Visualization of Isolated Poly(2-vinylpyridine)-*block*-Polyisoprene Chains Adhered to Isolated Palladium Nanoparticles[†]

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ABSTRACT: Isolated polymer chains adhered to isolated metal nanoparticles were directly visualized and characterized by atomic force microscopy (AFM) in order to gain insight into the stabilizing mechanism of the nanoparticles and their potential surface activities. For this purpose, nanoscaled Pd particles adhered and stabilized by poly(2-vinylpyridine)-*block*-polyisoprene (P2VP-*b*-PI), designated as Pd-(P2VP-*b*-PI), were prepared by reducing Pd^{2+} ions with 1-propanol at 85 °C for 45 h in a dilute solution of P2VP-*b*-PI and palladium acetylacetonate in benzene as a solvent and 1-propanol as a reducing agent. Thus, prepared Pd-(P2VP-*b*-PI) were purified to remove free P2VP-*b*-PI and unreacted salt, dissolved into a very dilute benzene solution containing $\sim 10^{-5}$ wt % of the particles, and transferred onto mica surface by dipping a sheet of mica into the solution. The surface of the sheet was further washed gently with a few drops (~0.1 mL/drop) of the benzene to obtain isolated Pd-(P2VP-*b*-PI) on the surface and observed by AFM with a tapping mode. The AFM images show isolated Pd-(P2VP-*b*-PI) with an average diameter of Pd particles of 8 nm and one to three adhered P2VP-*b*-PI chains. It was also revealed that only a part of segments of the chains adhered to the particles so that the particles had still a large surface area free from the polymers, and the adhered polymers had subchains free from the particles, thus stabilizing against coalescence of the particles due to entropic repulsion.

I. Introduction

Metal nanoparticles are currently an intensively discussed topic in various scientific fields including chemistry, electronics, and biotechnology from the viewpoint of their quantum effects and surface activities, etc.[1] One of mainstreams of the research along this line will be those concerning the formation of nanowires or ordered arrays of metal and semiconductor nanoparticles. The research is focused on eventual integration of small molecular-scale devices into useful nanometer-scale electronic circuits. There have been exciting reports concerning the formation of wires or chains of nanoparticles of silver,[2] palladium,[3] gold,[4] platinum,[5] and copper[6] from single molecule DNA templates or organization of platinum, gold, and silver nanoparticles using tobacco mosaic virus templates.[7] As for templates, single synthetic polyelectrolytes molecules,[8,9] amphipolar core−shell cylindrical brushes,[10] and unimolecular micelles[11] have also been utilized for metallization of palladium and gold into nanowires or for formation of ordered arrays of the particles.

Aside from the stream described above, we have been conducting a series of research in which we have been using the self-assembled domains of block copolymers as templates and aimed to selectively align nanoparticles in one of the domains. As one of the various methods to create this kind of nanohybrid, we have employed a self-assembly, via solvent-casting, of mixtures of block copolymer molecules and metal nanoparticles that are adhered and stabilized by the block copolymers comprised of the same component polymers. In this method, one of the key issues for the controlled alignments of metal nanoparticles is to elucidate characteristics of block copolymer chains adhered to particles and stabilizing particles from coagulation into larger particles. Up to now, the roles of surfactant[12−14] or polymers[15−17] on the stabilization of particles have been reported primarily on the basis of scanning probe microscopy. Calorimetric and spectroscopic investigations have been also reported on the amount and configuration of polymers adsorbed on particles such as silica.[18]

The following fundamental problems should be clarified on the characteristics of chains adhered to particles. (1) How many chains are adhered onto the surface of one metal nanoparticle? (2) As for a given chain adhered on the surface of a given particle, how many segments are adhered to the surface and how long are subchains (tails or loops) which are effectively free from the particle so that they can stabilize the particle against aggregate formation from other particles due to the steric or entropic repulsion? (3) What is the site fraction of the particle surface adhered to or free from polymers? These fundamental problems should reflect a basic problem concerning competing short-range interactions, involving interactions among solvents, polymer segments, and metal particles, and long-range molecular interactions, involving polymer conformational entropy when the particles adhering chains are in solution. In this work we will address some of the key issues described above on the basis of single-particles and single-polymers investigation under AFM.

