Chapter 4

Ionic liquid induced sphere-to-ribbon transition in Silver Nanoparticles

Abstract

Silver nanoparticles (AgNPs) are synthesized using amphiphilic block copolymer, P123 as a reducing agent. The spherical AgNPs undergo shape transition to ribbon like shape in presence of hydrophobic IL, C₈PyDs. The size and shape of AgNPs are correlated with the size and shape of micelles of amphiphilic block copolymers/C₈PyDs and alkyl chain length of IL. The AgNPs are characterized by TEM and DLS, while size of P123 and C₈PyDs micelles are determined by SANS and DLS.
4.1 Introduction

In recent years, noble and near noble metals such as Ag, Au, Pt, Pd nanoparticles (NPs) have been subject of attention by researchers due to their unique, optical, mechanical, magnetic, chemical, electronic and biological properties that are significantly different from those of bulk materials.\textsuperscript{1-5} These unique and special properties of nanoparticles could be attributed to their size and large surface area. Because of these reasons metallic NPs are widely used in various fields like catalysis, sensors, electronics, photonics, biology etc. In addition to the above mentioned applications, among all noble metals, Silver (Ag) has been extensively used in medicine to reduced infections\textsuperscript{6} and as it exhibits size dependent antimicrobial activity. Therefore, recently AgNPs as well as various silver based compounds containing ionic silver (Ag\textsuperscript{+})\textsuperscript{7,8} and metallic silver (Ag\textsuperscript{0})\textsuperscript{9,10} are in great demands.

In view of all above, the synthesis of novel nanostructures of different geometries like, spheres, wires, rods, porons, prisms, plates from Ag or Au metals has received due attention. The size, shape, color and physiochemical properties of the NPs depends on; (i) the method of preparation (chemical, sol-gel, sonochemical or photochemical), (ii) the concentration of reactants/stabilizers/capping agents, pH and temperature and (iii) the nature of reducing agents.\textsuperscript{11-15} Out of these methods, the most common synthesis of AgNPs is the chemical reduction of a silver salt by a reducing agent such as Sodium borohydride, hydrazine, ascorbic acid or sodium citrate.\textsuperscript{16-20} The use of a strong reductant such as NaBH\textsubscript{4}, resulted in small particles that were somewhat monodisperse, but controlling the generation of the larger particles became difficult. The use of weak reducing agents like citrate, resulted in a slower reduction rate, but the size distribution was far from narrow. Alternatively, a controlled synthesis of silver colloid particles was attempted using, a two step reduction process in order to control the particle size. In this process, first step involve a use of strong reducing agent to produce small AgNPs, which were than enlarged in a secondary step using a weaker reducing agent.\textsuperscript{21,22} But the problem with this method is reproducibility of initial sol and polydispersity. Moreover, use of these reducing agents is not viable environmentally or economically. Therefore, it has been of increasing interest to develop green synthesis of AgNPs. Recently, there are reports which focus on the synthesis of gold nanoparticles by environmentally benign and economical routes which involve only water and non-toxic commercially available
amphiphilic block copolymers (Pluronics® and Poloxomers®).\textsuperscript{23,24} Pluronics® are composed of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO), which belong to a class of block copolymers and are mainly used as stabilizers and templating agents in pharmaceutical applications, and for polymer gel electrolytes, etc.\textsuperscript{25–28} The aggregation behaviour of PEO–PPO–PEO block copolymers in water has been studied previously in order to examine their associative properties. The size, shape and crystalline phase of these block copolymers depends on the molar masses, PEO/PPO ratio, solvent type and the solvent/block copolymer composition.\textsuperscript{29–33} This block copolymer can be used for the preparation of nanoparticles while maintaining monodispersity because of their ability to reduce metal ions and acting as templating agents simultaneously. Alexandridis et al. and Aswal et al. used Pluronic® block copolymers for the synthesis of gold nanoparticles.\textsuperscript{34–37} They found that the nanoparticles size, shape, yield and stability depends on the molecular weight, PEO/PPO block length, concentration and temperature of the block copolymers. Thus, the modification of micelles of block copolymers can lead to the desired nanoparticle shape.

