Chapter 3

Behavior of poly(ethylene oxide) and poly(perfluorohexylethyl methacrylate) containing block copolymers in aqueous solution

3.1. Introduction

The ability of block copolymers to organize as micelles or other complex aggregates in selective solvents above a certain critical micelle concentration (CMC) has been studied for the last several decades. Block copolymers with hydrophilic and hydrophobic segments in particular have been a rich field of research due to the structural diversity formed in solvents selective for one block. Thus, amphiphilic block copolymers form various supramolecular structures such as spherical micelles, vesicles, cylindrical micelles and other complex aggregates in solution. The reason behind the keen interest in self-association of amphiphilic block copolymers has been their potential applications in different fields such as biomedical, pharmaceutical etc.

Amphiphilic block copolymers with long hydrophilic block attached with small hydrophobic block at one or both ends are also known as hydrophobically modified water-soluble polymers (HMWSP). These polymers are important because they exhibit characteristic rheological features that are markedly different from unmodified parent polymers. In aqueous solutions, the hydrophobic blocks of these polymers tend to associate forming hydrophobic microdomains to minimize their interaction with the unfavorable aqueous surrounding and interdomain bridges (especially the systems where the hydrophilic block is attached with hydrophobic blocks at both the ends). These interdomain bridges are assumed responsible for the unusual rheological features of these polymers. Though both the diblock (hydrophilic polymer with hydrophobic block at one end) and triblock copolymer (hydrophilic polymer with hydrophobic block at both the ends) form micelle like aggregates in water, yet the associated structures of these
Chapter 3 Behavior of poly(ethylene oxide) systems are significantly different. Diblock copolymers prefer to form individual micelles with little tendency for cluster formation, except at very high concentration, while the triblock copolymers have tendency to form intermicellar network structure, caused by bridges at higher concentration. Triblock copolymers in a solvent selective for the middle block are assumed to form flower-like micelles with the middle block looping in the micelle corona at low concentration, however, their existence is still controversial from both the theoretical and experimental point of view. There are conflicting reports in literature about the self-association behavior of triblock copolymers in solvent selective for the middle block. Entropy loss due to the loop formation of the middle block is considered to be the main barrier for such block copolymers to self associate into regular micelles. Several factors such as size of the molecule (molar mass), composition, architecture, and concentration of the amphiphilic block copolymer play a key role in aggregation behavior, size and shape of the microscopic self-assembled structures. Various methods can be used, to investigate the onset of micellization in solution, the structural parameters of the micelles and the effect of different factors such as mentioned above on the micellization process. Experimental techniques such as viscosimetry, fluorescence, surface tension measurements, laser light scattering, TEM etc. have been used.

Amphiphilic block copolymers with poly(ethylene oxide) (PEO) as hydrophilic block have been extensively studied for several years, especially pluronic type of block copolymers. PEO-based amphiphilic block copolymers with other hydrophobic blocks such as polystyrene, poly(butylene oxide) etc. have also been reported frequently. However, there are only a few reports dealing with fluorocarbon modified poly(ethylene oxide) systems.

Amphiphilic block copolymers of PEO as hydrophilic block and fluorine containing hydrophobic block might be of great potential interest because of the very peculiar properties of fluorine-containing materials such as low surface energy, high contact angle, reduced coefficient of friction, bio-compatibility and oleo- and
hydrophobicity. However, most of the literature available on the fluorine containing amphiphilic systems addresses low molar mass molecules, probably due to the difficulty in the synthesis of fluorine containing amphiphilic block copolymers. Only scarce literature is available on water-soluble fluorine-containing amphiphilic block copolymers. However, a number of investigations have been carried out on aggregation behavior of fluoroalkyl ended poly(ethylene glycol).

