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Effect of amphiphilic copolymer containing ruthenium tris(bipyridyl) photosensitizer on the formation of honeycomb-patterned film

Bong Seong Kim, C. Basavaraja, Eun Ae Jo, Dae Gun Kim, Do Sung Huh*

Department of Chemistry and Institute of Basic Science, Inje University, Obang 607 Gimhae City, Kyungnam 621-749, South Korea

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ABSTRACT

A new functional amphiphilic polymer (A_P) containing ruthenium tris(bipyridyl) photosensitizer was synthesized and a honeycomb-patterned film was fabricated by casting a polystyrene solution and different concentrations of A_P under humid conditions. The amphiphilic copolymer was obtained by the radical copolymerization of ruthenium (4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexaflurophosphate) with *N*-dodecylacrylamide and *N*-isopropylacrylamide. Without the addition of A_P, irregularly ordered porous films were obtained, while adding A_P in the casting solution resulted in highly ordered honeycomb-patterned films. In addition, the pore diameter and height of the porous structure increased with the increase of A_P amount in the solution. However, an excessive amount of A_P induced an irregularly structured pattern with small pore sizes.

1. Introduction

Highly ordered porous polymer films have attracted much attention due to their potential applications in areas such as tissue engineering [1,2], photonic band gap [3], and optoelectronic devices [4]. Porous films with ordered structures have been fabricated by a variety of methods [5,6], including lithography [7] or soft lithography [8,9], the use of colloidal crystals [10,11], emulsions [12], self-assembled rod-coil copolymers [13,14], and microphase-separated block copolymers [15,16].

Recently, a simple method to create ordered structure porous films was introduced by Pitois et al. [17]. Highly ordered polymer films were produced by evaporating a solution of polymer dissolved in a volatile solvent under humid conditions. Water vapor condensed onto the cooling surface due to rapid solvent evaporation, then the droplets were trapped in the solution surface by surface tension. In order to help the trapping of water droplets in the hydrophobic solution surface, an amphiphilic copolymer is generally used in the polymer solution, because the polymer forms a stable monolayer at the air–water interface. Shimomura et al. have synthesized many kinds of neutral or ionic amphiphilic copolymers [18]. Among them, the best-known amphiphilic copolymer is obtained by the copolymerization of *N*-dodecylacrylamide and 6-hexanoic acid [19,20]; *N*-dodecylacrylamide acts as a hydrophobic while 6-hexanoic acid acts as a hydrophilic component. Then, the polymers precipitated at the solution/water interface and effectively stabilized the droplets, thus preventing coalescence. The stabilized droplets were arranged in a well-ordered packing structure, induced by lateral capillary force and convection currents, which resulted from the temperature gradient in the solution. After the solvent and water completely evaporated, ordered traces (pores) were then obtained. These films have been fabricated from rod-coil block copolymers, polymers with ionic groups [21], amphiphilic copolymers [22], and star polymers [23,24].

Building and patterning inorganic nanoparticles into two- and three-dimensional organized structures by the manipulation of individual units is a potential route to the fabrication of chemical, optical, magnetic, and electronic devices with useful properties [25,26]. The synthesis and assembly of inorganic nanoparticles is currently an interesting issue. Composites formed from nanoparticles may possess unique applications in materials, such as batteries, electro-displays, molecular electronics, nonlinear optical materials, sensors, electromagnetic interference shielding, microwave absorption materials, and electrochromic devices [27–29]. Therefore, we introduce a new type of amphiphilic functional polymer including inorganic material of ruthenium.

Tris(2,2′-bipyridine)ruthenium(II) ion, or $Ru(bpy)_3^{2+}$, has received considerable attention from researchers because of its unique properties, such as strong luminescence, moderate excited-state lifetime, energy and electron transfer reactions, and chemical stability [30,31]. The luminescent excited state of $Ru(bpy)_3^{2+}$ is assigned to the metal-to-ligand charge-transfer (MLCT) state. Luminescence properties are very sensitive to the

* Corresponding author. Tel.: +82 55 320 3225; fax: +82 55 321 9718.
E-mail address: chemhds@inje.ac.kr (D.S. Huh).

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polarity and viscosity of the solvent because of the MLCT characteristic. Therefore, fabrication of metallopolymer films with highly ordered structures containing $Ru(bpy)_3^{2+}$ is an important subject in the construction of electrochemical and photochemical devices [32].

