Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 10410-10412

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15599A

Synthesis of Silver Nanorods Using Lamellar Liquid Crystal of Protic Ionic Liquids

QIU HONG LI*, PENG LI and XIAOLONG ZHANG

College of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, Shandong Province, P.R. China

*Corresponding author: E-mail: bingxueer79@163.com

(*Received*: 6 April 2013; *Accepted*: 18 November 2013) AJC-14414

Silver nanorods are prepared by reduction of silver nitrate in lamellar lyotropic liquid crystal mainly made of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (P123) and protic ionic liquids (PILs) EAN. Liquid crystal was characterized by polarized optical microscope and small-angle X-ray scattering measurements. Scaning electron microscopy (SEM) and UV-visible spectroscopy show the formation of nanorods. The effects of the concentrations of silver nitrate on the formation of the nano-products are discussed. The average diameter of silver nanorods with 30-50 nm can be observed and the length of nanorods is about 500 nm. The result indicates that the lamellar lyotropic liquid plays an important role for the consequent growth of nanorods by providing an ordered reaction medium and a limited growth space.

Key Words: Silver nanorods, Lyotropic liquid crystal, Protic ionic liquid.

INTRODUCTION

Metal nanoparticles have attracted attention in recent years due to their unique optical, electronic, magnetic and catalytic properties that are different from those of the bulk states[1]. Among the different metal particles, silver nanoparticles have attracted considerable interest because of their potential applications in areas such as nanoelectronics, electromagnetic interference shielding and surface-enhanced Raman scattering[2]. During the past few decades, many methods including both physical and chemical methods have been reported for the synthesis of silver nanoparticles[3-8].

At the same time, there is considerable interest in the use of room temperature ionic liquids as promising substitutes for volatile organic solvents. Ionic liquids are organic salts with melting points near room temperature, which have received a great deal of attention as green and designer solvents owing to their unique properties such as negligible vapor pressure, nonflammability, high chemical and thermal stability, high polarity, high ionic conductivity, wide electrochemical window and tunable physico-chemical properties including dissolving ability and solvent miscibility[9-12]. Protic ionic liquids (PILs) are a subset of ionic liquids that can be easily produced trough the proton transfer between Bronsted acids and bases. Protic ionic liquids exhibit some special qualities compared to aprotic ionic liquids because of the presence of the proton donor and acceptor sites, which makes them also useful in biology[13] and as proton-conducting media in polymer membrane fuel cells, double-layer capacitors, or dye-sensitized solar cells[14,15]. Meanwhile, the ease with which PILs form hydrogen-bonded network put them to be good candidates as nonaqueous self-assembling media[16]. Recently, the advantages of amphiphilic ionic liquid derivatives in the introduction of ordered self-organized structures have been reported. For example, long chain ionic liquids have been used as synthetic templates in the preparation of mesoporous silica[17-19]. But the use of liquid crystals formed by protic ionic liquids as templates in nanoparticle synthesis has been scarcely reported.

In this paper, we report on the formation of silver nanorods from lamellar lyotropic liquid crystals (LLC) made of poly-(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide) (PEO-PPO-PEO) block copolymers in PIL EAN. The small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM) and UV-visible absorption spectrum were employed to characterize the silver nanorods. In this process, $AgNO_3$ was reduced by the block copolymers PEO-PPO-PEO and there were no other reducing agents were added or other reductive methods were employed. The mechanism for oxidative degradation of ethoxyl groups of PEO-PPO-PEO[20] are shown in Fig. 1.

EXPERIMENTAL

The amphiphilic block copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mn = 5800) is purchased from Sigma. Silver nitrate ($AgNO_3$) is purchased from Shanghai Reagent Co.

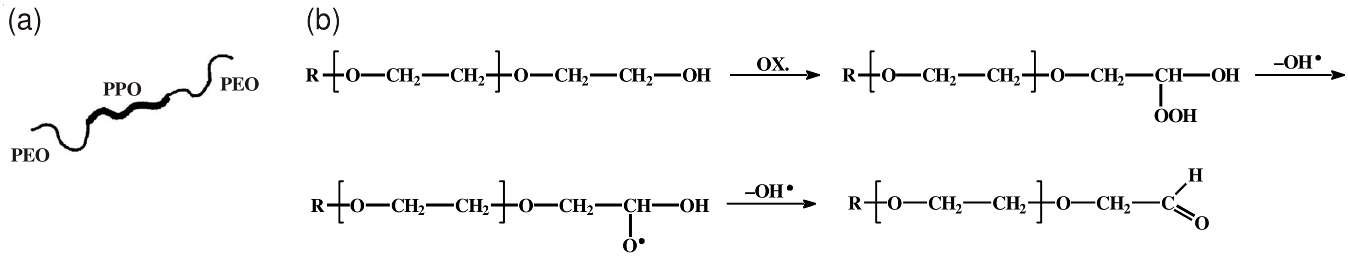

Fig. 1. Schematic diagram of molecular structure of P123 (a) and mechanism for oxidative degradation of ethoxyl groups (b)

Water used in the experiment was triply distilled. All chemicals are used as received without further purification.