In this chapter, self-association behavior of water-soluble fluorine containing amphiphilic di- and triblock copolymers having PEO as hydrophilic block and PFMA as hydrophobic block, synthesized by ATRP as explained in chapter 1, has been discussed. A diblock copolymer having PEO hydrophilic block and \( n \)-decylmethacrylate as hydrophobic block (PEO-\( b \)-PDMA), anionically synthesized has been included as well. The naming scheme for PEO and PDMA containing diblock copolymers is the same as that for PEO and PFMA containing diblock copolymers discussed in Chapter 2, i.e. PEO\(_x\)Fy-D for PEO and PFMA and PEO\(_x\)Dy-D for PEO and PDMA based block copolymers. Association properties in aqueous solution have been studied using surface tension measurements, dynamic light scattering (DLS) and transmission electron microscopy (TEM). Surface tension measurements have shown that the copolymers start aggregation above a characteristic concentration (CMC). DLS investigations were carried out above the CMC, where the existence of micelles could be expected. DLS studies reveal the existence of various scatterers in solution, including single chains, micelles and larger clusters. TEM investigations have shown spherical micelles; however, different initial concentrations have exhibited different morphologies.
3.2. Experimental section

3.2.1. Surface tension measurements

Surface tension measurements were carried out by pendant drop method using OCA 20 (Data Physics) at 20°C. For this purpose aqueous polymer solutions were prepared in double distilled water. Clear solutions were obtained after overnight stirring at room temperature. However, in some cases a few minute ultrasonic treatment in addition to stirring was given as well to get clear solutions. Freshly prepared stock solutions were diluted to different concentrations for surface tension measurements. The same solutions were also used for DLS and TEM studies.

3.2.2. Dynamic light scattering

DLS measurements were performed with ALV-5000 goniometer equipped with Nd:YAG DPSS-200 laser at a wavelength of 532 nm. The intensity time-correlation functions $g^2(\tau)$ were recorded with an ALV-5000E multiple-tau digital autocorrelator. The normalized field autocorrelation function $g^1(\tau)$ was derived from the $g^2(\tau)$ via Siegert relation. In the device, the thermostated sample cell is placed on a motor-driven precision goniometer (± 0.01°) which enables the photomultiplier detector to be moved from 20° to 150° scattering angle. A refractive index matching toluene surrounded the scattering cell. Experiments were done on the block copolymer solutions having concentration above CMC. The samples were prepared by filtering the solutions through cellulose acetate filters with 0.2 µm pore size directly into the dust free quartz cells. Measurements were made at an angle of 90°, otherwise mentioned. The experimental duration for each experiment was 15 to 30 min depending upon the scattering intensity. The correlation functions from dynamic light scattering were analyzed by the CONTIN method, giving information on the distribution of decay rate ($\Gamma$). Apparent diffusion coefficients were obtained from $D_{\text{app}} = \Gamma / q^2$ [with $q = (4 \pi n \lambda) \sin(\theta/2)$, $n =$ refractive index of the medium, $\lambda =$ wavelength of the light, $\theta =$ scattering angle] and the
corresponding apparent hydrodynamic radii ($R_{h,\text{app}}$, radius of the hydrodynamically equivalent sphere) via Stokes-Einstein equation $R_{h,\text{app}} = kT / (6\pi\eta D_{\text{app}})$, where $k$ is the Boltzmann constant and $\eta$ is the water viscosity at temperature $T$.

### 3.2.3. Transmission electron microscopy

TEM images were obtained using a LEO 912 TEM operating at an acceleration voltage of 120 kV. Samples were prepared by dipping carbon coated copper TEM grid into the copolymer solution. Extra solution was blotted with filter paper. The samples were then stained with RuO$_4$. 
3.3. Results and discussion

3.3.1. Micelle formation

Surface tension measurement over a wide range of concentration is one of the several methods used for the CMC determination of low molar mass surfactant or amphiphilic block copolymers. Surface tension measurements were carried out on aqueous solutions of the block copolymers in order to obtain information on the surface activity and micelle formation by the block copolymers. Figure 3.1a depicts the decreasing surface tension with increasing copolymer (PEO$_2$F12-D) concentration. It is clear from the plot that the surface tension decreases linearly with the logarithm of the copolymer concentration according to the Gibbs adsorption isotherm, i.e. a usual behavior of surface-active compounds. At a characteristic concentration, there is a clear inflection point above which the surface tension remains almost constant. This is a significant indication for a CMC and occurs for this sample at 2.14 g/L at 20°C. However, two inflection points can be seen in Figure 3.1b for PEO$_{10}$F11 above which the surface tension is still slightly decreasing. For comparison, we took the first inflection point as the CMC of the sample. For triblock copolymers PEO$_{10}$F5, PEO$_{10}$F9 and PEO$_{10}$F11 having the same PEO block length but different PFMA contents, the CMC values were calculated to be 1.1, 0.7,
and 0.4 g/L, respectively. Therefore, the CMC decreases with increase in fluoro content in the block copolymer; in other words high fluoro content enhances the surface activity of the copolymer.

