

Thermally Induced Nanocrystal Array of Poly(N-Vinylcarbazole) on Si-Wafer Substrate

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Abstract

Recently, nanostructures such as nanocrystals and nanoaggregates have attracted much attention in many quarters of materials, electronics, and biology to create higher-value-added functional nanoscale materials and films. In this research, the fabrication of nanoaggregates on ultrathin photoconductive films of poly(N-vinylcarbazole) (PVCz) by applying thermal treatment is demonstrated. The structure and size are discussed on the basis of the results of atomic force microscope images. As a result, after thermal treatment of these films above the glass transition temperature (T_g) of PVCz, different types of surface morphological changes were induced showing a dependence on the tacticity of PVCz. Radically polymerized PVCz(r) ultrathin film showed small aggregates with heights of ~8 nm on the film surface after thermal treatment, while cationically polymerized PVCz(c), which has higher isotactic diad fractions than PVCz(r), indicated similar aggregates on the film surface, although the number of aggregates was smaller than PVCz(r). It is considered that these different phenomena depend on the tacticity of PVCz and the interaction between PVCz molecules and the substrate surface.

Keywords

AFM, Poly(N-Vinylcarbazole), Structural Transfer, Thermal Treatment, Nanoaggregates

1. Introduction

Recently, nanostructures such as nanocrystals and nanoaggregates have attracted much attention in many quar-

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ters of materials, electronics, and biology to create the high-value-added functional nanoscale materials and films. Our research groups have also investigated the fabrication of functional films with nanostructures prepared by applying the selective doping method of photoactive chromophore [1] [2] and the laser ablation technique for gold nanoparticles/polymer films [3] [4]. However, photoconductive polymers have attracted increasing attention for producing nanodevices, such as optical sensors, photovoltaic cells, and so on. Poly(*N*-vinylcarbazole) (PVCz) is a photoconductive polymer, and it has received much attention as a representative photoconductive aromatic vinyl polymer. In addition, systematic studies have been carried out extensively covering photocurrent, luminescence, and absorption measurements in addition to structural studies in order to elucidate its mechanical, physical, chemical, and electronic properties [5] [6].

Concerning the structural studies, it was revealed that the tacticity of PVCz depends on the polymerization method (radical (r) or cationic (c) polymerization) on the basis of the nuclear magnetic resonance (NMR) spectra and glass transition temperatures (T_g) of PVCz [7]. Furthermore, other research groups had investigated the relation between the photophysical properties of PVCz and its tacticity, and the difference in tacticity was reflected in the drift mobility and in the thermal crystallization behavior [8] [9]. However, the thermal crystallization of PVCz(c) films is much more difficult than that of PVCz(r) films, and its mobility hardly changes with thermal treatment. In addition, it has been reported that PVCz(c) shows three different values of T_g , while PVCz(r) shows only one [10]-[12]. The triple T_g of the former was interpreted by the correspondence to the whole chain and the syndiotactic and isotactic stereoblocks, while the single T_g of the latter was interpreted by an absence of long sequences that behave as separate phases due to stereoblocks. That is, the length of each sequence in the stereoblock structure of PVCz(r) is considered to be too short to behave as a separate phase for T_g . However, these investigations focused on bulk samples such as thick film, bulk, or powder samples in order to measure the NMR, X-ray diffraction, and so on, and not on nanoscale samples such as ultrathin films on substrate. Therefore, it is very important to understand ultrathin PVCz films on a solid substrate at the nanoscale.

In this research, the thin films and ultrathin films of PVCz on Si-wafer substrate were prepared by the cast method, and these films were thermally treated in order to induce the crystallization of PVCz. The surface morphology changes of the PVCz films are discussed on the basis of the results of atomic force microscopy (AFM) observation.

2. Experimental

2.1. Synthesis of PVCz

N-vinylcarbazole (VCz) was purified by the usual method from commercial product. PVCz(r) was prepared by polymerization of a 1.0-M benzene solution of the purified VCz in the presence of azobisisobutyronitrile (0.4 mol%) in an evacuated sealed tube at 60°C for 9 h. PVCz(c) was prepared by polymerization of a 0.3-M toluene solution of purified VCz in the presence of 1 mol% boron trifluoride-diethyl ether (BF₃·OEt₂) under a nitrogen atmosphere at room temperature for 1.5 h. The PVCz samples were purified by reprecipitation 3 times from benzene with methanol. The chemical structure of PVCz is shown in **Figure 1**.