As discussed in Chapters in 1 and 3, ionic liquids (ILs) are of immense interest because of their wide applications as organic solvents, catalysts, electrolytes in advanced devices, metal ion absorbers, etc.\textsuperscript{38–43} Structurally, ILs are amphiphilic in nature and are generally composed of an alkyl imidazolium/pyridinium head group with a variety of anions. The solubility of ILs in water depends on the nature of anions as well as on the alkyl chain length of the cationic moiety. Due to their amphiphilic behavior, recently ILs have been used in the synthesis of titania, Au, Pd, Pt nanoparticles etc.\textsuperscript{44–49} Wang et al.\textsuperscript{47} reported the synthesis of gold nanoparticles (1–2 nm) which were stabilized by an amine-terminated IL. The IL mediated synthesis of palladium nanoparticles has been documented recently by Zhao et al., for their application in the electrooxidation of formic acid.\textsuperscript{44} In all of these reports, ILs have been used for the synthesis of small NPs (<10nm). The low interfacial tension of ILs promotes a high nucleation rate and weak Oswald ripening, which are essential requirements for the formation of smaller nanoparticles. Apart from these studies, chemical reducing agents were used in other cases of nanoparticles synthesis.

Herein we report the block copolymer mediated synthesis of silver nanoparticles without use of any additional reducing agents. The addition of IL induces a sphere-to-ribbon like
transition in the aqueous solution of block copolymer and silver nitrate. The size and shape of the NPs correlates with the micellar geometry of the block copolymer–IL systems. The effect of alkyl chain length of the cation as well as the anion on the geometry of AgNPs is also studied.

4.2 Materials and methods

The silver salt AgNO$_3$ (99.9%), octyl chloride (99%), pyridine (99.9%), Pluronic® P123 [$(EO)_{20}-(PO)_{70}-(EO)_{20}$] block copolymer (mol. wt. 5750 g mol$^{-1}$) and sodium dodecyl sulphate (SDS) (99%) were purchased from Sigma-Aldrich, India and were used as received. Dimethyl sulphate (99%) and diethyl sulphate (>97%) were purchased from Sisco Chem. and Spectrochem India respectively. Milli-Q grade water was used for the preparation of aqueous solutions.

4.2.1 Preparation of ionic liquids

N-Alkyl pyridinium dodecyl sulphates ($C_n$PyDs) were synthesized by a metathesis reaction between SDS and N-alkyl ($C_4$, $C_6$, and $C_8$) pyridinium chloride in acetone, leaving behind sodium chloride as a byproduct. The precipitated salt (NaCl) was removed by filtration and the filtrate was dried under vacuum. The resultant products were present as a brown colored waxy material which exhibited partial water solubility (~ 0.01–0.05% w/v). The synthetic procedure of N-methyl/ethyl pyridinium methyl/ethyl sulphate is given in Chapter 2. The detailed characterization and solubility in different solvents for all ILs is also documented in Chapter 2. The ILs used in this work along with chemical structures are given in Scheme 4.1.

4.2.2 Synthesis of Ag nanoparticles

AgNPs were prepared by the reduction of AgNO$_3$ solution using P123 in the presence and absence of ILs. In a typical procedure, 0.1 ml of 0.01 M AgNO$_3$ solution was mixed with 5 ml of 8.7 mM P123 solution. On addition, the initial colourless mixture slowly changed to a yellow colour. A similar procedure was adopted for the synthesis of AgNPs in presence of ILs, where the initial colorless solution changed to a dark brown colored solution.
In order to understand the role of these ILs, a controlled experiment was carried out for the synthesis of AgNPs using NaBH₄ (>99.0%, Sigma-Aldrich, India) as the reducing agent in presence of an IL (in the absence of P123). In this case, the initial colorless mixture changed to a black colored solution.

