Chapter 5

Correlating Block Copolymer Self-Assembly to the Gold Nanoparticle Synthesis

5.1. Introduction

In block copolymer-mediated synthesis of gold nanoparticles, block copolymers assist in reduction of gold salt, nucleation and growth of gold clusters and stabilization of gold nanoparticles [94-98]. The block copolymers required are amphiphilic, comprising two distinct hydrophobic and hydrophilic parts. It may be mentioned that in the case of homopolymer such as PEO the efficiency of formation of gold nanoparticles has been found to be very low [94-98]. While both hydrophilic and hydrophobic blocks in amphiphilic block copolymers contribute to the reduction of gold salt ion through the formation of crown ether-like domain, the contribution of hydrophilic is believed to be more dominant. The amphiphilicity of block copolymer helps in enhancing the nucleation as well growth of nanoparticles. The nucleation is enhanced by self-assembly of amphiphilic block copolymers to form gold clusters. Further, the adsorption of block copolymers on the surface of gold clusters as governed by the hydrophobicity of block copolymer decides the growth and stabilization of nanoparticles. It is therefore clear that amphiphilicity of block copolymer is important and can be varied to control the synthesis of gold nanoparticle [94-98].

The amphiphilic nature or self-assembly of block copolymers can be varied by varying their chemical architect and solution conditions such as temperature, pH, ionic strength etc [96,98,146]. These block copolymers self-assemble to micelle above a critical concentration (CMC) or critical temperature (CMT). There exists a concentration range at a
given constant temperature and similarly a temperature range at a given concentration when block copolymers coexist both as unimers and self-assembled micelles [119,120]. At much higher concentrations/temperatures than CMC/CMT leads to different micellar structures and liquid crystalline phases. The PEO-PPO-PEO block copolymers can be obtained having different block sizes of PPO and PEO to control the self-assembly. The higher the ratio of PPO to PEO enhances the propensity of self-assembly. The increased dehydration with increasing temperature is also known enhance the self-assembly. It is not clear how the synthesis will be influenced by the change of these structures. The correlation of self-assembly with the synthesis of gold nanoparticles has been addressed in the chapter.

The role of block copolymer self-assembly on the synthesis of gold nanoparticles has been studied by varying the block copolymer chemical structures and temperature [202-205]. The synthesis has been carried using three different block copolymers F88 (EO\textsubscript{103}PO\textsubscript{39}EO\textsubscript{103}), P85 (EO\textsubscript{26}PO\textsubscript{39}EO\textsubscript{26}) and P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}). Block copolymers F88 and P85 have the same hydrophobicity (same molecular weight of PPO block) but differ in their overall molecular weights, whereas P85 and P105 have different molecular weights with same ratio of hydrophilicity to hydrophobicity [94]. The block copolymer F88 forms spherical micelles over a wide temperature range whereas P85 and P105 show sphere-to-rod like micelle transition at higher temperatures. The gold nanoparticles have also been synthesized using F88, P85 and P105 at different temperatures. The synthesis of gold nanoparticles in these systems has been characterized by UV-visible spectroscopy, TEM, SANS and DLS.

5.2. Experimental Procedure

5.2.1. Materials

Pluronics block copolymers F88, P85 and P105 were obtained from BASF Corp., New Jersey. The gold salt of hydrogen tetrachloroaureate(III) hydrate (H\textsubscript{Au}Cl\textsubscript{4}.3H\textsubscript{2}O) was
purchased from Sigma-Aldrich. All the solutions were prepared in millipore H$_2$O other than those used in neutron scattering experiments for which D$_2$O (99.9 atom %D Sigma Make) was used. All products were used as received.

5.2.2. Synthesis of Gold Nanoparticles

The synthesis of the gold nanoparticles for each block copolymer was carried out by varying the concentration of gold salt at a fixed concentration of block copolymers. The block copolymer concentration used was 1 wt% and the concentration of gold salt varied in the range from 0 to 0.02 wt%. After mixing all the components for synthesis, samples were kept at room temperature without any disturbances for about 3 hours for the completion of the reaction. The transparent solution of block copolymers in the presence of gold salt was observed to become coloured on the formation of nanoparticles. For temperature-induced synthesis, before mixing, all the components were maintained at that particular temperature and kept at that temperature for the time required to reaction to be completed.