Direct evidence for the presence of micelles in solution can be obtained from DLS investigations. Hence, further investigations on the aggregation behavior of the block

![Graphs showing decay-rate distributions for different block copolymers.](image)

**Figure 3.2.** Decay-rate distributions for (a) PEO$_{10}$D$_{13}$-D ($c = 4$ g/L), (b) PEO$_2$F$_{12}$-D (4.0 g/L), (c) PEO$_{10}$F$_5$ (4.0 g/L), and (d) PEO$_{10}$F$_{11}$ (4.25 g/L) obtained from the respective time correlation functions, measured at $\theta = 90^\circ$, using CONTIN method.$^{132}$ The measurements were carried out at 20°C.
copolymers were carried out with DLS. Distributions of decay rates \( \Gamma \) were obtained by analysis of the dynamic correlation functions \( g^{(1)}(\tau) \) by CONTIN.\textsuperscript{132} Figure 3.2 shows decay rate distributions for different samples. The distribution for sample PEO\textsubscript{10D13-D} reveals one prominent peak and another very small peak as shown in Figure 3.2a. The fast (I) and the intermediate (II) mode correspond to aggregates with apparent hydrodynamic radii \( R_{h, \text{app}} = 2.7 \) and 31 nm, respectively. Figure 3.2b, shows one prominent peak (II) for decay rate distribution for the sample PEO\textsubscript{2F12-D} corresponding to aggregates of \( R_{h, \text{app}} = 15 \) nm and a very small peak (III) at lower decay rate distribution representing some large scatterers. The PEO block length in PEO\textsubscript{2F12-D} is roughly five times shorter and \( R_{h, \text{app}} \) is approximately half of the value for PEO\textsubscript{10D13-D} copolymer. This suggests that the same scaling behavior as for Gaussian chains, \( R_{h, \text{app}} \sim M_w^{0.5} \), is applicable. However, the length of an extended PEO chain with \( M_w = 2000 \) g/mol, with approximate \( R_{h, \text{app}} \) of 16 nm, is in the same range. Therefore, the PEO chains seem to be nearly full extended as no change in shape or structure of the micelles could be detected by TEM (discussed below). The triblock copolymers, however, show quite a different behavior. The \( \Gamma \) distributions are far from single mode as shown in Figure 3.2c and d for sample PEO\textsubscript{10F5} and PEO\textsubscript{10F11}, respectively. Figure 3.2c clearly reveals three modes of decay rate representing three types of aggregates in the solution. Peak I, II, and III for fast, intermediate, and slow modes correspond to \( R_{h, \text{app}} = 3, 16, \) and 85 nm, respectively. In Figure 3.2d three peaks are also identified, corresponding to aggregates of \( R_{h, \text{app}} = 1.7, 18 \) and 84 nm respectively. The aggregates of intermediate size, \( R_{h, \text{app}} = 31, 15, 16, 18 \) nm in the solutions of samples discussed above can be regarded as micelles with hydrophobic block making the core and hydrophilic PEO block constitutes the corona of the micelle. The fast mode (peak I in Figure 3.2a, c, and d) can be attributed to the single chains in the solution and the slow mode (peak III in Figure 3.2c and d) can be assigned to large clusters. The difference in the \( R_{h, \text{app}} \) values of micelles for the triblock copolymers (PEO\textsubscript{10F11}, PEO\textsubscript{10F5}) (18 and 16 nm) and diblock
copolymer PEO\textsubscript{10}D13-D (31 nm) with approximately the same PEO block length suggests that the PEO middle block in triblock copolymer micelles form loop in the micellar corona, resulting in the formation of flower-like micelles as has been suggested for block copolymers with this type of architecture,\textsuperscript{41,118} (i.e. hydrophilic middle block attached with hydrophobic blocks at its two ends). However, a very broad decay rate distribution peak for PEO\textsubscript{10}D13-D and very small hydrophobic blocks in triblock copolymers makes it difficult to interpret the data with certainty. Several groups have reported the presence of large aggregates in addition to regular micelles in aqueous solution of PEO containing block copolymers.\textsuperscript{126} However, in our investigations, the presence of large aggregates or clusters were more evident in triblock copolymer solution, an expected observation for this type of amphiphilic triblock copolymers.