Synthesizing a new type of amphiphilic functional polymer including $Ru(bpy)_3^{2+}$ and observing the effect of this polymer in the formation of honeycomb-patterned porous polymer films is induced by the consideration regarding on the possibility for the application of this polymer to overcome the limit of self-organizing process for the honeycomb pattern formation. To date, one major limitation in the formation of honeycomb-patterned microstructures with the assistance of water-droplet is that the diameter/height ratio and interdroplet distance could not be separately controlled. This is because the formation of a highly ordered pattern by evaporation of a polymer solution dissolved in a volatile solvent under humid conditions is a self-organized process, though it can be controlled to achieve a narrow size distribution of the droplets [33]. It is difficult, however, to control the diameter/height ratio and interdroplet distance separately even if a stabilizing amphiphilic polymer for the regular package of water-droplet is used. An additional control factor is necessary to adjust the height/diameter ratio and interdroplet distance separately in self-organized microstructures.

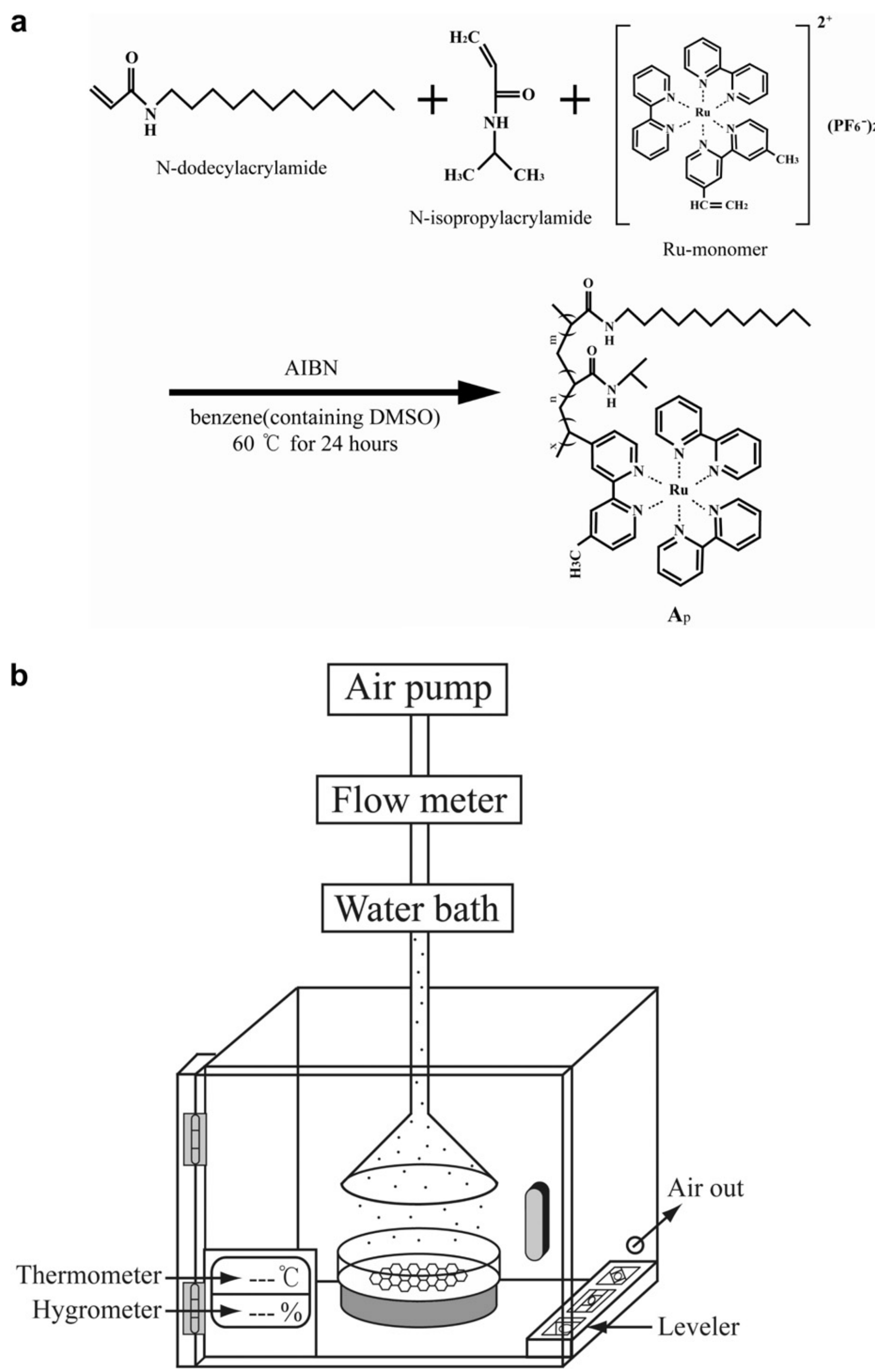

Fig. 1. (a) The scheme for the synthesis of A_P and (b) the overall experimental scheme for the pattern formation of honeycomb structure by the assistance of water-droplet.