### 4.2.3 Characterization of Ag Nanoparticles

The synthesized AgNPs were characterized spectrophotometrically using a UV-visible spectrometer from Shimadzu, Japan (UV-160). A BIC 90 Plus (Brookhaven) instrument equipped with a 35 mW solid state laser operating at 660 nm and an avalanche photodiode detector was used for the particle size distribution measurements by DLS. The TEM measurements were performed on a Philips, Holland Model Techai-20 instrument operated at an accelerating voltage of 200 kV. Samples for the TEM studies were prepared by placing drops of the AgNP solution on carbon-coated TEM Cu grids. The
film on the TEM grid was allowed to dry in air for 10 min. The SANS experiments were carried out on micellar solutions of the PEO–PPO–PEO triblock copolymer P123. All of the final solutions used for the neutron scattering measurements were prepared in D$_2$O (99.9 atom % D, Sigma-Aldrich, India). This provides a very good contrast between the micelles and the solvent in the SANS experiment. The detailed geometry and methodology adopted for SANS instruments is discussed in Chapter 2.

4.3 Results and discussion

4.3.1 Role of block copolymer (Pluronic® P123)

Upon mixing the aqueous solutions of silver salt and block copolymer at room temperature, a change in color of the mixture (colorless to faint yellow) was observed within few minutes. Figure 4.1(a) shows the time-dependant UV-Vis spectra for the sample prepared by mixing 0.01 M AgNO$_3$ and 8.7 mM P123 solution under ambient conditions, which exhibit a strong absorption band at ~ 400 nm. The faint yellow color is a result of the Surface Plasmon Resonance (SPR) of AgNPs. The concentrations of both the block copolymer and silver salt were optimized on the basis of their maximum absorbance of the SPR band. SPR is the collective oscillation of excited free electrons in metallic nanostructures when it is irradiated with light. The prime requirement for Plasmon resonance is that the particle size should be much smaller than the wavelength of the radiation.

For small particles in the quasi static limit, the absorption cross-section is given by the following equation:\(^5\)

\[
\sigma_{abs.} = \frac{2\pi}{\lambda} I_m \left( 3V \frac{\varepsilon - 1}{\frac{\varepsilon}{\varepsilon_m} + 2} \right)
\]  

(1)

where, \(V\) is volume of the particle, \(\varepsilon\) is the permittivity of the metal and \(\varepsilon_m\) is the permittivity of the surrounding medium. For very large particle sizes, the plasmon modes are reduced due to multiple oscillations, thereby leading to a reduction in the scattering efficiency of the particles. Hence, from equation (1) it is clear that the volume or size of the particles affects the absorption cross-section.
Besides size, the peak position is influenced by the nanostructure shape and the surrounding media, including the nature of the ligand shell and the interparticle distances in dispersions. In the case when anisotropy is added to the nanoparticle, such as growth of nanoparticles, and the optical properties of the nanoparticles change dramatically. Thus the magnitude of SPR peaks depends on the size, shape and concentration of the AgNPs.

Surprisingly, the absorbance of the SPR peak decreased along with narrowing of the bands as a function of time i.e. the SPR peak becomes increasingly Gaussian in shape. This reduction of the band width may be attributed to aggregation of the AgNPs which may affect the stability of the nanoparticles. A similar decrease in absorption as a
function of time was reported recently by Angelescu et al. for AgNP synthesis using Pluronic F127 as a stabilizing agent.\textsuperscript{52} From Figure 4.1(a), it is clear that AgNPs attain an equilibrium within \( \sim 50 \) min, and after that no appreciable change was observed, which indicates that the AgNPs are stable. The inset of Figure 4.1(b) shows the color of the AgNPs after stabilization. The time required for obtaining the equilibrium for the nanoparticles by this method is better than in the recent reports on the reduction of metal ions under ultrasonication and by biocompatible reducing agents.\textsuperscript{53} In order to gain information on the size and shape of the AgNPs, DLS and TEM measurements were performed.

Figure 4.3 depicts a TEM image and the DLS distribution of AgNPs, which shows that the AgNPs are polydispersed in size and exhibit a spherical shape, with mean diameter of \( \sim 20 \) nm. The TEM image also confirms the spherical shape of the particles. It can be seen that the nanoparticle concentration is low, which may be due to the slow reduction power of the block copolymer.\textsuperscript{54}

![Figure 4.3](image)

**Figure 4.3** (a) TEM image of AgNPs synthesized in presence of P123 (without ILs) and (b) The DLS particle size distribution.