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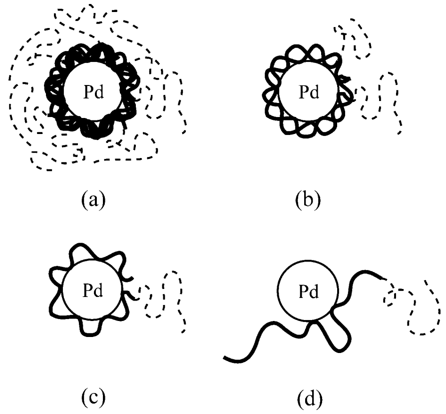

Figure 1. Schematic representation of possible configurations of P2VP-*b*-PI adhered to a palladium nanoparticle. P2VP and PI chains are shown by solid and broken lines, respectively.

II. Special Motivation for This Study

Let us describe first a primary motivation of our studies in this paper. In this study we used poly(2-vinylpyridine)-*block*-poly(isoprene) (P2VP-*b*-PI) in which one of the blocks, poly(2-vinylpyridine) (P2VP), selectively adheres to palladium nanoparticles, but the other blocks, polyisoprene (PI blocks), are free from the particles. We designate the particles adhered by the polymers as Pd-(P2VP-*b*-PI). We consider controlled alignments of the particles Pd-(P2VP-*b*-PI) in nanodomain of P2VP-*b*-PI as templates. The Pd-(P2VP-*b*-PI) nanoparticles were selectively incorporated into the lamellar microdomains of P2VP blocks by means of a self-assembly of a mixture of a small amount of Pd-(P2VP-*b*-PI) and a large amount of lamella-forming P2VP-*b*-PI via the solution-cast process with benzene as a solvent.[19−21] Moreover, it is shown that the nanoparticles can be aligned in the P2VP lamellae preferentially along the interfaces with the PI lamellae,[19,20] near the middle of the P2VP lamellae,[20,21] or more or less uniformly in the P2VP lamellae,[20] depending on molecular weight of P2VP-*b*-PI forming the lamellar microdomains templates and molecular weight of P2VP-*b*-PI in Pd-(P2VP-*b*-PI). It may be needless to say that important information required for understanding such controlled alignment of the particles as described above is conformation of the block copolymer chains adhered to the particles. To facilitate understanding of our arguments, below we shall briefly describe a few possible conformations.

Figure 1 shows some conceivable conformations of the P2VP-*b*-PI block chains in Pd-(P2VP-*b*-PI). Part a shows the case where many block chains are adhered to single Pd particle. The P2VP block chains isotropically cover the Pd particle to form a shell for the Pd particle from which the PI block chains emanate and shield more or less uniformly the P2VP shell. Part b is the case where a smaller number of the block chains are involved in Pd-(P2VP-*b*-PI) than the case in part a, so that the PI block chains cannot uniformly shield the P2VP block chains. Here a large fraction of the P2VP segments per P2VP block chains are adhered to the particle as in the case of part a. The center of mass of the Pd particle and that of adhered P2VP are essentially identical, but they locate at a position different from that of the PI blocks ("polarized" configuration of adhered block copolymer chains). A simplified case of part b is shown in parts c and d where a single block chain of P2VP is adhered to the Pd particle: In part c a large fraction of the P2VP segments are adhered so that the PI block chain is emanating from the surface of the particle, while in part d only a minor fraction of the P2VP segments in the P2VP block are adhered to the particles; the adhering position may be anywhere along the P2VP block chain, i.e., near the junction with PI block, middle or a free end of the P2VP block chains.