Two opposing thermodynamic parameters play important role in the formation of flower-like micelles by the triblock copolymers; (i.e. having hydrophilic middle block and hydrophobic end blocks) the loss of entropy due to looping of the middle block and the free energy gain on the association of hydrophobic ends in the micellar core.\textsuperscript{118} The combined free energy of loop formation can be estimated from:

$$\Delta G_{\text{looping}} = \Delta G_{\text{back folding}} + \Delta G_{\text{hydrophobic}}$$

Stable flower-like micelles will form only when the net looping energy is negative. Alami et al.\textsuperscript{116} have reported such estimations for the hydrophobically modified poly(ethylene oxide) (C\textsubscript{12}E\textsubscript{460}C\textsubscript{12} systems). However, perfluorohexylethyl methacrylate blocks rather than \textit{n}-alkyl groups, modify the PEO in the polymers discussed here. In this case, it becomes very much complicated to assess the net free energy of looping process. However, simplifying the case and taking into consideration that CF\textsubscript{2} is more hydrophobic than CH\textsubscript{2}, i.e. 1 CF\textsubscript{2} \textasciitilde 1.7 CH\textsubscript{2},\textsuperscript{133} 12 CH\textsubscript{2} groups can be assumed in each FMA unit. Using Equation 2 and 3, net looping energy ($\Delta G_{\text{looping}}$) can be calculated.
\[ \Delta G_{\text{back folding}} = -2.6RT + 1.5RT \ln N_{\text{EO}} \]  
(3.2)

\[ \Delta G_{\text{hydrophobic}} = (-0.3 \text{ to } -0.5)RTN_{\text{CH2}} \]  
(3.3)

Hence, for PEO (10 000 g/mol) having 227 EO units and FMA with 12 CH\text{2} groups, \( \Delta G_{\text{looping}} = -0.5RT \). This simple picture predicts that a single FMA unit at each end would be sufficient for the PEO chain of 227 EO units to make energetically stable loop. From the net composition of the copolymer, it can be calculated that each chain of PEO is attached to approximately 3-4 FMA units in total, i.e. there is a high probability to have at least one FMA unit at each end. Therefore, the formation of flower like micelles would be preferred by these triblock copolymers.

### 3.3.2. Effect of concentration, temperature, ultrasonic treatment, and time

For detailed DLS investigations, the PEO\textsubscript{10}F11 sample was chosen due to its architecture and good scattering intensity as compared to other copolymers. Investigations were carried out over a range of concentration (above the CMC region) and each concentration was measured at several temperatures from 15°C to 50°C. Concentration dependent DLS data at two representative temperatures (30°C and 50°C) have been shown in Figure 3.3. Two large overlapping and one much smaller peak can be seen for all concentrations. The assignment of these peaks has been discussed earlier. The much smaller peak that appears at higher relaxation rate (\( \Gamma \)) corresponds to scattering species with \( R_{\text{h,app}} \) in the range of \( 2.2 \pm 0.5 \) nm for all concentrations. The value is close to that deduced from the empirical relationship for unmodified PEO in water at 30°C:\textsuperscript{134}

\[ R_{\text{h}} = 0.0145M_{w}^{0.57\pm0.009} \text{ (nm)} \]  
(3.4)

\( (M_{w} \text{ in g/mol}) \). This relation gives \( R_{\text{h}} = 2.79 \) nm, for PEO with \( M_{w} = 10 \) 000 g/mol. A smaller value would be expected for copolymer chains where both the hydrophobic ends come close to each other to avoid interaction with unfavorable environment (water) with
the PEO loop in the surrounding. However, from the data it is difficult to assign this small peak either to single unassociated polymer chains or to unimolecular self-assembled structures. As the CONTIN program could not resolve the two overlapping peaks, the correlation functions were fitted to a bi-exponential function to obtain the apparent hydrodynamic radii for the intermediate and slow mode. A single exponential function could not fit the data. In order to check if real particles are detected by our measurements,