The mechanism of the nanoparticle synthesis using block copolymer is composed of three main steps:\textsuperscript{55} (i) reduction of Ag\(^+\) by the block copolymer in solution and the subsequent formation of Ag clusters, (ii) adsorption of the block copolymer on the Ag cluster and the reduction of metal ions on the surface of these Ag clusters and (iii) growth of the AgNPs using step (ii) and finally stabilization by the block copolymers. In the case of the PEO–PPO–PEO block copolymers, the PEO dominates in the reduction of the metal ions. In the later stages of growth, PPO facilitates the adsorption of the block copolymer onto the Ag
clusters. Steps (ii) and (iii) are responsible for the definite size and shape of the nanoparticles. Thus, the size and shape of the nanoparticles depends on the micellargeometry. In order to correlate the micellar morphology with the geometry of the AgNPs, we have characterized the micelles of P123 block copolymers in aqueous solution by DLS and SANS measurements. Figure 4.3(b) depicts the particle size distribution of 15% P123 micelles in aqueous solution, obtained from DLS. It is revealed that the micelles are polydisperse in nature, possessing a mean diameter in the range of 15–23 nm. These diameter values are in good agreement with the size distribution profile of the AgNPs. In order to gain exact information on the shape as well as size of the micelles, further SANS measurements were performed (Figure 4.4). The experimental SANS profiles were analyzed by using different geometries such as spherical, ellipsoidal, cylindrical etc. and of these shapes, we could best fit the SANS data by considering hard sphere geometry of micelles.

![Figure 4.4](image)

**Figure 4.4** SANS data of 10% (w/v) P123 in aqueous solution at 30 °C. The inset indicates DLS particle size distribution of the block copolymer.

The detailed theory of SANS analysis including form and structure factor’s contributions to coherent differential scattering cross-section, $d\Sigma/d\Omega$ can be found in Chapter 2. The parameters obtained from the above SANS analysis for the hard sphere model are given in Table 4.1. Apart from $R_C$, the $R_{HS}$ volume fraction, $\phi = 0.152$ and polydispersity $= 0.49$ were also obtained from the analysis. These values indicate that the micelles are polydispersed with spherical shape, and exhibit inter-micellar interactions. The obtained micelle diameter is ~ 17.8 nm, which is close to the average value of the hydrodynamic
diameter obtained from DLS as well as the size of the AgNPs. The slightly lower value of the micelle diameter may be due to the assumption made (scattering from the core only) during SANS analysis.

### Table 4.1 Parameters obtained from SANS, DLS and TEM

<table>
<thead>
<tr>
<th>System</th>
<th>Micellar size</th>
<th>Nanoparticles</th>
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<tbody>
<tr>
<td></td>
<td>SANS*</td>
<td>DLS®</td>
</tr>
<tr>
<td></td>
<td>$R_C$ (nm)</td>
<td>$R_{HS}$ (nm)</td>
</tr>
<tr>
<td><strong>Spherical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P123</td>
<td>3.6</td>
<td>8.4</td>
</tr>
<tr>
<td><strong>Disk</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L$ (nm)</td>
<td>$R$ (nm)</td>
<td></td>
</tr>
<tr>
<td>C$_8$PyDs</td>
<td>7.1</td>
<td>98.5</td>
</tr>
<tr>
<td>C$_6$PyDs</td>
<td>2.4</td>
<td>100.7</td>
</tr>
<tr>
<td>C$_8$PyDs</td>
<td>6.3</td>
<td>102.0</td>
</tr>
<tr>
<td>C$_1$PyMs</td>
<td>-</td>
<td>-</td>
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<tr>
<td>C$_2$PyEs</td>
<td>-</td>
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</tr>
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*R_C* = core radius, *R_{HS}* = hard sphere radius, *R_h* = hydrodynamic radius, $L$ = thickness of disk, $R$ = radius of disk, *#* uncertainty is ± 2%, *@* 5%

Thus, from the DLS and SANS analysis, we can say that the size of the nanoparticles depends on the geometry and dimension of the block copolymer micelles. This conclusion supports the second and third steps of the proposed mechanism of the block copolymer mediated nanoparticle synthesis.