2.2. Sample Preparation

PVCz films were cast on silicon (Si) wafers of approximately 10 × 10 mm² from a 1,2-dichloroethane solution at room temperature and dried in vacuo for several hours. The average thickness of the amorphous PVCz film was estimated from the weight and density of a film with known area. Thermal treatment of PVCz films on Si wafer substrate was carried out at 583 K above the T_g under high vacuum for 1 h.

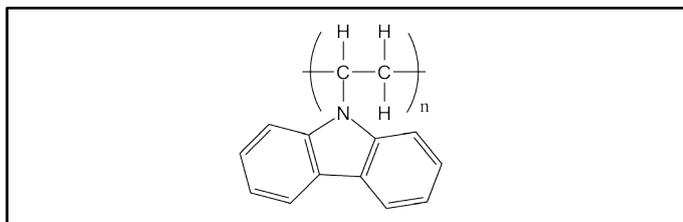


Figure 1. Chemical structure of poly(*N*-vinylcarbazole) (PVCz).

2.3. DSC Measurement and WAXD Measurement

Differential scanning calorimetry (DSC; DSC2920, TA Instruments, New Castle, Delaware) was conducted in a nitrogen atmosphere at a temperature range of 50 - 350°C with a heating rate of 20°C/min for the purpose of investigating the thermal properties of the PVCz films. Wide-angle X-ray diffraction (WAXD) patterns were taken on an X'Pert-Pro MPD X-ray diffractometer for PVCz(r) and PVCz(c) samples.

2.4. AFM Observation

An atomic force microscope (Seiko Instruments, Inc., SPI 3800N/SPA-400 system) was used in dynamic force mode under ambient conditions. Si single crystal tips with a cantilever length of 125 μm were used. Both height and phase images were recorded simultaneously. Since the soft amorphous material is more compliant than the hard crystalline material, a phase difference between the two materials provides a distinct contrast between these states in the phase image.

3. Results and Discussion

3.1. Thermal Properties of PVCz with DSC and WAXD Measurement

DSC and WAXD measurement were performed for PVCz(r) and PVCz(c) powder. The results of DSC and WAXD of PVCz(r) and PVCz(c) are shown in **Table 1**. For the DSC measurement, the base line shift which was corresponding to glass transition temperature (T_g) were observed at 502 K and 518 K, respectively. Accordingly, thermal treatment of PVCz films on Si wafer substrate was carried out at 583 K above the T_g in this investigation. On the other hand, heating of PVCz films to a temperature above T_g under high vacuum resulted in the appearance of a narrow crystalline X-ray scattering peak at $2\theta = 8.39^\circ$, which indicates the occurrence of paracrystalline lamellar [9]. The value of the peak width at half height (FWHM) ($\Delta 2\theta$) of PVCz(r) was smaller than that of PVCz(c). Therefore, it is considered that the significant difference between the thermally treated PVCz(r) and PVCz(c) samples in the results of DSC and WAXD is attributed to the difference in their thermal crystallization behavior.

3.2. AFM Observation of Thin PVCz Films with a Thickness of ~10 μm

AFM images of PVCz(r) and PVCz(c) films cast on Si wafer substrate before and after thermal treatment shown in **Figure 2**. The scales of the height images are 10 nm in **Figures 2(a)-(c)** and 150 nm in **Figure 2(d)**. The surface of both the as-cast films was smooth, and no difference between PVCz(r) and PVCz(c) films in the surface morphology was found. However, a large difference between thermally treated PVCz(r) and PVCz(c) films was observed: the AFM image of the thermally treated PVCz(r) films showed a vein-like structure and large lumps with a difference in height of more than 100 nm, while no such structure and lumps were observed for the thermally treated PVCz(c) films. That is, thermal treatment at a temperature above T_g under high vacuum induced a drastic change in the surface morphology of cast PVCz(r) films, whereas the surface morphological change of PVCz(c) films was slight. These results indicate that the thermal treatment of thin PVCz films under high vacuum results in tacticity-dependent change in the surface morphology of PVCz of a homopolymer.