Let us now try a thought experiment on a self-assembly of Pd-(P2VP-*b*-PI) and the lamella forming P2VP-*b*-PI which forms a matrix phase for Pd-(P2VP-*b*-PI). In this case the configuration of the block chains such as shown in part a will result in incorporation of Pd-(P2VP-*b*-PI) in the PI lamellae, simply because the particle is shielded by the PI blocks. This case was never found in our experiments, which indicates that this configuration is not feasible in our case. The experimental evidence also rules out the possibility that the Pd particles are adhered by PI block chains. The configuration shown in parts b and c will always align the particles near the interfaces of the P2VP lamellae.[19] Our experiments show that this is not always the case,[20,21] suggesting that this configuration is also not plausible. Our experimental results,[20,21] showing a more or less uniform distribution of the particles in the P2VP lamellae, strongly infer the configuration shown in part d. Thus, it is crucial to explore the configuration of the P2VP-*b*-PI in Pd-(P2VP-*b*-PI) for the controlled alignments of Pd particles in the block copolymer microdomain.

In this work we aim to clarify the configuration of the block chains in Pd-(P2VP-*b*-PI) by a direct visualization of isolated Pd-(P2VP-*b*-PI) under AFM. This type of study of isolated particles and isolated chains adhered to particles would have an advantage in obtaining direct *qualitative* information concerning adhered chains but have a disadvantage in obtaining *quantitative* statistical information, compared to the conventional calorimetric and/or spectroscopic studies of the amount and configuration of polymer chains adsorbed on solid particles.[18] It should be stressed that the direct method may have a serious disadvantage from the viewpoint that the characteristics of adsorbed chains may be altered in the sample preparation process for AFM studies. The clarification of this problem is open to the public for future works. Here in this work we challenged whether we can visualize isolated adhered chains and their loops and tails. From the viewpoint of a direct observation of isolated single synthetic polymer chains, this work is an extension of our earlier studies reported by Hashimoto and co-workers.[22,23] However, to our best knowledge, the direct observation of the isolated chains adhered to isolated metal nanoparticles has never been reported so far, although there are some reports on arrays of nanoparticles formed from single macromolecules templates,[1−11] as described in section I.

We think that from the AFM images one can distinguish the model shown in Figure 1d from those shown in Figure 1b,c, though the distinction between those in Figure 1b,c may be difficult. To facilitate our investigation on validity of the model shown in Figure 1d inferred from our previous work,[20,21] we deliberately chose such a model P2VP-*b*-PI block copolymer that has molecular weight of a P2VP block much larger than that of a PI block. Moreover, as will be discussed later, PI blocks cannot spread on mica so that they may tend to form very small globules and only P2VP can spread on mica with expanded chain configurations. This situation

Table 1. Block Copolymers Used in This Work

polymer	M_n[a]	W_{P2VP}[b]
P2VP-*b*-PI-L	337-*b*-23	93.5
P2VP-*b*-PI-S	249-*b*-19	92.8

[a] In *X*-*b*-*Y*, *X* and *Y* designate number-average molecular weights of P2VP and PI, respectively, in units of thousand. *X* and *Y* were evaluated by the molecular weight of PI block precursor determined by GPC and the molar ratio of 2-vinylpyridine and isoprene monomer units determined by ^{1}H NMR. [b] Weight fraction of P2VP in the block copolymer.

would facilitate a distinction of the model 1d from the models 1b and 1c because long tails and loops can be seen in the model 1d only.

III. Experimental Method

III.1. Block Copolymers. P2VP-*b*-PI block copolymers used in this work were prepared by living anionic polymerization and were characterized as described in Table 1. Further details have been described elsewhere.[19]