#### 4.3.2 Influence of ionic liquid on the nanoparticles

As discussed in the above section, in order to tune the size and shape of the nanoparticles, one has to tune the micellar geometry of the block copolymer. In view of this, we have synthesised the AgNPs using P123 in the presence of ILs. The ILs used in present study are depicted in **Scheme 4.1**. The 0.01 M AgNO$_3$ solution was added to a premixed solution of block copolymer (8.7 mM P123) and C$_8$PyDs (0.01% w/w). Within a few minutes, the initial transparent solution turned yellow and darkened as time progressed.
Figure 4.5 (a) Plot of absorbance at $\lambda_{\text{max}}$ (401 nm) versus time for AgNPs synthesized using Pluronic P123 in the presence of an IL ($C_8$PyDs). The inset indicates the variation of absorbance as a function of time. (b) UV-Vis spectra of AgNPs synthesized using Pluronic P123 in the presence of an IL ($C_4$PyDs, $C_6$PyDs and $C_8$PyDs) after 30 h.

Figure 4.5 represents the UV-Vis spectra of silver nanoparticles in presence of an IL as a function of time. From Figure 4.5, it can be seen that the absorbance of the SPR band increases with time but with little change in the absorption value, which indicates that the presence of IL facilitates growth of the particles, and the equilibrium is reached within a short time. The absorbance value at equilibrium is $\sim 2.0$ (Figure 4.5(b)) which is quite high (almost 3 fold) compared to AgNPs prepared without the IL (Figure 4.1(b)). Apart from this, the following observations are made upon comparison of the UV-Vis spectra (Figure 4.1(b) and Figure 4.5(b)) of AgNPs prepared in the absence and presence of an IL: (i) the absorption values of the SPR band are quite high, (ii) an additional band appears at $\sim 500$ nm and (iii) the time required to attain equilibrium is low. The presence of the additional band indicates that the system contains particles with a different size.

In order to confirm the morphology of the AgNPs synthesized using ILs, DLS and TEM measurements were carried out (Figure 4.6(a)) which showed particles of $\sim 20$ nm and $\sim 140$ nm in size. A close look at the intensity values (Figure 4.6(a)) reveals that the population of larger sized particles is higher than that of the smaller sized particles. The TEM image shows AgNPs with a flexible cylindrical (ribbon)-type shape along with spherical particles, which confirms that the presence of IL not only increases the growth of the nanoparticles but also induces a sphere-to-ribbon-like transition, i.e. the IL is also
performing a shape-directing role in the block copolymer mediated nanoparticle synthesis.

Figure 4.6 TEM images of AgNPs reduced by P123 in the presence of (a) C₈PyDs, (b) C₄PyDs, (c) C₃PyMs and (d) C₂PyEs and right side their corresponding DLS particle size distributions.
To see the actual effect of the IL on the morphology of AgNPs, a control experiment was carried out in which a silver salt was reduced by a simple reducing agent such as NaBH$_4$ (instead of P123) in the presence of C$_8$PyDs. **Figure 4.7** depicts the UV-Vis spectrum and a TEM image of AgNPs prepared under the control experiment. The UV-Vis spectrum (**Figure 4.7(a)**) has a similar nature to that exhibited by the AgNPs when reduced by P123, i.e. the presence of multiple SPR bands which confirm the larger polydispersity and particle size. Moreover, from the TEM image, it is confirmed that the AgNPs possess a non-spherical (cylinder or disk) geometry. This indicates that the change in the morphology of the nanoparticles from spherical to cylindrical is only due to C$_8$PyDs (IL) and not because of the reducing agent (amphiphilic block copolymers).