Synthesis of silver products: According to the previous report, Pluronic P123 can form a lamellar phase at higher concentration (weight percentage of 66-90 %) when mixed with EAN at room temperature[21]. In our study, 80 % P123 is selected where lamellar liquid crystal can be formed. To prepare silver nanoparticles, silver nitrate solution in PIL EAN instead of water is used to construct lamellar phase with PEO-PPO-PEO. The samples are sealed in glass tubes and left at room temperature for further study.

Small-angle X-ray scattering (SAXS) measurement: Phase behaviours of lyotropic liquid crystals (LLCs) are investigated by SAXS on a HMBG-SAX X-ray small angle system (Austria) with Ni-filtered CuK_α radiation (0.154 nm) operating at 50 kV and 40 mA. The sample-to-detector distance is 27.8 cm. The temperature is kept at 25 °C. The relative positions of SAXS scattering peaks along the scattering vector (q) axis are used to determine the lyotropic phase structure. For lamellar structure, the peak positions should obey the relation 1:2:3:4.

Characterization of Products: Polarized optical micrographs were observed by a Motic B2 polarized optical microscope (POM) with a CCD camera (Panasonic Super Dynamic II WV-CP460). Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F system (operated at 3.0 kV). The sample was prepared by casting the solution of silver nitrate onto a clean silicon slide, followed by drying under vacuum at room temperature. The optical properties of obtained gold products dispersed in water are characterized on a HP 8453E UV-visible spectrometer.

RESULTS AND DISCUSSION

Fig. 2 shows the photographed textures of sample for liquid crystal template and hybrids with different silver atom concentrations (P123 80 %) by polarized optical microscopy (POM). The typical "thread-like" textures can be assigned to a lamellar liquid crystalline phase (La)[22]. Further structural informaiton on such lamellar liquid crystalline phases is extracted by small-angle X-ray scattering (SAXS) measurement (Fig. 3). As can be seen, all of them exhibit two clear and typical scattering peaks, accompanying with the third nearly undistinguishable peaks. The ratio of the scattering factors (q) at the 1st, 2nd and 3rd Bragg peaks is 1:2:3, indicating a lamellar structure, which is kept well when lyotropic liquid crystal is added into $AgNO_3$. Moreover, the first peak position shift to left with the increase $AgNO_3$ concentration, which indicate the increase of the typical repeat distance (d) for lyotropic liquid crystal determined from the first peak position (q1). The reason

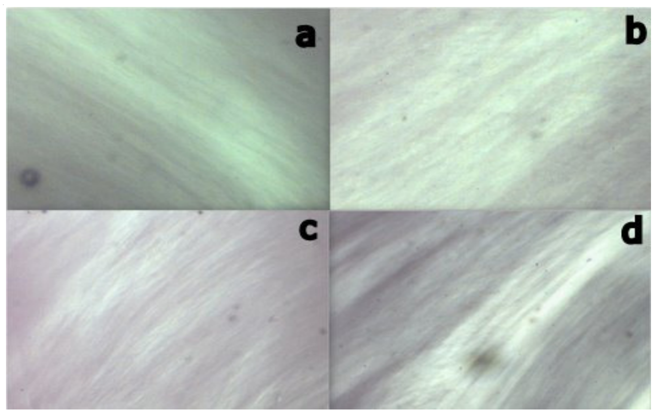

Fig. 2. Polarized optical microscopy photographs of P123 (80 %) lamellar liquid crystal phases measured 20 days after preparation. Concentrations of $AgNO_3$ (mol L^{-1}) are: (a) 0, (b) 0.01, (c) 0.03 and (d) 0.05