5.2.3. Characterization of Gold Nanoparticles

The formation of gold nanoparticles is confirmed using UV-visible spectroscopy [19]. The measurements were carried out using 6505 Jenway UV-visible spectrophotometer. The instrument was operated in spectrum mode with a wavelength interval 1 nm and the samples were held in quartz cuvettes of path length 10 mm.

SANS is used to correlate concentration dependence of self-assembly of block copolymer with the synthesis of gold nanoparticles. The measurements were performed on the SANS instrument at the Guide Tube Laboratory, Dhruva Reactor, BARC, India [188]. The data were recorded in the accessible $Q$-range of 0.015 – 0.35 Å$^{-1}$. Some of the measurements requiring higher sample to background and wider $Q$-range were also carried out at SANS-I facility, Swiss Spallation Neutron Source SINQ, Paul Scherrer Institut,
Switzerland [189]. The wavelength of neutron beam used was 6 Å. The experiments were performed at sample-to-detector distances of 2 and 8 m to cover $Q$-range of 0.007 to 0.32 Å$^{-1}$. The scattered neutrons were detected using two-dimensional 96 × 96 cm$^2$ detector.

DLS experiments were also performed to probe the variation of the size of the nanostructures in the system with different chemical structure of block copolymers [63]. Measurements were carried out using Autosizer 4800 (Malvern Instruments, UK) equipped with 7132 digital correlator and coherent (Innova 70C) Ar-ion laser source operated at wavelength 514.5 nm with a maximum output power of 2 W.

The direct visualization of nanoparticles has been obtained by TEM [169]. Conventional transmission electron microscopy was carried out using a JEOL 2000 FX transmission electron microscope. All TEM microphotographs were taken at acceleration voltage 160 kV, recorded on a photographic film.

5.3. Results and Discussion

The self-assembly of block copolymers is tuned by varying its chemical structure and solution temperature, whose effect on the synthesis of gold nanoparticle has been examined [202-205].

5.3.1. Tuning of Block Copolymer Self-Assembly

The self-assembly of block copolymer is known to be strongly dependent on the chemical structure of the block copolymer [197]. We have used three different block copolymers F88, P85 and P105 for studying the effect of chemical structures of the block copolymers on the self-assembly [202-204]. The details of the chemical structures of these block copolymers are given in Table 5.1. Block copolymer P85 and P105 have different molecular weights with same ratio of hydrophilicity to hydrophobicity. On the other hand, F88 and P85 have the
same hydrophobicity (same molecular weight of PPO block) but differ in their overall molecular weights [94].

**Table 5.1.** Details of chemical structure of the PEO-PPO-PEO block copolymers used.

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>Formula</th>
<th>Mol. Wt.</th>
<th>Hydrophilicity (PEO wt%)</th>
<th>PPO Block Mol. Wt.</th>
<th>PEO Block Mol. Wt.</th>
<th>CMT for 1 wt% (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F88</td>
<td>EO&lt;sub&gt;103&lt;/sub&gt;PO&lt;sub&gt;39&lt;/sub&gt;EO&lt;sub&gt;103&lt;/sub&gt;</td>
<td>11400</td>
<td>80</td>
<td>2280</td>
<td>9120</td>
<td>38.0</td>
</tr>
<tr>
<td>P85</td>
<td>EO&lt;sub&gt;26&lt;/sub&gt;PO&lt;sub&gt;39&lt;/sub&gt;EO&lt;sub&gt;26&lt;/sub&gt;</td>
<td>4600</td>
<td>50</td>
<td>2300</td>
<td>2300</td>
<td>29.0</td>
</tr>
<tr>
<td>P105</td>
<td>EO&lt;sub&gt;52&lt;/sub&gt;PO&lt;sub&gt;56&lt;/sub&gt;EO&lt;sub&gt;37&lt;/sub&gt;</td>
<td>6500</td>
<td>50</td>
<td>3250</td>
<td>3250</td>
<td>21.5</td>
</tr>
</tbody>
</table>

**Figure 5.1.** SANS data of pure 1 wt% block copolymer solutions. The solid lines are the theoretical fits to the experimental data.