As mentioned in the experimental section, C$_8$PyDs was prepared by the metathesis of N-octyl pyridinium chloride and sodium dodecyl sulphate. SDS was used as a shape directing, as well as stabilizing agent in the synthesis of AgNPs.$^{56}$ Mafune et al.$^{56}$ reported that AgNPs prepared using the laser ablation method in the presence of C$_n$H$_{2n+1}$SO$_4$Na (n = 8, 10, 12, 16) are spherical in shape. Thus, we can say that as a stabilizing agent, SDS plays a vital role in determining the morphology of nanoparticles. In addition to this, replacement of the Na head group of SDS with a pyridinium cation induced a spherical to cylindrical shape transition in the AgNPs. This indicates that the cationic moiety also plays an important role in determining the geometry of AgNPs. In order to study the influence of alkyl chain length of the cation and anion on the geometry...
of AgNPs, as described in the experimental section, two types of ILs were prepared, (i) by varying the alkyl chain length on the cation, keeping the anion constant (dodecyl sulphate), and (ii) by shortening the alkyl chain of both the cation and anion. These ILs, along with the amphiphilic block copolymer reducing agents were used in the synthesis of the AgNPs. **Figure 4.5(b)** shows the SPR band in the UV-Vis spectra for AgNPs prepared in the presence of \( \text{C}_4\text{PyDs} \) and \( \text{C}_6\text{PyDs} \). As with \( \text{C}_8\text{PyDs} \), for these two ILs additional SPR bands are present at \( \sim 501 \text{ nm} \), which indicates that the system is composed of polydispersed particles. The obtained particle size from DLS measurements in the presence of \( \text{C}_4\text{PyDs} \) and \( \text{C}_6\text{PyDs} \) are depicted in the last column of **Table 4.1**. The data shows that the size of the AgNPs is almost independent of the alkyl chain length of the IL, featuring the same anion. To gain information on the shape of the AgNPs prepared with \( \text{C}_4\text{PyDs} \), a TEM image was obtained (**Figure 4.6(b)**), which clearly shows that the AgNPs possess a non-spherical (flexible ribbon or cylindrical) shape with an elongated length \( L = \sim 110 \text{ nm} \). This value is closer to the one obtained using \( \text{C}_8\text{PyDs} \). A close look at the TEM images (**Figure 4.6(a, b)**) confirms that an increase in the alkyl chain length results in flexibility of the cylindrical form of the AgNPs. The increase in the alkyl chain length from \( \text{C}_4 \) to \( \text{C}_8 \) does not lead to any remarkable change in the size and shape of the AgNPs (the morphology is independent of the alkyl chain length of the cation (keeping same anion) in the ILs).

Similarly, \( \text{C}_1\text{PyMs} \) and \( \text{C}_2\text{PyEs} \) were used to study the effect of anions on the morphology of AgNPs with P123 as the reducing agent. The DLS particle size distribution and TEM images of AgNPs prepared in the presence of \( \text{C}_1\text{PyMs} \) and \( \text{C}_2\text{PyEs} \) are shown in **Figure 4.6(c, d)**. Looking at the results, to our surprise, in both cases the AgNPs possess spherical shapes of size \( \sim 20–30 \text{ nm} \). On closer inspection, we found that these ILs do not form any micelles in water but their addition may charge the P123 micelles which upon the reduction of \( \text{Ag}^+ \) ions leads to ILs adopting the shape of the P123 micelles, thus giving spherical shape to AgNPs. This observation supports the hypothesis that the alteration or growth of AgNPs in the presence of ILs and P123 as a reducing agent depends on micelles of the IL. If they are absent then P123 may determine the shape of the AgNPs. As discussed above, the size and shape of the AgNPs depends on ILs, and in order to correlate the geometry of AgNPs with the IL micelles, we have characterized the IL micelles in aqueous solutions by DLS and SANS measurements. Out of the five ILs used
in this study (mentioned in Scheme 4.1), C_4PyDs, C_6PyDs and C_8PyDs have poor solubility in water while the remaining two (C_1PyMs and C_2PyEs) are fully miscible with water, which shows the former produce micelles in water, while the later do not form micelles. Figure 4.8 shows the SANS curves for the aqueous solutions of C_nPyDs (n = 4, 6, 8). The inset depicts the average diameter of the IL micelles, showing the average particle diameters to be ~150, 155, 160 nm (considering a spherical shape) for C_4PyDs, C_6PyDs and C_8PyDs respectively, indicating that the size of the micelle is almost independent of the alkyl chain length on the pyridinium cation.

