Preparation of Surface-Tethered Polymer Thin Films by Vapor Deposition Assisted by Thiol-ene Reaction

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Abstract

Polymer thin films that are covalently tethered on inorganic surface were obtained by vapor-depositing vinyl carbazol monomers on the substrate modified with selfassembled monolayers (SAMs) having thiol terminal units under UV irradiation. The UV irradiation initiated polymerization of the monomers on any surfaces. However, the SAM modification enabled remarkable improvement in film morphology owing to the covalent tethering at the film/substrate interface

1. Introduction

Variety of interfacial layers have been utilized at the organic/inorganic junctions with an aim to control the electron injection barrier or film growth morphology. On the other hand, little attention has been paid on the presence of chemical bonds at the organic/inorganic interfaces. We have demonstrated that the chemical tethering at the organic/inorganic interface can be a promising strategy not only to improve the physical stability but also to enhance the charge injection at the interface [1]. This paper reports formation of carbazole polymer films that are covalently tethered at the film/substrate interface by combining a self-assembled monolayer (SAM) and vapor-deposition polymerization.

In order to achieve this strategy, it is required to deposit the monomers on a SAM that has a function of polymerization initiator. So far, the SAMs having benzophenon- [2] or azo-terminal groups [3] were shown to have a capability of growing surface-tethered polymers. However, these SAMs tend to have complicated structures that might impede smooth transport of carriers. This paper explores the possibility of using a thiol-terminated SAM for this purpose. The thiol terminal of the SAM can initiate the polymerization of vinyl monomers by thiol-ene reaction. In addition, this SAM can be prepared by a simple single step reaction. We examined the effect of thiol-SAM on the surface morphology and polymerization reaction of a carbazole monomer.

2. Experimental Procedure

Scheme 1 shows the procedure for preparing the surfacetethered polymer thin films. An aluminum film was vapor-deposited on the surface of a glass substrate. The substrate was processed in a UV-ozone cleaner to oxidize its surface, and then immersed in 5 mM toluene solution of (3-mercaptopropyl)trimethoxysilane for 1 h. The substrate was rinsed with toluene and was annealed at 100°C in nitrogen for 1 h. The aluminum surface had a water contact angle of 6° after the UV-ozone cleaning, which increased to 59° after forming the SAM.

9-vinylcarbazole (VCz) was vapor-deposited on the substrate at an evaporation temperature of 120°C for 30 min to obtain thin films of about 200 nm in thickness. The substrate temperature was about 30°C. With a purpose to initiate radical polymerization of VCz, UV light from a low-pressure mercury lamp was irradiated to the substrate during the vapor deposition at a power of 5 mW/cm². The deposition was achieved both on a bare and the SAM-modified aluminum surfaces.

Polymerization of VCz was characterized by IR spectroscopy using the reflection-absorption method. In addition, the films were dissolved in tetrahydrofuran (THF) to estimate the molecular weight by gel-permutation chromatography (GPC). The surface morphology of the films were observed with a scanning probe microscope (SPM).

As an application for photopatterning, VCz was vapordeposited both on the bare and the SAM-modified surfaces without UV irradiation, and then irradiated with UV light in air at a power of 15 mW/cm² for 15 min through a photomask. The UV-irradiated films were rinsed by THF and then observed with an optical microscope.

3. Results and Discussion

Figure 1 shows IR spectra of the VCz monomer (a) and the films deposited on the bare (b) and the SAM-modified (c)



Scheme 1 Procedure for preparing surface-tethered polymer film.

substrates. Both of the vapor-deposited films have absorption bands of alkyl C-H stretching at wavenumbers around 2900 cm⁻¹, suggesting the formation of alkyl backbone by vinyl polymerization of VCz. The results of their GPC analyses are shown in Fig. 2. Both of the films have clear signals at retention times of 8 to 9 min, indicating the presence of polymer component. The average molecular weight M_w were 1.9×10^4 and 2.5×10^4 for the films on the bare and the SAM modified substrates, respectively. It is considered that the UV irradication can induce polymerization of VCz regardless of the substrate.

Although the vapor deposition of VCz under UV irradiation yielded polymer thin films on any substrate, a marked difference was observed in surface morphology for the films deposited on the bare and the SAM-modified surfaces. Figure 3 shows the SPM images of the films deposited on bare (b1-3) and SAM modified (a1-3) surfaces for deposition times of 30 to 180 s. On the bare substrate, the film grew in island structure and no uniform film was obtained even by extending the deposition time. On the SAM, the film grew in two-dimensional flat morphology from an early stage of the deposition. It is considered that the monomers deposited



Fig. 1 IR spectra of VCz monomer (a) and the films deposited on bare (b) and SAM modified (c) aluminum.



Fig. 2 GPC charts of VCz monomer (a) and the films deposited on bare (b) and SAM modified (c) aluminum.



Fig. 3 SPM images of the films deposited on SAM modified (a1a3) and bare (b1-b3) surfaces for different deposition times. Note the large difference in height scale.



Fig. 4 Optical micrographs of photopatterns formed on SAM modified (a) and bare (b) surfaces.

on the SAM were immobilized by the thiol-ene reaction, preventing the coagulation into island structure.

Figure 4 shows optical micrographs of VCz films vapor deposited on the SAM modified (a) and the bare (b) surfaces after the UV irradiation through a photomask followed by rinsing in THF. The film deposited on the SAM left a clear image of photomask while that on the bare surface was mostly delaminated. This result confirms that the vapor deposition on the thiol-terminated SAM combined with UV irradiation results in stable tethering at the film/substrate interface.

4. Conclusions

Carbazole polymer thin films that are covalently tethered on aluminum surface were prepared by vapor-depositing VCz monomer on a SAM that have thiol terminal group. Although polymerization can proceed without the SAM, interfacial tethering via the SAM had a profound effect in improving the film morphology. It is also expected that this method is effective in improving the film stability. Photopatterning of polymer thin films is also possible by utilizing this method.

References

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