**Table 5.2.** Fitted structural parameters of self-assembled micellar structures of block copolymers.
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<table>
<thead>
<tr>
<th>Block Copolymer System</th>
<th>Micellar Fraction (%)</th>
<th>Radius of Gyration of Unimers $R_{gu}$ (nm)</th>
<th>Micellar Parameters</th>
<th>Aggregation Number $N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% F88</td>
<td>0</td>
<td>3.5</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1 wt% P85</td>
<td>15</td>
<td>2.4</td>
<td>3.6</td>
<td>1.2</td>
</tr>
<tr>
<td>1 wt% P105</td>
<td>26</td>
<td>2.8</td>
<td>4.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

SANS studies have been performed on block copolymers to study the self-assembly of block copolymers. Figure 5.1 shows the SANS data of pure 1 wt% block copolymer solutions in D$_2$O at room temperature ($30^\circ$C). The $Q$-dependence of the scattering is observed to be quite different for three block copolymers indicating differences in their propensity to self-assemble. Block copolymer are known to self-assemble above their CMT to form micelles consisting of core of PPO block surrounded by hydrated PEO shell. At CMT, both unimers and micelles coexist and the population of unimers converting into micelles increases with temperature. The low scattering from highly hydrophilic block copolymer F88 (measurement temperature is below the CMT) is because of this system consists of only unimers. In the case of P85 and P105, the build-up of scattering in the low-$Q$ region, suggests the formation of micelles. As the volume of the scattering object increases on the formation of micelles, therefore scattering intensity increases. Table 5.2 gives the structural details of block copolymer micelles as obtained from SANS analysis. It is found that F88 consists of only unimers. On the other hand, both unimers and micelles coexist in case of P85 and P105. These two block copolymers (P85 and P105) have the same percentage of hydrophilicity but P105 has the higher molecular weight and this gives rise to
higher fraction of micellization in this system. These block copolymers also form the micelles with different sizes and aggregation numbers.

**Table 5.3.** Hydrodynamic size of self-assembly of block copolymers as obtained by DLS.

<table>
<thead>
<tr>
<th>Block Copolymer System</th>
<th>Hydrodynamic Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% F88</td>
<td>4.4</td>
</tr>
<tr>
<td>1 wt% P85</td>
<td>7.5</td>
</tr>
<tr>
<td>1 wt% P105</td>
<td>9.0</td>
</tr>
</tbody>
</table>

The above SANS results of self-assembly of block copolymers have been further confirmed by DLS data of the intensity autocorrelation function $[g^I(\tau)]$ from the 1 wt% block copolymer samples. The functionality of the autocorrelation function depends on the diffusion coefficient of the particles and the data obtained suggest that three block copolymers show different autocorrelation functions indicating different structures in these systems. The calculated hydrodynamic sizes are given in **Table 5.3.** The effective size corresponding to micellar fraction and size is found to be largest for P105 than F88 and P85 similar to as observed by SANS. In all, both the SANS and DLS results suggest that P105 has higher tendency to self-assemble as compared to F88 and P85.
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(a) 1 wt% F88
   - 30 °C
   - 50 °C
   - 75 °C

(b) 1 wt% P85
   - 30 °C
   - 50 °C
   - 75 °C

(c) 1 wt% P105
   - 30 °C
   - 50 °C
   - 75 °C
**Figure 5.2.** SANS data of 1 wt% block copolymer systems with varying temperature for (a) F88, (b) P85 and (c) P105. The solid curves are theoretical fits to the experimental data.