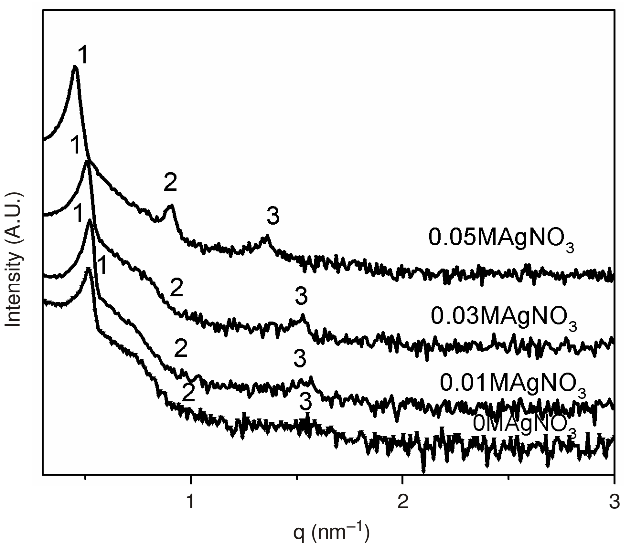

Fig. 3. SAXS patterns of P123 (80 %) lamellar liquid crystal phases measured 20 days after preparation at different $AgNO_3$ concentration

may be the swelling effect of particles formed in lyotropic liquid crystal phase.

Morphology Characterization of Silver Products: In the lamellar lyotropic liquid crystal system self-assembled from P123, the reduction occurs and PEO blocks will slowly reduce AgI ions to Ag through oxidation of their oxyethylene groups[23,24]. SEM images for samples produced from 0.03 M $AgNO_3$ are shown in Fig. 4. The regular silver nanorods with diameter 30-50 nm can be observed and the length of nanorods is about 500 nm. Herein, the lamellar lyotropic liquid crystal structure plays an important role on the formation of rod-like products[25].

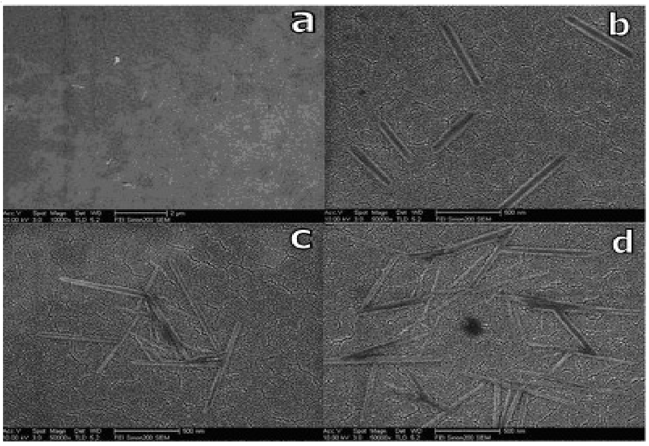

Fig. 4 SEM images of silver nanorods obtained from P123- $AgNO_3$ (0.03 M) systems measured 20 days after preparation. Magnification factor: (a) 10000, (b) 50000, (c) 50000 and (d) 50000

Optical properties: Optical properties of prepared silver nanorods are strongly related to their shape and size. To further study such manipulation effect and monitor the products formation, the optical absorption properties of obtained product dispersions are recorded. As shown in Fig. 5, the UV-visible absorption curves for investigated samples show two absorption peaks with the wavelength about 310 and 400 nm, reflecting the formation of anisotropic nanoparticles, which is in line with the results observed by SEM. In addtion, the broad absorption peak shows the strong interaction between silver nanoparticles and substrate. With the increase of $AgNO_3$ concentration, the shape of absorption peak does not change obviously, indicating the little influence of concentration on the morphology[26].

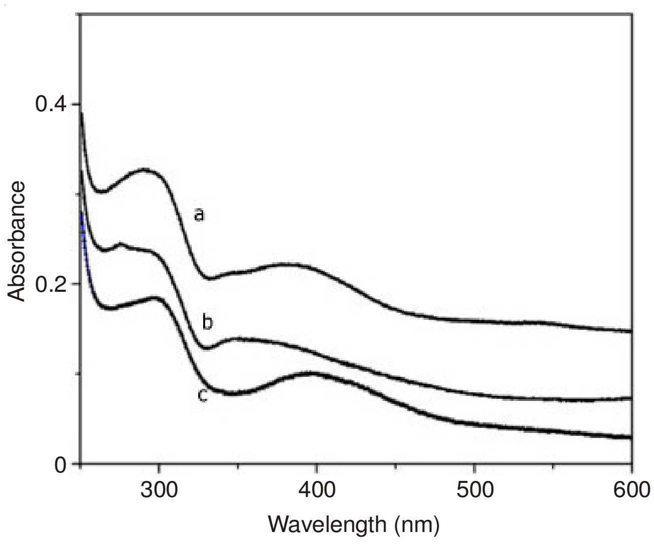

Fig. 5. UV-visible absorption spectra of silver products prepared from P123 (80 %) $AgNO_3$ systems with $AgNO_3$ concentration (mol L^{-1}) at (a) 0.05, (b) 0.03 and (c) 0.01.