![Graph showing decay rate distributions obtained by DLS for PEO₁₀F₁₁ at different concentrations at (a) 30°C and (b) 50°C.](image)

**Figure 3.3.** Decay rate distributions obtained by DLS for PEO₁₀F₁₁ at different concentrations at (a) 30°C and (b) 50°C.
an angle dependent measurement of the decay rates was performed. Figure 3.4 shows that the relaxation rates of the fast and slow modes are proportional to the square of the scattering vector, indicating that the observed peaks come from diffusive aggregates. Therefore, the calculation of the apparent diffusion coefficient via \( D_{\text{app}} = \Gamma/q^2 \) is correct for these modes. Apparent hydrodynamic radii of the aggregates in solutions having different concentrations were calculated from the data via Stokes-Einstein equation. Each concentration was measured at several temperatures between 15 and 50°C. Figure 3.5 shows the effect of concentration on the apparent hydrodynamic radius of the micelles and clusters for three temperatures. The error bars in the figure give the error on fitting the mean value. With concentration, a slight but significant increase (~ 2 nm) in the apparent hydrodynamic radius of micelles was observed for all the three temperatures. This effect can be due to the micellar structure, i.e. flower-like micelle having some

**Figure 3.4.** Plot of the relaxation rate as function of \( \sin^2(\theta/2) \) for both the intermediate mode (micelles) (■) and slow mode (clusters) (●) at 20°C and \( c = 3.0 \) g/L. The data are derived from the bi-exponential fitting to the DLS data.
PFMA ends extended into the solvent. These extended chains may result in transient linking, providing an attractive contribution to intermicellar interaction. Yang et al. have reported similar results for ethylene oxide and butylene oxide containing triblock copolymers (BₐEₘBₙ). On the other hand, temperature had no effect on the micellar radii. Similar effect of temperature on PEO containing block copolymer micelles in water has been observed, and regarded as a compensation between an increase in aggregation number and a decrease in expansion of the PEO block fringe in the water that becomes poorer with temperature. An effect of concentration on the clusters was even more significant as can be seen by an increase of the hydrodynamic radius. For the highest concentration under investigation (5.7 g/L), the apparent hydrodynamic radius increased to 119 nm, whereas at 1 g/L only 72 nm was obtained. This could be because of a

![Figure 3.5. Effect of concentration on the apparent hydrodynamic radii of the clusters and micelles at 15°C ( ), 30°C (•) and 50°C (▲).](image-url)
stronger attractive interaction among the clusters as compared to the micelles or to a real growth of the clusters. An effect of temperature can also be seen for clusters, at least at lower temperatures for higher concentrations. The value of $R_{h, app}$ changes from 119 nm at 15°C to 101 nm at 30°C and remains then almost constant. Different groups have reported the presence of larger aggregates of PEO homopolymer or copolymers of PEO in water and even in organic solvents such as methanol, acetonitrile.\textsuperscript{126,136} These are generally interpreted as loose aggregates, some kind of aggregates due to impurities in the sample, or incomplete dissolution of the polymer. Duval\textsuperscript{137} has recently suggested that PEO aggregates as result of the history of preparation of the sample and that exposure of PEO to water at high temperatures greater than 89°C but lower than the critical solution temperature (~102°C) of PEO correlates with the observation of irreversible aggregation. To get more insight into the origin of the larger aggregates observed here; one solution (4.25 g/L) was treated with ultrasound for one hour at room temperature before the DLS experiments were carried out. Figure 3.6 shows the DLS data of the untreated solution (a) and immediately after one hour ultrasound treatment (b). The

![Figure 3.6](image)