**Table 5.4.** Fitted structural parameters of self-assembled micellar structures of block copolymers F88, P85 and P105 with varying temperature. The dimension of spherical micelles is represented by radius \( R \), ellipsoidal micelles by semi-major axis \( a \) and semi-minor axis \( b = c \), and rod-like micelles by radius \( R \) and length \( L \). The fitted values of radii of gyration of unimers for F88, P85 and P105 are 3.5, 2.4 and 2.8 nm, respectively.

<table>
<thead>
<tr>
<th>Block Copolymer System</th>
<th>Temperature (°C)</th>
<th>Micellar Fraction (%)</th>
<th>Micellar Parameters</th>
<th>Shape of the Micelle</th>
<th>Dimensions</th>
<th>( R_g ) of PEO Chain (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% F88</td>
<td>30</td>
<td>0</td>
<td>F88 exists as unimer ( (R_g = 3.50 \text{ nm}) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>Spherical</td>
<td>( R = 3.12 \text{ nm} )</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>100</td>
<td>Spherical</td>
<td>( R = 3.59 \text{ nm} )</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>1 wt% P85</td>
<td>30</td>
<td>15</td>
<td>Spherical</td>
<td>( R = 3.60 \text{ nm} )</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>Ellipsoidal</td>
<td>( b = c = 4.27 \text{ nm} )</td>
<td>( a = 6.36 \text{ nm} )</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>100</td>
<td>Rod-like</td>
<td>( R = 4.30 \text{ nm} )</td>
<td>( L &gt;&gt; R )</td>
<td>1.2</td>
</tr>
<tr>
<td>1 wt% P105</td>
<td>30</td>
<td>26</td>
<td>Spherical</td>
<td>( R = 4.35 \text{ nm} )</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>Ellipsoidal</td>
<td>( b = c = 4.85 \text{ nm} )</td>
<td>( a = 8.06 \text{ nm} )</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>100</td>
<td>Rod-like</td>
<td>( R = 5.10 \text{ nm} )</td>
<td>( L &gt;&gt; R )</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Figure 5.2** shows the SANS data from aqueous solution of 1 wt% block copolymers (F88, P85 and P105) at varying temperature. SANS data of all the three block copolymers...
show strong build-up of scattering intensity in the low-$Q$ region with increase in the temperature. This is an indication of enhanced micellization with the increase in the temperature for all the block copolymers. Unlike F88, it is observed for P85 and P105 that the scattering at higher temperature (75 °C) show a linear $Q$-dependence on log-log scale in low-$Q$ region, suggesting temperature-induced sphere-to-rod-like transition for P85 and P105 micelles. This is expected as a result of dehydration of PEO shell. On the other hand, highly hydrophilic F88 block copolymers form spherical micelles even up to at higher temperature. The fitted micellar parameters in these systems are given in Table 5.4.

Table 5.4 shows that micelles coexist with unimers at lower temperature (30 °C). The micelles fraction depends on the hydrophilicity and increases in the order F88 < P85 < P105 as the hydrophilicity of the block copolymer decreases. As the temperature increases, more and more unimers convert to micelles. It is found that there are only micelles at 50 °C for all the block copolymers. The shape of the micelles remains same (spherical) for F88 whereas P85 and P105 micelles become ellipsoidal. As the temperature is increased to 75 °C, both P85 and P105 transform to rod-like micelles. It may be mentioned that since no lower cut-off in the SANS data for rod-like micelles are seen, the micelles are fitted having length greater than that can be measured from the accessible range ($> 2\pi/Q_{min} \sim 100$ nm) of the present data.

The role of self-assembly of block copolymer has been used to correlate with the synthesis of gold nanoparticles. The self-assembly is tuned as discussed above by varying chemical structure of block copolymer and temperature.
5.3.2. Gold Nanoparticle Synthesis with Different Block Copolymers

![Graphs of SPR peaks with varying HAuCl₄·3H₂O concentration](image)

**Figure 5.3.** The gold salt concentration normalized SPR peaks of (a) 1 wt% F88 and (b) 1 wt% P105 with varying HAuCl₄·3H₂O concentration.