Conclusion

Present study has demonstrated that protic ionic liquid, EAN, can form lyotropic liquid crystal with P123 in the system containing $AgNO_3$, which can be used as soft templates to prepare silver nanorods. SAXS results indicate the formation of lamellar liquid crystal and the typical repeat distance (d) for lyotropic liquid crystal increase when $AgNO_3$ is added because of the swelling effect of particles formed in lyotropic liquid crystal phase. SEM measurements and UV/visible spectra of the products show the formation of nanorods. Obtained results suggest that the lyotropic liquid crystal phase provides an ideal reaction environment to control the shape of silver nanorods.

ACKNOWLEDGEMENTS

The authors are thankful for the financial support from Shandong Provincial Science Fund (Project No. ZR2012BQ-008), Development of Young Teachers Program of Shandong University of Technology (Project No. 112015) and Starting Researh Fund from Shandong University of Technology (Project No. 411011).

REFERENCES

1. M.-C. Daniel and D. Astruc, *Chem. Rev.*, **104**, 293 (2004).
2. A.C. Templeton, A.W.P. Wuelfing and R.W. Murray, *Acc. Chem. Res.*, **33**, 27 (2000).
3. K.S. Chou and C.Y. Ren, *Mater. Chem. Phys.*, **64**, 241 (2000).
4. C. Luo, Y. Zhang, X. Zeng, Y. Zeng and Y. Wang, *J. Colloid Interf. Sci.*, **288**, 444 (2005).
5. Z.Y. Tang, S.Q. Liu, S.J. Dong and E. Wang, *J. Electroanal. Chem.*, **502**, 146 (2001).
6. D.G. Li, S.H. Chen, S.Y. Zhao, X.-M. Hou, H.-Y. Ma and X.-G. Yang, *Thin Solid Films*, **460**, 78 (2004).
7. A. Kameo, T. Yoshimura and K. Esumi, *Colloids Surf. A*, **215**, 181 (2003).
8. Z. Zaheer and Rafiuddin, *Colloids Surf. B*, **90**, 48 (2012).
9. H. Weingärtner, *Angew. Chem. Int. Ed.*, **47**, 654 (2008).
10. V.I. Pârvulescu and C. Hardacre, *Chem. Rev.*, **107**, 2615 (2007).
11. F. van Rantwijk and R.A. Sheldon, *Chem. Rev.*, **107**, 2757 (2007).
12. S.G. Lee, *Chem. Commun.*, **10**, 1049 (2006).
13. J. Pernak, I. Goc and I. Mirska, *Green Chem.*, **6**, 323 (2004).
14. A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, **107**, 4024 (2003).
15. W. Ogihara, J. Sun, M. Forsyth, D.R. MacFarlane, M. Yoshizawa and H. Ohno, *Electrochim. Acta*, **49**, 1797 (2004).
16. T.L. Greaves and C.J. Drummond, *Chem. Rev.*, **108**, 206 (2008).
17. Y. Zhou and M. Antonietti, *Chem. Commun.*, 2564 (2003).
18. Y. Zhou and M. Antonietti, *Adv. Mater.*, **15**, 1452 (2003).
19. T. Wang, H. Kaper, M. Antonietti and B. Smarsly, *Langmuir*, **23**, 1489 (2007).
20. M. Andersson, V. Alfredsson, P. Kjellin and A.E.C. Palmqvist, *Nano Lett.*, **2**, 1403 (2002).
21. G.D. Zhang, X. Chen, Y.R. Zhao, F.M. Ma, B. Jing and H.Y. Qiu, *J. Phys. Chem. B*, **112**, 6578 (2008).
22. F.B Rosevear, *J. Am. Oil Chem. Soc.*, **31**, 628 (1954).
23. L.M. Liz-Marzán and I. Lado-Touriño, *Langmuir*, **12**, 3585 (1996).
24. L. Qi, Y. Gao and J. Ma, *Colloids Surf. A*, **157**, 285 (1999).
25. Z.W. Sun, X. Chen, L.Y. Wang, G.D. Zhang and B. Jing, *Colloids Surf. A*, **326**, 23 (2008).
26. P. Mulvaney, *Langmuir*, **12**, 788 (1996).