**Figure 3.6.** Effect of ultrasound treatment on the aggregates. Decay rate distribution (a) before ultrasound treatment and (b) after one hour ultrasound treatment at room temperature. The data in (b) were obtained immediately after the ultrasound treatment.
effect of ultrasound treatment was dramatic on the relative amplitude of the two main peaks. However, the existence of the clusters is still evident in the solution. In another experiment the copolymer solutions were stored at room temperature for several months. After approximately four months, DLS measurements were carried out on the solutions to study the effect of time on the aggregates in solutions. As shown in the Figure 3.7a and b for concentrations 2.0 g/L and 3.0 g/L respectively. The decay rate distributions reveal the same two main scatterers, i.e. micelles and clusters, in solution as found before (Figure 3.3). However, by now the micelles are the main contributors to the scattering intensity of the solution. As discussed before, the DLS measurements after a limited time ultrasound treatment of solutions has produced similar results (see Figure 3.6). There are several reports on the aggregation behavior of the telechelic associative polymers, particularly on fluorocarbon associative polymers.\textsuperscript{31-32,138-140} From the literature as cited above, and the observation we have made on our triblock copolymer systems in water, it can be assumed that the observed large clusters in aqueous solution of the triblock copolymers are loose or random aggregates\textsuperscript{120} formed by the intermicellar connection through bridges. Figure

![Graph](attachment:image.png)

**Figure 3.7.** Decay rate distributions for aqueous solutions of PEO\textsubscript{10}F11, stored for four months at room temperature, having concentration (a) 2.0 g/L and (b) 3.0 g/L.
3.8 shows the schematic illustration of the flower-like micelle and the intermicellar network (formed by the intermicellar bridges through the dangling chains) formation. The individual micelles are flower-like micelles with some free chains dangling in solution, which are responsible for the formation large clusters. The schematic presentation of a star-like micelle formation by the diblock copolymer in solution is also given in Figure 3.8. The intermicellar network is loose in the sense, that the bridges that hold the structure together break and form continuously, i.e. it can be regarded as equilibrium between the individual micelles and large clusters. However, this equilibrium shifts towards micelles with time (in untreated solutions) or by limited time high energy input (in the form of ultrasound) to the system.

**Figure 3.8.** Schematic presentation of the star-like micelle formation by diblock copolymer, the flower-like micelle, and the intermicellar network formation by triblock copolymer (hydrophilic block having hydrophobic blocks attached at both the ends).
3.3.3. **Morphology of solvent evaporated samples**

The morphology of the copolymer aggregates in aqueous solution has been investigated by TEM after transferring the aqueous solution to carbon coated copper grids, as shown in Figure 3.9 and 3.10. The block copolymers mainly form spherical micelles. In Figure 3.9 TEM micrographs of sample (a) PEO₁₀D₁₃-D and (b) PEO₂F₁₂-D, obtained from initial concentration of 4.0 g/L for both the copolymers, are depicted. The mean radius of the aggregates as calculated from the pictures is 15.6 nm with a standard deviation of 2.8 nm and 21 nm with standard deviation of 2.9 nm for PEO₂F₁₂-D and PEO₁₀D₁₃-D copolymers respectively. For triblock copolymer PEO₁₀F₁₁, TEM micrographs were obtained from different initial concentrations as shown in Figure 3.10. TEM picture (Figure 3.10a) from low initial concentration (2.5 g/L) reveals only small individual

![Figure 3.9](image1.png)

**Figure 3.9.** TEM pictures of sample (a) PEO₁₀D₁₃-D and (b) PEO₂F₁₂-D, after transferring the copolymer solutions to the carbon coated copper grids. The scale bars are 200 nm and 100 nm respectively.
micelles (average radius of the micelles calculated from the picture is ~ 21 ± 2.7 nm), and a small incomplete network formation as shown with arrows in the picture, where the

(a) ![Image](image1.png)  (b) ![Image](image2.png)

(c) ![Image](image3.png)