The synthesis of gold nanoparticles similar to that for P85 (see Chapter 4) has also been carried out with block copolymers F88 and P105. These block copolymers vary in their...
overall molecular weight and their propensity to self-assemble. The synthesis of gold nanoparticles for F88 and P105 is carried out and compared to that for P85 at a fixed block copolymer concentration (1 wt%) and varying the gold salt concentration. Figure 5.3 shows UV-visible absorption spectra for 1 wt% F88 and 1 wt% P105 as a function of varying concentration of gold salt. Similar to P85, all the spectra show a SPR peak confirming the formation of gold nanoparticles in all these systems irrespective of the different block copolymers used. The maximum absorbance at SPR (proportional to yield of gold nanoparticles) for 1 wt% F88 and 1 wt% P105 have been found to be for 0.004 wt% and 0.006 wt% HAuCl₄·3H₂O, respectively. This trend is also consistent with the earlier data that the normalized SPR peak with respect to salt concentration shows a strong decrease in yield beyond a certain gold salt concentration. These concentrations seem to depend on the molecular weight of the block copolymer that decides the number of molecules available for reduction of the gold ions. The alcohol (hydroxyl) functionality at the two ends of a PEO-PPO-PEO block copolymer molecule is known to act as reductant for the metal ions [147,148]. Therefore the higher reduction is expected for the block copolymer with lower molecular weight. The molecular weight of P85 is the lowest and hence amongst all block copolymers for a given concentration (1 wt%) provides more number of block copolymer molecules which can reduce more number of gold ions. Figure 5.4 shows the comparison of SPR peaks of the block copolymers used. The yield follows the trend in the order P105 > P85 > F88. It does not have the same trend to that of the gold salt concentration (P85 > P105 > F88) corresponding to the maximum yield of the block copolymer. The yield of gold nanoparticles follows the trend in the order P105 > P85 > F88 as governed by the order of self-assembly of the block copolymer in aqueous solution. On the other hand, the amount gold salt concentration for the maximum yield depends on the molecular weight and
thus follows the order P85 > P105 > F88 decreasing with the increase in molecular weight of block copolymer (Table 5.1).

![SPR Peak](image)

**Figure 5.4.** Comparison of SPR peaks for 1 wt% block copolymers (F88, P85 and P105) with gold salt concentration corresponding to their maximum yields.

![Time-dependent variation of yield of gold nanoparticles](image)

**Figure 5.5.** Time-dependent variation of yield of gold nanoparticles for 1 wt% block copolymers (F88, P85 and P105) at their corresponding gold salt concentrations of maximum yields.
The rate of formation and stability of gold nanoparticles for different block copolymers have also been examined. Figure 5.5 shows the time dependence of yield for 1 wt% block copolymers at gold salt concentrations corresponding to their maximum yields. The formation rate is observed to be faster for the system having higher yield, as slope of the formation region is higher for P105 > P85 > F88. This higher tendency of P105 in self-assembling leads to the highest yield as well as faster formation rate of gold nanoparticles amongst three block copolymers used. However, the yield saturation is obtained at almost similar time (~ 1 hr) for all the block copolymers with high stability for a longer period of time. The self-assembly is utilized to control the nucleation and growth and hence the synthesis of nanoparticles.

Figure 5.6. SANS data of 1 wt% block copolymer solutions without and with the gold salt corresponding to their maximum yields.

The comparison of SANS data without and with the addition of gold salt corresponding to maximum yields is given in Figure 5.6. There are no significant changes observed with gold nanoparticles. Block copolymers in salt solutions can either participate in
the formation of gold nanoparticles or form their own micelles. In the case of nanoparticles, they get coated on the particles, and will have a very different scattering pattern than that of the micelles. Therefore, the scattering from block copolymer coated gold nanoparticles is expected to be significantly different than from the micelles. The fact that the scattering curves do not change in presence of gold nanoparticles, suggests the formation of a very small fraction of gold nanoparticles in these systems. This behaviour can be understood on the basis if most of the block copolymers form their own micelles and the fraction associated with the gold nanoparticles is small as the gold nanoparticle concentration is much smaller than the block copolymer concentration.

