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Photo-controlled fabrication of self-organized structures in honeycomb-patterned thin films with light-sensitive amphiphilic copolymer

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ABSTRACT

The structures of honeycomb-patterned thin polymer films fabricated by casting polystyrene solution under humid conditions were controlled by illumination of ultraviolet (UV) light by the assistance of an added light-sensitive amphiphilic copolymer (A_{ls}) in the casting solution. A_{ls} was synthesized through the radical copolymerization of ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexaflurophosphate) with *N*-vinylcarbazole. The synthesized A_{ls} was characterized using spectroscopic methods and a thermogravimetric analyzer. An appropriate duration of light illumination in a suitable concentration of A_{ls} minimized the irregularity of the honeycomb pattern. However, irregular patterns were induced by an excessive amount of A_{ls} or by excessive illumination time.

1. Introduction

Macroporous polymer films with highly ordered pore patterns have attracted considerable attention because of their potential application in areas such as tissue engineering, photonic band gap, and optoelectronic devices [1–3]. Porous films with ordered structures have been fabricated by a variety of methods such as lithography, the use of colloidal crystals, self-assembly, and the rod-coiled copolymers process [4–7]. The common method for preparing such patterned films involves top-down engineering techniques using photolithography and soft lithography [8,9].

Bottom-up approaches using self-assembled templates have recently received interest because they allow for the preparation of large areas of highly ordered porous films at a low cost. Widawski et al. [10] introduced a simple method for creating porous films with ordered structures. Highly ordered polymer films are produced by evaporating a polymer solution dissolved in a volatile solvent under humid conditions. Water vapor condenses on the cooling surface because of rapid solvent evaporation to produce water droplets, which are then trapped on the solution surface via surface tension. An amphiphilic copolymer is used to hold the water droplets on the hydrophobic solution surface because it can form a stable monolayer at the air–water and the water-organic phase interfaces [11,12].

Despite the advantages of a simple and low-cost procedure, one major limitation in the formation of honeycomb-patterned microstructures with the assistance of water droplets is that the diameter to height ratio and interdroplet distance could not be separately controlled. This is because the formation of a highly ordered pattern by the 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-sized distribution through the variation of initial experimental conditions such as temperature, humidity, and air flow rate [13]. Additional control factors are necessary to control separately the parameters in self-organized microstructures. Based on this perspective, our earlier report aimed to introduce a photoactive amphiphilic copolymer containing a $Ru(bpy)_3^{2+}$ photosensitizer [14]. However, the photoactive amphiphilic copolymer was not adequately light-sensitive because its primary component, which serves as its hydrophobic constituent, was non-photosensitive *N*-dodecylacrylamide.

The current paper reports on the control of microstructures of honeycomb-patterned thin films obtained via the fabrication process of a polymer solution through UV illumination. Performance was controlled by the assistance of a newly synthesized light-sensitive amphiphilic copolymer (A_{ls}) containing *N*-vinylcarbazole (NVC) and $Ru(bpy)_3^{2+}$. This novel amphiphilic copolymer was synthesized based on NVC and $Ru(bpy)_3^{2+}$ because of the photo-sensitivity both materials. $Ru(bpy)_3^{2+}$ has received considerable attention because of its unique properties, namely, strong luminescence, moderate excited-state lifetime, energy- and

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electron–transfer reactions, and so on. On the other hand, poly(*N*-vinylcarbazole) (PVK) is considered an ideal model of a non-conjugated, photo-conducting polymer with strong electron-donor properties.

2. Experimental

2.1. Materials

A polystyrene standard (PS, average Mw = 400,000 g mol^{-1}) was purchased from John Mattey Co. NVC (98%), chloroform ($CHCl_3$, ≥99.8%), dimethyl sulfoxide (DMSO, ≥99.9%), α,α′-azobis(isobutyronitrile) (AIBN, 99%), and tetrahydrofuran (THF, 99.8%) were purchased from Aldrich Co. Ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexaflurophosphate) (hereafter abbreviated as Ru-monomer) was obtained from Fuji Molecular Planning Co. All reagents were used as received without further purification. Deionized water was used in all experimental processes.

2.2. Synthesis of A_{ls}

NVC (5 mmol) was dissolved in 20 mL of THF. DMSO (2 mL) containing 0.18 mmol Ru-monomer was then added to the solution. The resulting solution was transferred into a three-necked round bottom flask equipped with a thermometer, a nitrogen stopcock, and a reflux funnel. The solution was thoroughly stirred to ensure an almost uniform media. AIBN (0.2 mmol) was then added to initiate the polymerization process. The mixture was degassed via three freeze-evacuate-thaw cycles. The experiment was performed under a dry nitrogen atmosphere.

