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Formation of polymer nanoparticles by self organized precipitation method

S. Enkhtuul[1], M. Munkhshur [1,2]

[1]*Institute of Chemistry and Chemical Technology, MAS, Peace avenue, Ulaanbaatar 13330, Mongolia*
Department of Energy and Mechanical engineering, Gyeongsang National University,Cheondaegukchi-Gil 38, Tongyeong, Gyeongnam 650-160, Republic of Korea

Abstract: Polymer nanoparticles have been investigated with great interest due to their potential applications in the fields of electronics, photonics and biotechnology. Here, we demonstrated the formation of polymer nanoparticles from a tetrafydrofuran/water mixture solution. Polymer nanoparticles remained as dispersed particles in the poor solvent (water) when good solvent (THF) is evaporated. Homogeneous nucleation and successive growth of polymer particles takes place during the dynamic nonequilibrium process of solvent evaporation. The size of the particles ranging from hundreds of nanometers to micrometers scale depends on the solvent mixing ratio. With suitable combinations of solvents, this procedure is applicable to a wide variety of polymers.

Keywords: polymer nanoparticles, self-organized precipitation method, poor and good solvent

INTRODUCTION

The synthesis of nanostructured materials with tunable properties is central to the development of varying applications in nanoscale science and techno-logy. The convergence of physics, chemistry and biology will actually lead to an explosive increase in possibilities of R&D directions. Polystyrene (PS) nanoparticles are useful for a wide range of applications ranging from applications in fields of photonics [1], nanotechnology [2, 3], and life science [4, 5] to fundamental studies in the behavior of colloidal suspensions, like the role of hydrodynamic [6] and   entropic [7] forces and studies on phase transition [8] and crystallization [9].

There are many preparation methods of polymer nanoparticles including milling of bulk materials, emulsion polymerization, seed polymerization and reprecipitation [10]. However emulsion based methods for nanoparticle synthesis are two-step procedures that comprise an initial emulsion formation and, subsequently, an actual nanoparticle formation via a process such as evaporation or diffusion [11]. In contrast, reprecipitation methods for organic nanoparticle synthesis are single-step procedures based on the mixing of a solution of the organic compound with a poor or nonsolvent. During recent years, the majority of investigations in the field of nanotechnology have focused on the fabrication of polymeric nanostructures using different methods such as self-organized precipitation method or supercritical fluid technology. Both self-organized precipitation method and supercritical fluid techniques used in the synthesis of nano

* corresponding author: e-mail: enkhtuulls@yahoo.com

materials can be seen as a special form of the reprecipitation method [10]. The supercritical fluid can act either as the good or poor solvent for the polymer compound.

A new methodology based on self-organization [11] is widely applicable to nano- and micro- fabrication of polymer materials without conventional lithographic procedures [12-15]. Self-assembly of nanometric particles will definitely play an important role in this. Nonlithographic approaches based on thermo-dynamically driven self-organization processes are especially appealing because of their potential for large-scale production with very small infrastructure investments [16]. Different types of organic nano-particles ranging from dye molecules to polymers have been prepared using those techniques [11].

In this paper, we have demonstrated the possibility to fabricate polymer nanoparticles using self-organized precipitation method. The characterization of fabricated nanoparticles such as size, size distribution, shape and functionality are the important factors for understanding their properties and considering their applications.

EXPERIMENTAL

Preparation of polymer nanoparticles : All chemicals were purchased from SX Biotech Co., Ltd, Mongolia. Polystyrene (1 mg) was dissolved in 2 ml of good solvent tetrahydrofuran (THF) and 2 ml of poor solvent water was slowly added to the THF solution through a syringe pump with dropping speed of 1ml/min. The polymer solution remained still optically transparent after mixing. The solution stayed

clear at room temperature when the solution kept closed tightly. However, when the mixed solution was left open at room temperature for evaporation of good solvent, the solution stayed clear for a while and then turned turbid (see Fig. 1, left). The time course of the optical transmittance of the evaporating solution at 600nm was measured by Shimazu 160 UV spectrophotometer.

RESULTS AND DISCUSSIONS

A scanning electron microscopy image of polystyrene particles generated in the transparent solution is shown in Fig. 1 (right). In order to measure by SEM

100µl of the evaporating polymer solution was sampled and dropped onto mica substrates, and then coated by spattering platinum after drying.