![Figure 5.7](image)

**Figure 5.7.** TEM images of gold nanoparticles synthesized using 1 wt% block copolymers (a) P105, (b) P85 and (c) F88 with gold salt in samples corresponding to their maximum yields.

We have observed that the yield (Figure 5.4) and formation rate (Figure 5.5) of synthesis of gold nanoparticles depend on the propensity of the self-assembly of block copolymers. Further, TEM has been used to find the structure of gold nanoparticles in these
systems. Figure 5.7 shows transmission electron micrographs of gold nanoparticles for the block copolymers corresponding to the samples of their maximum yields. It is observed that the size of the nanoparticles depends on the block copolymer. The block copolymer F88 mostly consists of block copolymer cross-linked small gold nanoparticles while the size of the nanoparticles for P85 is ~ 15 nm. The P105 block copolymer having highest tendency of self-assembly forms the nanoparticles with largest sizes (~ 30 nm). These studies thus show that the self-assembly of block copolymers controls the yield and formation rate as well as the structure of the gold nanoparticles.

5.3.3. Temperature-Induced Synthesis

Micelle formation, in aqueous solutions of amphiphilic block copolymers, is critically dependent upon temperature [96,98,146]. This is a result of the successive dehydration of PO and EO chains upon the increase in temperature. At low temperatures, both types of blocks within block copolymer molecules are hydrated and therefore they are soluble in water. When the temperature increases, the PO block dehydrates and becomes insoluble, resulting in the formation of micelles. The temperature at which micelles are formed is referred to as the CMT and for most of the block copolymers it has value in the range of 25 to 40 °C.
Figure 5.8. UV-visible absorption spectra of 1 wt% block copolymers with HAuCl₄·3H₂O corresponding to their maximum yields with varying temperature.

UV-visible absorption spectra of 1 wt% block copolymers at gold salt concentrations corresponding to their maximum yields with varying temperature are shown in Figure 5.8. All the three systems show SPR peaks whose position, height and width depend on the block copolymer and temperature used. The peak height (maximum absorbance, \( \text{Abs}_{\text{max}} \)), peak position (\( \lambda_{\text{max}} \)) and peak width (\( FWHM \)) of the SPR peak in absorption spectra in these
Figure 5.9. (a) Absorbance ($Abs_{max}$), (b) maximum wavelength ($\lambda_{max}$) and (c) full width at half-maximum ($FWHM$) of SPR peak of gold nanoparticles containing 1 wt% block copolymers as a function of temperature.

In the case of F88 block copolymer there is change in the SPR peak height and position, which suggests to the increase in the yield and size of the nanoparticles, respectively with increase in the temperature. These results can be explained
based on the enhanced micellization of F88 with increasing temperature that leads to higher yield and larger sizes of the nanoparticles. Unlike F88, P85 and P105 mostly show SPR peaks shift and broaden with increasing temperature. Also there is build-up of absorption spectra at higher wavelengths for higher temperature. The broadening of SPR is because of increase in the size of the nanoparticles. Though there is build-up at higher wavelengths but not as expected for nanorods if one expects them to be formed from the rod-like micelles at those temperatures [206]. It is possible that along with mostly spherical particles there exists a small fraction of nanorods or different asymmetric particles for the build-up of the absorption spectra at higher wavelengths.