Figure 4.8 SANS data of 0.05% (w/v) C_4PyDs, C_6PyDs, C_8PyDs in a pure aqueous solution at 30 °C. The inset indicates the mean diameter of C_nPyDs (n = 4, 6, 8)

The SANS measurements of C_4PyDs, C_6PyDs and C_8PyDs were carried out on a 0.05% w/v solution of the ILs at 30 °C. In all of the curves the dΣ/dΩ correlation value increases by decreasing the scattering vector, q, and there is an absence of correlation peaks (S(q) = 1). These SANS profiles could be best reproduced with a cylindrical (or disk) shape (using eqn. (2), (3) and (5)). The parameters obtained from the fits are given in Table 4.1. The probability of the cylindrical shape is omitted by a log–log plot of dΣ/dΩ and q, for q values in the range 1/R < q < 1/L (slope ~ -2, which is for the disk shape). The values of R and L mentioned in Table 4.1 are almost constant within the uncertainty limit, which means that the micellar size is almost independent of the increase in alkyl chain length from C_4 to C_8 on the pyridinium cation. As mentioned earlier, ILs are synthesized from SDS and C_nPyCl, and it is very well documented that SDS produces micelles spherical in shape, but C_4PyCl and C_6PyCl do not produce micelles while C_8PyCl can be micellized.
at a very high concentration in water.\textsuperscript{57} However, just by a metathesis process we can increase the hydrophobicity which is responsible for making very well organized micelles.

The micellar dimensions and the shape of ILs in aqueous solution are in good agreement with the geometry possessed by the AgNPs prepared by P123 in the presence of ILs. This indicates that the presence of ILs not only increases the growth but also induces a spherical to cylindrical (flexible ribbon-type in the case of C\textsubscript{8}PyDs) transition, i.e. ILs also plays a shape-directing role in block copolymer mediated nanoparticles synthesis. As the nanoparticles possess the shape of IL micelles, rather than of the block copolymer, we conclude that the nucleation of nanoparticles is taking place in the IL.

\textbf{Scheme 4.2} Schematic representation of AgNPs prepared by the block copolymer mediated method in the presence of ILs

This is further supported from the behavior of the AgNPs in the presence of C\textsubscript{1}PyMs and C\textsubscript{2}PyEs where ILs do not produce micelles in aqueous solution, and thus the nanoparticles adopt the shape of the block copolymer. This confirms that ILs are responsible for the shape transition as well as the growth of AgNPs. The mechanism of Ag\textsuperscript{+} ion reduction by the PEO–PPO–PEO block copolymer in aqueous solution is the same as proposed by
Sakai et. al.\textsuperscript{54} with the only difference being that, due to the electrostatic attraction of silver ions towards the anions of the IL (\textit{Scheme 4.2}), nucleation is taking place on the cylindrical (disk) IL micelles and later on they are reduced by the PEO–PPO–PEO block copolymer. Apart from this, the mechanism follows all of the other steps (ii and iii) as described previously.

4.4 Conclusions

The Ag nanoparticles were synthesized using a block copolymer mediated process, where PEO–PPO–PEO acts as a reducing, templating and stabilizing agent. The AgNPs possess a spherical shape. For a given block copolymer, the shape and size of the AgNPs solely depends on the geometry of the block copolymer micelles. The addition of an IL (C\textsubscript{n}PyDs) induced a sphere to flexible cylinder (ribbon)-like transition in the AgNPs, which was confirmed by TEM. The morphology and geometry of the AgNPs correlates with the dimension and shape of the ILs micelles. Thus, we show that ILs have a shape directing as well as growth enhancing role in the block copolymer mediated synthesis of AgNPs.
Chapter 4

4.5 References

34. Sakai, T.; Alexandridis, P. Nanotechnology 2005, 16, S344.