NOTES

Scanning Tunneling Microscopic Observation of Shape of Iodine Doped Poly(*N*-vinylcarbazole) Deposited on Graphite Surface

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The study of polymer adsorption on an interface is of interest because of diverse applications to colloid stability, adhesion, chromatography and reinforcement. In these studies, it is crucially important to know the conformations of polymers. Theories developed in the past two decades have been mostly concerned with the calculation of $\langle z^2 \rangle$ and $\langle |\rho^2| \rangle$ for chains with one end attached to a wall. Here, z measures the end-vector distance orthogonal to the wall, and ρ is the projection of the end vector in the $z=0$ plane of the wall.¹⁻⁷ Because of a higher polymer density near the surface, theories of polymer adsorption for an single isolated chain predict that $\langle |\rho^2| \rangle^{1/2}$ is larger than the root mean square end-to-end distance $\langle r^2 \rangle^{1/2}$ in free space. Therefore, the adsorbed shape of polymers on a surface is spreaded form. Dickinson has also reached a similar conclusion by his computer simulation of adsorbed shapes of deformable polymers on a surface.⁸

However, experimental techniques such as ellipsometry and hydrodynamic methods developed until now have been mostly concerned with the measurement of the thickness of the adsorbed layer in the plateau region of adsorption isotherm, where many chains intermingle near the surface. Therefore, $\langle z^2 \rangle^{1/2}$ and $\langle |\rho^2| \rangle^{1/2}$ measurements have been im-

possible.

In an attempt to observe adsorbed shape of an isolated polymer chain, we employed here the scanning tunneling microscope, which was invented by Rohrer and Binning.⁹ For imaging a molecule deposited on a surface, there are two problems. First, it is necessary to reduce molecular motion or diffusion on a surface. The second is to give contrast for the molecule. The former problem may be dissolved in the case of polymer adsorption, since number of segments per molecule interact with the substrate is large.¹ For the latter problem, although the contrast generation is still a matter of debate, we considered that this problem may be dissolved by giving conductivity to polymer chains with addition of doping agent, although recent study showed that poly(ethylene oxide) can be visualized without doping.¹⁰ However, doping probably brings a sacrifice in observation of molecular structure, but will allow us to observe global shape of deposited polymer on a surface, although successful STM observations of DNA, proteins and liquid crystals *etc.* have been reported.¹²⁻¹⁴

As a sample, poly(*N*-vinylcarbazole) (PVCz) was selected and it was purchased from Tokyo Kasei Co. PVCz was dissolved in chloroform, precipitated by addition of acetone, and dried

in vacuo. The molecular weight of PVCz was determined from intrinsic viscosity measurement in chloroform at 25°C according to the viscosity equation¹¹

$$[\eta] = 19.6 \times 10^{-3} M_w^{0.67} \quad (1)$$

and the molecular weight was 8.1×10^5 .

Solutions of PVCz doped with iodine were prepared as follows. For a specified concentration of chloroform solutions of PVCz, I₂ was added, so that the ratio of I₂ to monomer unit of PVCz equals unity.

Figure 1. STM image of I₂ doped PVCz deposited from CHCl₃ solution ($C_p = 0.35 \text{ g dl}^{-1}$). The tunneling current, 1.7 nA; The bias voltage, 50 mV. The line segment corresponds to 100 nm.

A droplet of the solution was applied on a freshly cleaved, highly oriented pyrolytic graphite (HOPG, Union Carbide, grade ZYA) substrate and then was allowed to dry at room temperature in a clean box.

STM observation was carried out by Nanoscope I (Digital Instruments, Inc.) at constant current mode. The particular conditions of tunneling were typically 50 mV sample bias and 2 nA tunneling current.

The STM image which was observed for PVCz–I₂ complex deposited from either concentrated (0.35 g dl^{-1}) or dilute (0.002 g dl^{-1}) solutions, exhibits bundle like aggregation of molecules whose width is as large as 10 nm as shown in Figure 1, and observation of isolated polymer chains was unsuccessful. While the STM images of PVCz deposited from the polymer solution whose concentrations are intermediate *i.e.*, 0.023 – 0.18 g dl^{-1} showed different shape as shown in Figure 2, although the reason why this intermediate concentration allowed the observation of these shapes is not clear. Its diameter is about 100 nm and probably the image corresponds to an isolated polymer chain.

For glass transition temperature of PVCz, rather conflicting values 357,¹⁵ 423,¹⁶ and

(a)

(b)

Figure 2. STM images of I₂ doped PVCz deposited from CHCl₃ solutions. The line segment corresponds to 100 nm. (a) $C_p = 0.18 \text{ g dl}^{-1}$. Tunneling current 3.5 nA and bias voltage 90 mV. (b) $C_p = 0.023 \text{ g dl}^{-1}$, 2.0 nA and 30 mV.

481 K,¹⁷ respectively, were reported and exact T_g value has not yet been settled. Nevertheless, these values are higher than room temperature 298 K, hence we may suppose that the molecular motion of PVCz on the graphite surface is hampered. Comparison of the radius r of PVCz deposited on the graphite surface with the compact radius R of PVCz in free space was made. R is given by $R = (3M/4\pi dN_A)^{1/3}$, where M is the molecular weight, d is the density of PVCz, respectively and N_A is Avogadro number. Taking $d = 1.2 \text{ g cm}^{-3}$,¹⁸ we obtain $R = 14 \text{ nm}$, which is considerably smaller than the radius of the PVCz images 50 nm.

de Gennes¹⁹ has pointed out that when the glass transition temperature of bulk polymers is higher than room temperature, the first few adsorbed layers near the wall may become glassy. Then we expect the freezing of motion of monomer units which were directly attached to the surface and the occupied area of PVCz adsorbed from solution does not change even in the process of evaporation of solvent. Although we could not evaluate $\langle |\rho^2| \rangle^{1/2}$ for PVCz, however, since we may consider that probably the diameter D of PVCz images and $\langle |\rho^2| \rangle^{1/2}$ do not differ appreciably, we may also expect the diameter D will be slightly larger than the root mean square end to end distance of PVCz in solution. In order to test this hypothesis, comparison of the observed diameter D of PVCz images and the root mean square end to end distance of PVCz with and without I_2 doping is made. The root mean square end-to-distance $\langle r^2 \rangle^{1/2}$ were estimated from intrinsic viscosity measurements of PVCz in chloroform as well as the iodine added chloroform solution by using Flory-Fox equation and the results were shown in Table I. The larger $\langle r^2 \rangle^{1/2}$ for PVCz- I_2 complex probably originates from excluded volume effect of the complex or charge effect. The comparison of the diameter D (100 nm) and $\langle r^2 \rangle^{1/2}$ (81 nm) indicates that D is slightly larger than the mean square end-to-end

Table I.

$[\eta]$	$\langle r^2 \rangle^{1/2}$	Concentration of iodine
dl g ⁻¹	nm	g dl ⁻¹
1.24	78.6	0
1.42	81.2	0.030

distance as is expected.

Since the height of deposited polymer chain could not be measured at present stage, what we can say at most from the observed diameter is that collapse of adsorbed chains probably happened. The most serious obstacle for imaging of deposited polymer on graphite surface is low success rate of observation, which in turn prevents statistical average calculation of sizes.

In conclusion, although we could not observe the detailed polymer structure of PVCz- I_2 complex deposited on graphite, we could observe slightly collapsed global shape of deposited PVCz- I_2 complex when compared with the shape of a random coil in free space.

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