Under a polarizing microscope, a bright image was observed for the thermally treated PVCz(r) films. For the thermally treated PVCz(c) films, however, a dark image was observed, and growth of spherulite morphology was not observed. These tacticity-dependent results were interpreted as the thermal crystallization of PVCz(r) films being much easier than that of PVCz(c) films. Hence, the significant difference between the thermally treated PVCz(r) and PVCz(c) films in the AFM images is attributed to the difference in their thermal crystallization behavior. **Figure 2** shows the tacticity-dependent thermal crystallization behavior of a homopolymer as a

Table 1. Results of DSC and WAXD measurement for PVCz samples.

	T_g (K)	2θ	FWHM
PVCz(r)	502	8.39°	0.13°
PVCz(c)	518	8.39°	0.30°

*FWHM = "full width at half maximum".

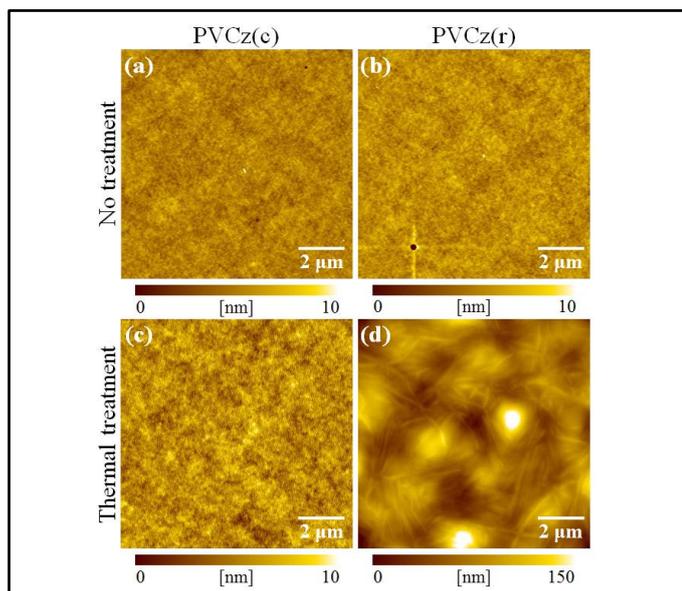


Figure 2. AFM images of thin PVCz films with 10 μm thickness cast on silicon wafer substrate before and after thermal treatment at 583 K under high vacuum for 1 h.

surface-morphological change in AFM images.

As expected from the above results, the AFM phase images of the thermally treated PVCz(r) and PVCz(c) films were quite different: no contrast was found in the phase image of the PVCz(c) films, while the phase image of the PVCz(r) films exhibited distinct contrast revealing a veined surface structure.

3.3. AFM Observation of Ultrathin PVCz Films with a Thickness of ~ 10 nm

The ultrathin films the 10 nm thickness cast from very dilute PVCz solutions was prepared on Si wafer in order to investigate the morphological changes with thermal treatment above the T_g of PVCz. These films were observed by AFM, and the results are shown in **Figure 3**. As shown in this figure, the ultrathin PVCz film before thermal treatment has a flat surface; however, the surface shape was drastically changed by thermal treatment, *i.e.*, small aggregated islands with unique shapes appeared on the ultrathin film surface. The number of unique aggregates for ultrathin PVCz(r) film was larger than for ultrathin PVCz(c) film. It is considered that the PVCz(r) allows the growth of crystals on the ultrathin films under thermal treatment as compared with PVCz(c), and this phenomenon is consistent with the result of the dependence of tacticity for PVCz molecules as shown in **Figure 2**.

Figure 4 shows magnified height and phase images, a lateral image, and an aggregate image of ultrathin PVCz(r) film. From the phase image in **Figure 4(a)**, the small aggregated islands correspond to a crystal structure with a low phase shift as compared with the flat surface area, because the hard part, which corresponds to the crystal area, indicates a weaker interaction between the Si-tip of AFM and the ultrathin film surface as compared with the soft part of the amorphous area. In addition, these small aggregated islands have a unique shape and size with ~ 8 nm height as shown in **Figure 4(b)**.

