6A/2013G533

Synthesis of Pd Particles in Surfactant Aggregates in Ionic Liquids

Masafumi HARADA*[1], Chihiro ASANO[1], and Kenji SAIJO[2]
[1]Department of Clothing Environmental Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8506, Japan
[2]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

1 Introduction

In recent years, ionic liquids (ILs) have been paid much attention as novel green media for the synthesis of inorganic materials [1,2]. Micellar aggregations of nonionic surfactants in ILs have been also studied intensively [3]. However, few reports have described the synthesis of metal particles in micellar aggregates in ILs. In this study we have performed the size-controlled synthesis of Pd particles in a series of micellar aggregates consisted of nonionic surfactant Brij in various ILs based on the 1-alkyl-3-methylimidazolium cation by means of SAXS measurements.

2 Experimental

Colloidal dispersions of Pd particles were synthesized by the decomposition of palladium acetylacetonate, $Pd(acac)_2$, in the mixture of nonionic surfactant (Brij-30, Brij-52, Brij-56, Brij-58, Brij-35, Brij-700) and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF_4]) (or 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIm][PF_6])) at fixed weight ratio. For example, in the case of Brij-52/[OMIm][BF_4] binary system, 1.2 g of Brij-52 was added to 2 mL of [OMIm][BF_4], followed by the addition of 11 mg $Pd(acac)_2$ and mixed vigorously. Subsequently, the mixture solution was poured into a cell (optical path length 1 mm), and the sample was stepwise heated from RT to 333, 353, 373, 393, 413, 433, and 453 K. The in-situ SAXS measurements were performed at each temperature at BL-6A. The scattering data was detected by a PILATUS 1M.

3 Results and Discussion

Fig. 1 shows the SAXS profiles of the colloidal dispersions of Pd particles at different temperatures (up to 453 K) in the presence of Brij-52 or Brij-58 mixed with [OMIm][BF_4]. These SAXS profiles show that all the samples have a broad peak (centered around 1.7 nm^{-1} for Brij-52/[OMIm][BF_4] and 2.2 nm^{-1} for Brij-58/[OMIm][BF_4]) observed in a q range larger than 1.5 nm^{-1} and a second inner shoulder peak in a q range shorter than 1.2 nm^{-1}. The former is characteristic of the interference peak due to the existence of ordering for ILs, and the latter is related to interferences due to the interaction between two neighboring Pd particles. The intensity of the second peak increases and its position shifts to lower q with increasing temperature. The variation of average size of Pd particles with temperature is listed in Table 1. The detailed analysis is in progress.

Table 1 Average particle size (nm) of Pd particles synthesized at different temperature in various binary systems

Sample	353K	373K	393K	413K	433K	453K
Brij-30/[OMIm][BF_4]	2.4	3.0	4.1	5.9	6.2	6.5
Brij-52/[OMIm][BF_4]	1.4	1.4	1.8	2.2	3.1	-
Brij-56/[OMIm][BF_4]	1.6	-	1.6	2.4	3.4	-
Brij-58/[OMIm][BF_4]	-	2.2	2.5	2.9	3.8	4.8
Brij-56/[OMIm][PF_6]	-	-	1.9	3.0	4.3	4.5
Brij-35/[OMIm][PF_6]	-	2.4	2.7	3.5	4.0	5.2
Brij-700/[OMIm][PF_6]	-	2.9	3.9	4.4	4.4	4.7

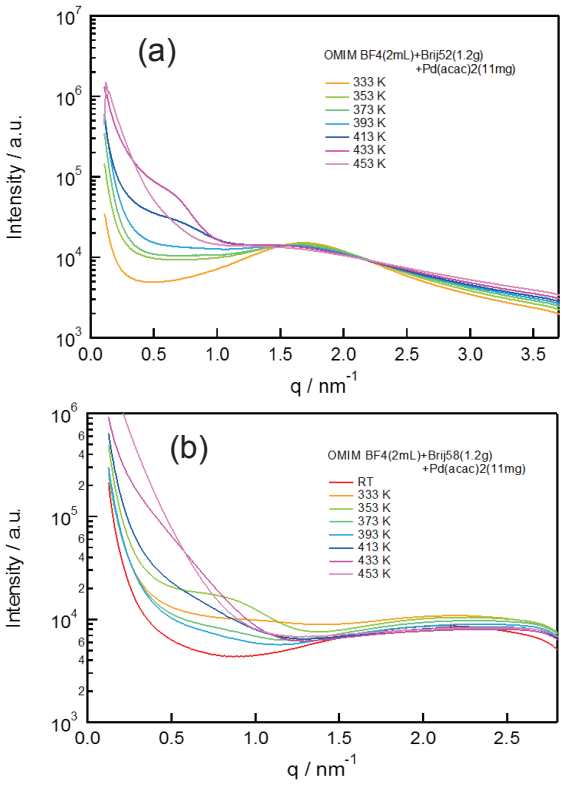

Fig. 1. SAXS profiles of the Pd colloidal solutions synthesized during stepwise raising the reaction temperature in the binary system of (a) Brij-52/[OMIm][BF_4] and (b) Brij-58/[OMIm][BF_4].

References

[1] Z. Ma et al., *Adv. Mater.* **2010**, *22*, 261.
[2] J. Dupont et al., *Chem. Soc. Rev.* **2010**, *39*, 1780.
[3] R. Rai, S. Pandey, *Langmuir* **2014**, *30*, 10156.
*harada@cc.nara-wu.ac.jp