Figure 3.10. TEM micrographs of the associated structures of PEO_{10}F_{11} block copolymer obtained on a carbon coated copper grid after water evaporation from different initial concentrations 2.5 g/L (a), 3.5 g/L (b), and 5.7 g/L (c). The scale bar represents 200 nm (a), 1000 nm (b), and 200 nm (c). The inset in (b) shows the high magnification view of the fibrous network (scale bar 100 nm).
micelles are tending to coalesce together. By close observation, even some of the individual micelles, seem group of several individual micelles (as shown by dark arrow). Figure 3.10b with relatively high initial concentration (3.5 g/l) reveals a fibrous network and several large structures. Apparently, the fibrous network has the appearance of thread-like or worm-like micelles. However, in high magnification as shown as inset in Figure 3.10b, the network structure looks like a string of beads (single micelles). These can be assumed as individual micelles, connect with each other as the water evaporates. The apparent reason for this fusion could be the bridge formation as discussed earlier. Lee et al. have also reported similar fibrous network (formed by individual micelles) morphology for polypeptides. Looking to the details of the large spherical structures, it can be observed that the boundary wall is not smooth but appears a beaded ring. The origin of these structures is not yet clear. These could be simple rings of interconnected micelles formed as the water droplet evaporates or it could be spherical structures. The former idea, however, would be of more worth as there are some incomplete rings associated with the fibrous network (shown with arrow) and furthermore, even the complete ring-like structures are usually connected with the network structure. Different morphologies have been reported for block copolymer associated structures, like individual spherical micelles, vesicles, compound micelles, tubular, thread-like micelles. However, the observed type of micellar arrangement is unique. It can be argued that with evaporation of the solvent, concentration of the solution increases, leading to an increase in the number density of the micelles and a corresponding decrease in their distance, and hence the formation of fibrous network occurs. However, this specific morphology was associated only when the initial concentration was 3.5 g/L. It implies that the initial concentration of the block copolymer solution plays an important role in fibrous network formation when the rate of evaporation of the solvent is fixed. Furthermore, still at higher concentration the tendency of film formation by the amphiphilic block copolymer is obvious as shown in Figure 3.10c. The block with the smaller interfacial tension to substrate compared to the other block tries to spread on the
surface. In this case, the spreading started but the polymer concentration of 5.7 g/L is not large enough to form a homogeneous film on the carbon film.

The ability of amphiphilic block copolymers to cover colloidal metal particles is used for many applications. To test the covering tendency of the polymers under investigation, colloidal particles can be added to the solutions. The suitability for using the micelles as nanoreactors for producing metal particles in nanometre scale depends on

Figure 3.11. TEM images of gold colloid (dark particles) covered with (a) PEO$_{10}$D$_{13}$-D and (b) PEO$_{10}$F$_{11}$ block copolymer chains, obtained after transferring the water solutions to carbon coated copper grid. The scale bars are 200 nm and 100 nm respectively.

their affinity and stability. For this purpose, a dilute solution of colloidal gold (4.5 x 10$^{-5}$ wt.-% in water) was mixed with the polymer solution. TEM investigations were carried out after approximately 10 min ultrasound treatment of the solutions at room temperature. Figure 3.11 depicts the TEM pictures of sample (a) PEO$_{10}$D$_{13}$-D and (b) PEO$_{10}$F$_{11}$ with gold colloids. The pictures reveal that the gold particles (dark circular spots in the
picture) are engulfed by the block copolymer (comparatively less dark surrounding). The effect of covering gold particles by amphiphilic block copolymers is well known and is used for the formation of nanoparticles.\textsuperscript{142}

### 3.4. Conclusion

Aggregation behavior of poly(ethylene oxide) and poly(perfluorohexylethyl methacrylate) containing amphiphilic block copolymers in aqueous solution has been investigated by different techniques. Surface tension measurements have shown a clear inflection point in surface tension vs. concentration plots. The concentration corresponding to the inflection point was interpreted as the CMC. The CMC decreased with an increase in the PFMA content in copolymers. Dynamic light scattering studies have revealed the existence of different types of aggregates in solutions, including single chains, micelles, and large clusters. However, the large clusters as the dominant scatterers were detected only in triblock copolymer solution. Micelle size was found resistant to changes in temperature, however, a slight but significant increase in apparent hydrodynamic radius was observed with an increase in concentration, while both the temperature and concentration affected the large clusters, especially in concentrated solution. TEM investigations, carried out after transferring the aqueous solutions to carbon coated copper grids, has shown that the initial concentration of samples used for TEM has an influence on the morphology of the aggregates formed. Depending upon the initial concentration, single micelles, a fibrous network with circular structures, and some irregular morphology (tendency towards film formation at high concentration) were revealed by TEM studies. Lastly, by adding colloidal gold particles to the copolymer solutions, the typical covering by the polymer was observed by TEM as well.