Figure 5 shows graphs of frequency distributions for the unique aggregates, and these distributions correspond to Gaussian distributions. The peak value of crystal width is ~ 200 nm, and the peak value of crystal length is ~ 400 nm. Therefore, it is considered that these nanoaggregates grew from crystal nucleations on the amorphous film of PVCz after thermal treatment. In addition, we show in the schematic illustrations of the crystal growth process of PVCz that the nanocrystals consist of small lamella structures on the ultrathin PVCz film as shown in **Figure 6**.

In this investigation, we prepared the ultrathin PVCz films with ~ 15 nm thickness on Si-wafer substrate. It is noted that the average thickness of the flat area is most probably less than twice the radius of gyration of the PVCz molecules in the neat films [13], although the radius of gyration of the PVCz(r) and PVCz(c) molecules in

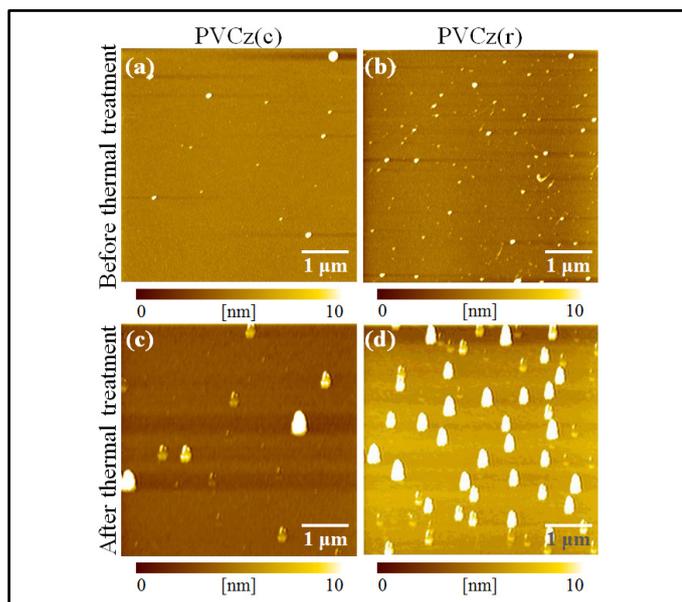


Figure 3. AFM images of ultrathin PVCz films with 10 nm thickness cast on silicon wafer substrate before and after thermal treatment at 583 K under high vacuum for 1 h.

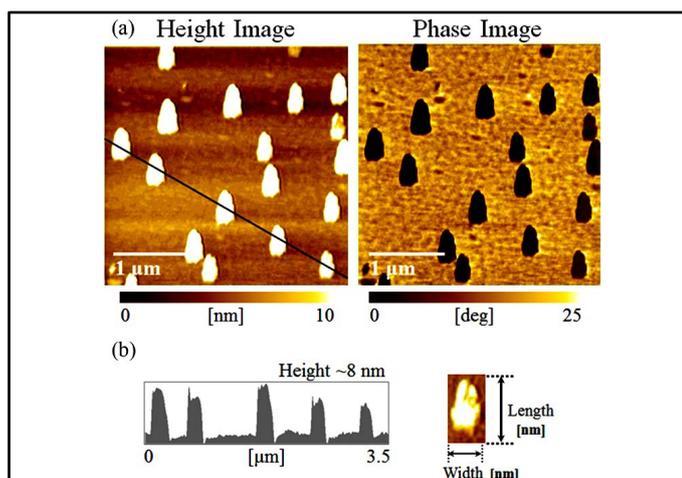


Figure 4. Typical AFM images of ultrathin PVCz(r) film after thermal treatment at 583 K under high vacuum for 1 h, (a) height and phase image and (b) lateral image of PVCznanocrystals.

the neat films is generally unknown. However, we succeeded in fabricating a nanocrystal array of PVCz on ultrathin PVCz films by applying thermal treatment above the T_g under high vacuum condition. In addition, the dependence is on the tacticity of PVCz. That is, the ultrathin PVCz(r) film prepared by radical polymerization showed small aggregates with a height of ~8 nm on the film surface after thermal treatment, while cationically polymerized PVCz(c), which has higher isotactic diad fractions than PVCz(r) also indicated the same aggregates on the film surface, although the number of aggregates is lower than that on PVCz(r). Therefore, it is considered that these different phenomena depend on the tacticity of PVCz and on the interaction between PVCz molecules and the substrate surface.