Free-radical polymerization was conducted in an oil bath at 80 °C under a nitrogen atmosphere for 24 h. After polymerization, acetonitrile was poured into the reaction mixture to precipitate the synthesized polymer. The polymer powder was collected by filtering the precipitate, and was then washed with water to remove the unreacted monomer. Finally, the product was dried in vacuo. FT-IR and UV–Vis spectroscopies were used to characterize the interaction between the components of the synthesized A_{ls}. The overall scheme for the synthesis of the random copolymer of A_{ls} is shown in Fig. 1(a).

The IR spectra of PVK, Ru-monomer, and A_{ls} were obtained using an FT-IR spectrometer (Perkin–Elmer Model 1600). The samples were prepared by cryogenically grinding the synthesized polymer with KBr (polymer: KBr = 1:20) and compressing the mixture on a disk. Approximately 60 scans were signal-averaged in the 500–4000 cm^{-1} frequency range at a resolution of 2 cm^{-1}. On the other hand, UV–Vis spectra of PVK, Ru-monomer, and A_{ls} were recorded using a Shimadzu UV–Vis-NIR spectrophotometer (UV–3101PC). The thermal properties of the samples were obtained using a thermogravimetric analyzer (TGA) (Perkin–Elmer model TGA 7) in the range of 25–800 °C at 10 °C min^{-1} under nitrogen atmosphere.

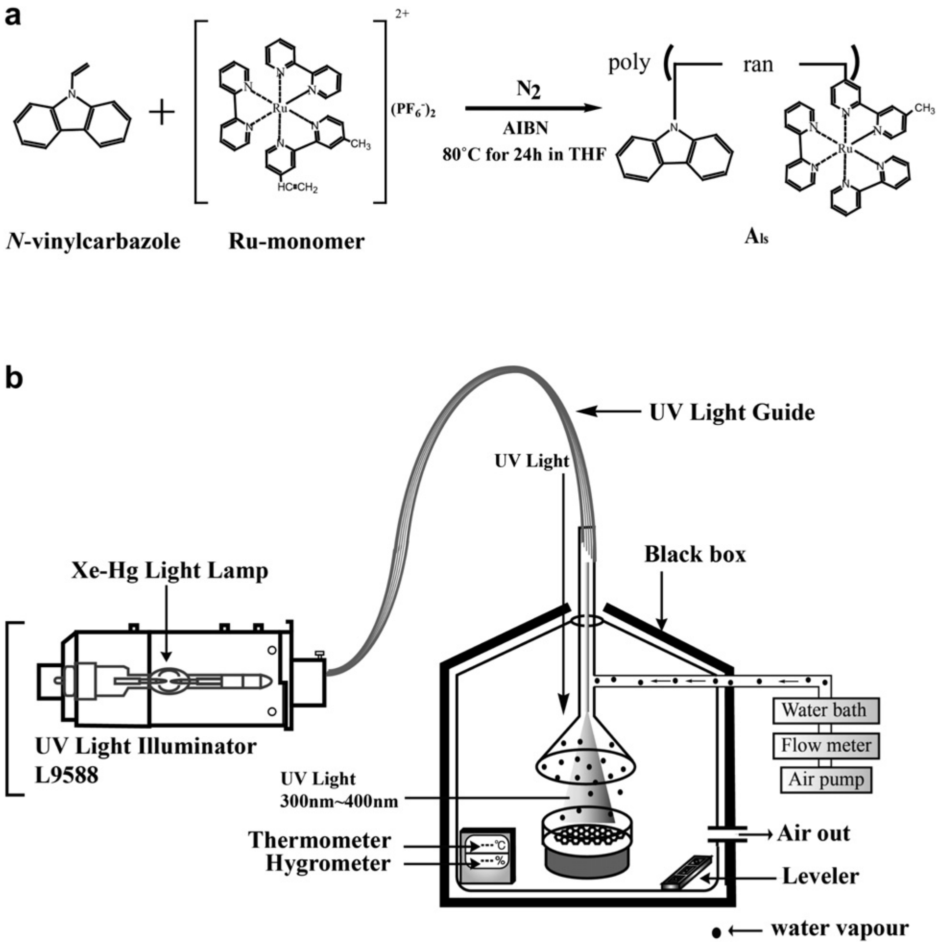

Fig. 1. (a) Overall scheme for the formation of the light-sensitive amphiphilic copolymer A_{ls}, and (b) Overall experimental setup for studying the effect of UV illumination in the fabrication of honeycomb-patterned thin films.