Uniformity of the particle is not that great, however when the particle size was in the sub-wavelength region, the solution kept transparent. The polymer solution abruptly became opaque 300 min after starting evaporation. The size of the polymer particle could be affected by the polymer concentration and the mixing ratio of the solvents.
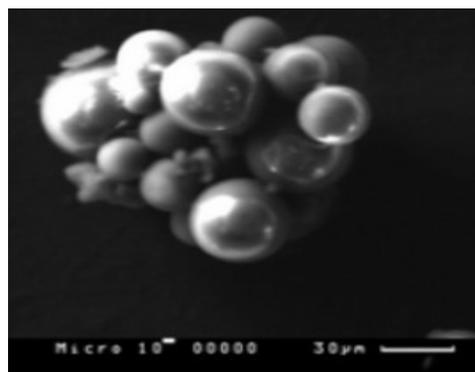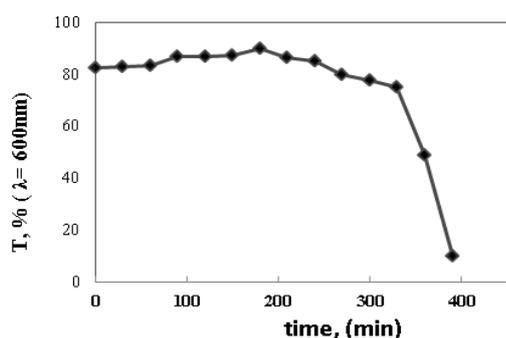

Fig. 1. Time course of turbidity change during the solvent evaporation process (left). SEM image of fabricated nanoparticles (right).

As Yabu et. al also had suggested previously, we propose a temporary schematic model of the mechanism of nanoparticle formation mechanism during the evaporation of good solvent (see fig. 2). Due to the solvation by the good solvent, polymer molecules are dissolved in a random coil structure.

As the amount of poor solvent is increased due to the evaporation of good solvent, desolvation of polymer molecules begins and then compact folding of polymer chain occurs as a result, the polymer molecules grow to small nuclei.
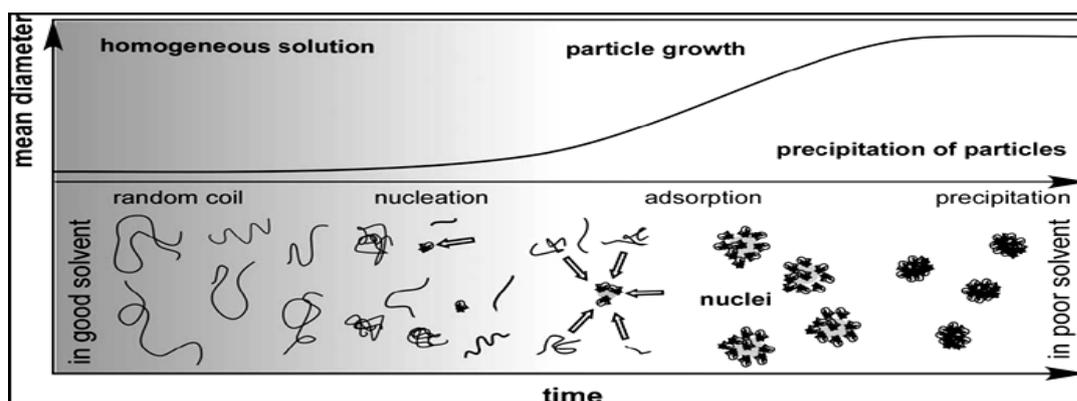

Fig. 2. Schematic representation of nanoparticle formation mechanism during dynamic process of solvent evaporation.

The equilibrium between random coils and nuclei dynamically shifts toward nuclei as the amount of good solvent decreases during evaporation. This change in equilibrium during evaporation may be a driving force for the formation of homogenous nuclei and the successive growth of polymer nanoparticles. After complete evaporation of the good solvent, nanoparticles are dispersed in the poor solvent.

CONCLUSIONS

We have demonstrated a novel method to fabricate polymer nanoparticles based on self-organized nonequilibrium processes in slowly evaporating polymer solutions. Miscibility of the two solvents is essential for this method, and in order to ensure preferential evaporation of the good solvent, the boiling point of the good solvent must be lower than that of the poor solvent. Due to the physical

generality of the formation mechanism, this method is applicable to a wide variety of polymers. Chemical and physical modifications of the particle surface will provide functionality and can be promising for a many novel applications.

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