4. Conclusion

In this research, we demonstrated a thermally induced nanocrystal array of poly(N-vinylcarbazole) on Si-wafer

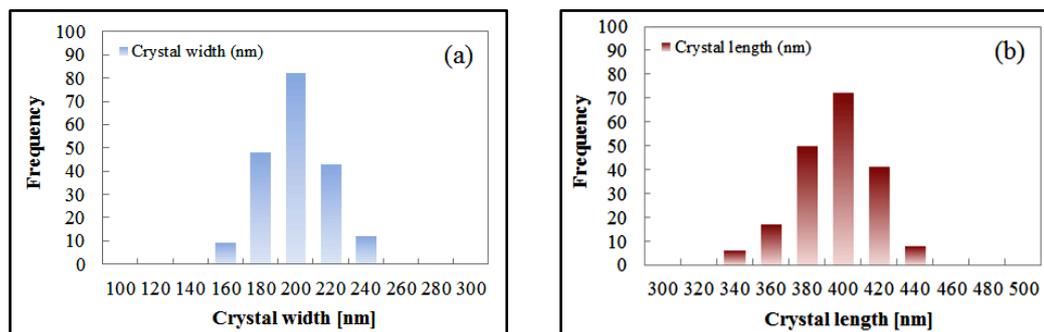


Figure 5. Histograms of PVCz nanocrystal size: (a) width [nm] and (b) length [nm].

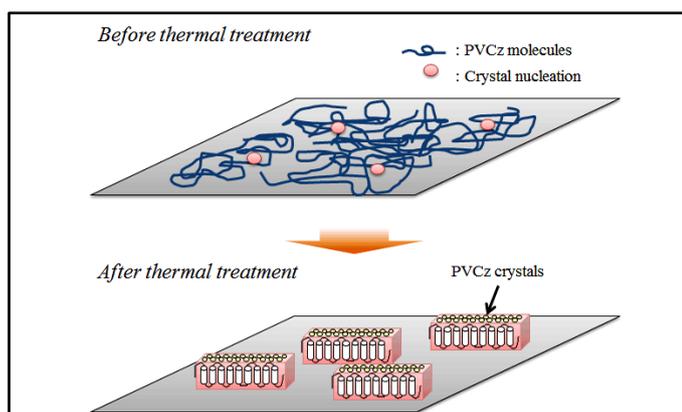


Figure 6. Schematic illustration of the crystal growth process of PVCz nanocrystal on the ultrathin PVCz films.

substrate. The thin films and ultrathin films of PVCz on Si-wafer substrate were prepared by a cast method, and these films were thermally treated in order to induce the crystallization of PVCz. For PVCz film with $\sim 10 \mu\text{m}$ thickness, it was found that thermal treatment above T_g under high vacuum induces a drastic change in the surface morphology of cast PVCz(r) films, whereas the surface morphological change of PVCz(c) films is slight. These results indicate that thermal treatment of thin PVCz films under high vacuum causes tacticity-dependent change in the surface morphology of PVCz of a homopolymer. However, for an ultrathin PVCz film with $\sim 15 \text{ nm}$ thickness, we succeeded in fabricating a nanocrystal array of PVCz on ultrathin PVCz films by applying thermal treatment above T_g under high vacuum. In addition, the dependence is on the tacticity of PVCz. The present results suggest that both the AFM images of ultrathin PVCz films and the surface morphological change induced by thermal treatment are very sensitive to the substrate surface property. In order to elucidate further the origin of these phenomena and to control the arrangement of small PVCz crystal aggregates, detailed studies of the surface-property dependence will be carried out in near future.

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