The effect of temperature on the gold nanoparticle synthesis has been further investigated by SANS [205]. Figure 5.10 shows SANS data of gold nanoparticles from 1 wt% P85 with 0.2 wt% HAuCl₄·3H₂O and in presence of Na₃Cit. It may be mentioned that SANS requires sufficiently high concentration of gold nanoparticles to able to get enough scattering from the sample. The high-yield of gold nanoparticles with block copolymers can be obtained with the help of additional reductant such as Na₃Cit, the details of which are discussed in the next chapter. The SANS data in Figure 5.10 are also taken for the solvent (85% H₂O in H₂O and D₂O mixture) where the block copolymers are contrast-matched. All the data show similar features irrespective of the temperature at which nanoparticles have been synthesized. The data are fitted with the polydispersed spherical nanoparticles. The fitted size parameters are given in Table 5.5. It is seen that the size of the nanoparticles and polydispersity increases with the increase in the temperature. Thus SANS clearly show while P85 forms rod-like micelles at higher temperatures but nanoparticles synthesized at that temperature are spherical similar to that formed at low temperatures.
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Figure 5.10. SANS data of 1 wt% P85 with 0.2 wt% HAuCl₄·3H₂O in presence of 0.2 wt% Na₃Ct at different temperatures. The solid curves are theoretical fits to the experimental data. The data of 50 and 75 ºC are shifted vertically for clarity.

Table 5.5. Fitted structural parameters of gold nanoparticles as obtained by SANS in 1 wt% P85 with 0.2 wt% HAuCl₄·3H₂O in presence of 0.2 wt% Na₃Ct at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Mean size (nm)</th>
<th>Polydispersity σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10.1</td>
<td>0.41</td>
</tr>
<tr>
<td>50</td>
<td>11.6</td>
<td>0.36</td>
</tr>
<tr>
<td>75</td>
<td>12.7</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The direct visualization of the structures of synthesized gold nanoparticles has also been carried out by TEM. Figure 5.11 shows TEM images of gold nanoparticles at different temperatures from the nanoparticle system used in SANS studies in Figure 5.10. It is observed that irrespective of the temperature of synthesis nanoparticles formed are mostly spherical. The average size of the nanoparticle is of the order similar to that found by SANS.
We have also observed that a small fraction of non-spherical nanoparticles are also formed at higher temperature, which could be the reason for the build-up of SPR at higher wavelengths as observed in Figure 5.8. The fact that the presence of rod-like micelles does not lead the formation of rod-like nanoparticles, suggests interplay of different driving forces for block copolymer to self-assemble to micelles and synthesizing nanoparticles.

![Figure 5.11. TEM images of gold nanoparticles in 1 wt% P85 with 0.2 wt% HAuCl₄·3H₂O in presence of 0.2 wt% Na₃Ct) at different temperatures.](image)

### 5.4. Conclusions

The role of self-assembly of block copolymers to the gold nanoparticle synthesis has been studied. The self-assembly is tuned by varying the chemical structure of the block copolymer and solution temperature. The self-assembly has been studied for three different block copolymers F88, P85 and P105, which not only have varying molecular weight but also differ in hydrophobicity to hydrophilicity ratio. The propensity of these block copolymers to self-assemble to micelles has been found in the order P105 > P85 > F88. The self-assembly is enhanced with decreasing hydrophilicity (P85 > F88) and increasing molecular weight for the block copolymers with similar percentage of hydrophilicity (P105 > P85). The micelles remain spherical even up to very high temperature for highly hydrophilic block copolymer (F88) whereas sphere-to-rod transition of micelles has been observed for the block copolymers with low hydrophilicity (P85 and P105) as the temperature is increased. The
synthesis has been carried out using these three block copolymers at different temperatures. It has been found that the yield of gold nanoparticles increases in the order F88 < P85 < P105. As a fact that P105 has higher tendency to self-assemble, it results in higher yield as compared to F88 and P85. The formation rate is also found faster for the system having higher yield. Block copolymer P105, having the highest tendency of self-assembly, forms the nanoparticles with largest sizes whereas the size of the nanoparticles decreases for F88 and P85. It is also found that F88 unlike P85 and P105 mostly consists of block copolymer cross-linked small gold nanoparticles. Temperature dependent synthesis show that irrespective of shape of block copolymer micelles the synthesis carried out at different temperature gives rise to the formation of spherical nanoparticles in all the cases. This is believed to be because of the differences in the driving force of block copolymer to self-assemble to micelles and in synthesizing nanoparticles. However, it has been found that increasing temperature increases the reaction kinetics drastically, resulting in much faster synthesis of nanoparticles.