of solvents on the formation of various morphologies. One factor is the different dimensions or stretching degrees of the core-forming chains and another one is the different repulsive interactions between shell-forming chains in different solvents during micellization.

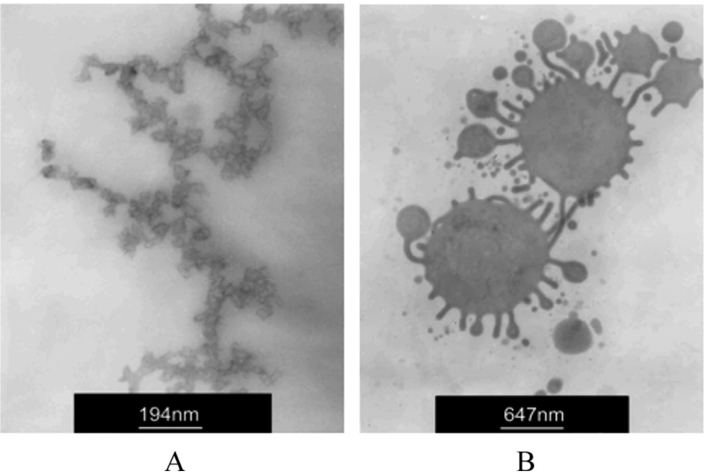

FIGURE 4 TEM images of various morphologies obtained form poly($FOMA_{10k}$-*b*-EO_{20k}) in DMF (A), and methanol (B).

TABLE 3 Summary of the Structural Parameters of Micelles Formed by Copolymers in Different Solvents, as Observed with TEM

	$CHCl_3$		CFC-11		DMF		Methanol	
Block copolymer	Morphology	Size (nm)	Morphology	Size (nm)	Morphology	Size (nm)	Morphology	Size (nm)
Poly($FOMA_{10k}$-b-EO_{20k})	Spheres	15	Network	200	Vesicles	20	Lamellar with rods	700
Poly($FOMA_{20k}$-b-EO_{20k})	Spheres	26	Network	200	NA*	–	NA*	–
Poly($FOMA_{80k}$-b-EO_{20k})	Rods	25	Network	50	NA*	–	NA*	–

NA*: No micelle formed.

As mentioned earlier, when the solvent was $CHCl_3$, the resultant aggregates were core-shell spheres with diameter of about 15 nm. The different types of aggregates in different solvents can be explained by the solubility parameters of the PEO in particular solvents. For example, the solubility parameter of $CHCl_3$ ($\delta = 18.7\,MPa^{1/2}$) is closer to that of PEO ($\delta = 19.9\,MPa^{1/2}$) than that of DMF ($\delta = 24.7\,MPa^{1/2}$) or methanol ($\delta = 29.7\,MPa^{1/2}$) [31]. Thus, $CHCl_3$ is better solvent for PEO chains than DMF or methanol. In DMF or methanol, the dimension of PEO corona is smaller than that in $CHCl_3$ solvent at the same conditions because of smaller repulsive interaction of the corona PEO chains. Thus crew-cut type micelles were formed for selective solvent DMF or methanol. In DMF, the resultant aggregates were vesicular with 20 nm in diameter (see Fig. 4A). The vesicular morphology is evidenced from a higher transmission in the center of the aggregates than that of their periphery. On the other hand, when methanol was used as the solvent, as can be seen in Figure 4B, lamellae with protruding rods-like aggregates with a diameter of 700 nm were formed. In methanol, the aggregates were bigger due to its bad solubility for PFOMA ($\delta = 13.5\,MPa^{1/2}$) in comparison with other selective solvents. The low chain mobility and weak interaction between PEO chains and the solvent led to fast growth of the lamellae with rods. The results show that the natures of the selective solvents are important factors influencing the morphologies. The micellar morphologies of poly(FOMA-*b*-EO) copolymers having different FOMA block lengths in various organic solvents are listed in Table 3.

4. CONCLUSION

The self-assembly behavior of poly(FOMA-*b*-EO_{20k}) with different PFOMA block lengths was investigated in solutions at various conditions. In $CHCl_3$, the micellar film morphologies of poly($FOMA_{10k}$-*b*-EO_{20k}) and poly($FOMA_{20k}$-*b*-EO_{20k}) were found to be well-ordered spherical with the diameters of 15 nm and 26 nm, respectively, whereas poly($FOMA_{80k}$-*b*-EO_{20k}) produced interconnected rods morphologies. The morphology also depended on the solution concentration. At low concentration, spherical micelles with fairly long-range order were observed. With an increase in concentration, the micelles were transformed from spherical to sphere necklace due to the interaction between micelles. In CFC-11, the morphological phase of block copolymers was inverted, leading to micellar films of PEO domains in the PFOMA matrix. Morphological tuning was also achieved by different solvent types such as DMF and methanol. While the aggregates were vesicles in DMF, lamella with rods morphology was formed in methanol.

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