III.2. Preparation of Palladium Nanoparticles Stabilized by P2VP-*b*-PI. Pd-(P2VP-*b*-PI) were prepared by reducing Pd^{2+} ions (Pd(II)) with 1-propanol at 85 °C for 48 h in a dilute homogeneous solution of P2VP-*b*-PI and palladium acetylacetonate, $Pd(acac)_2$. For this purpose 0.05 g of P2VP-*b*-PI, 0.12 g of $Pd(acac)_2$, and 10 mL of 1-propanol were dissolved into 70 mL of benzene, and a homogeneous solution was prepared by stirring. The reduction was conducted by refluxing the solution under a nitrogen gas atmosphere. After the alcohol reduction, the solution was stored at room temperature typically for a few hours. Then benzene and 1-propanol were evaporated. Thus, obtained Pd-(P2VP-*b*-PI) were immediately dissolved in chloroform solution and precipitated into acetone to remove unreacted salt. The precipitates were again dissolved immediately by benzene and purified by centrifugation three times to remove free P2VP-*b*-PI. The purified precipitates were immediately dissolved again by benzene and left at room temperature for a few days. Finally, black powders of Pd-(P2VP-*b*-PI) were obtained by freeze-drying of the benzene solution. The purified powers were used as a starting material for this experiment.

III.3. Transmission Electron Microscopy. The purified Pd-(P2VP-*b*-PI) was dissolved in benzene to prepare an extremely dilute solution of 2×10^{-5} wt %. One drop of Pd-(P2VP-*b*-PI) solution was dropped onto an electron microscope grid covered with a thin film of poly(vinyl formal). After drying specimens on the grid the specimens were subjected to morphological studies under transmission electron microscopy with a JEOL JEM-2000 FXZ operated at 120 kV.

III.4. Atomic Force Microscopy. Isolated block copolymers, free from Pd (designated as P2VP-*b*-PI-L) and those adhered by Pd [designated Pd-(P2VP-*b*-PI-S)], were observed under atomic force microscopy (AFM) on mica. To prepare the samples for the observations, the samples were transferred onto mica substrates by dipping the substrates into a very dilute benzene solution of P2VP-*b*-PI-L or of the purified Pd-(P2VP-*b*-PI-S) (solution concentration being about 2×10^{-5} wt % in both cases) and then by pulling out the substrates from the solution. Then the samples transferred on the substrates were gently washed further by a few drops of benzene. The last process was necessary to obtain isolated block chains of P2VP-*b*-PI-L and isolated adhered block chains on isolated Pd particles of Pd-(P2VP-*b*-PI-S) on the substrates.

The samples thus made were observed in air (with relative humidity of 50−60%) by a tapping mode AFM (Nano Scope III, Digital Instruments) with a silicon cantilever (resonance frequency: 300−400 kHz; spring constant: 70−90 N/m). AFM images are shown in the height mode without any image processing. The samples were observed by AFM immediately after the sample preparation.

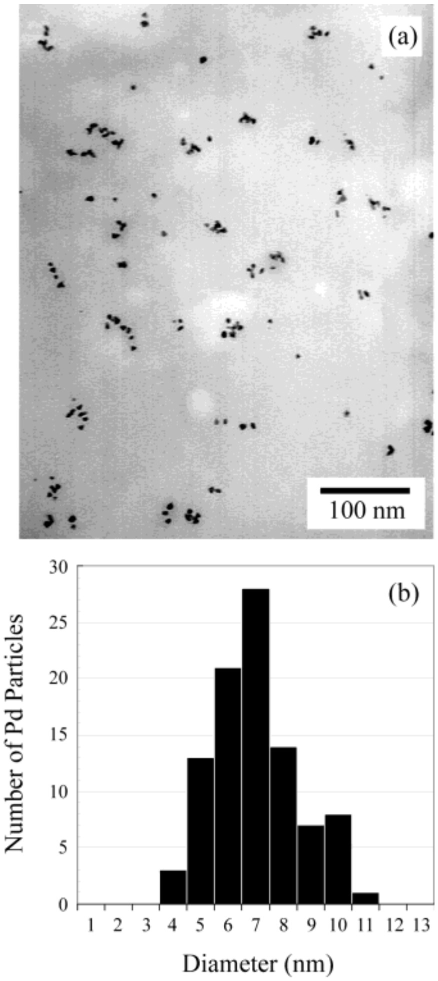

Figure 2. (a) Transmission electron micrograph of Pd-(P2VP-*b*-PI−S) and (b) histogram for diameter of Pd particles.

IV. Results and Discussion

We would like to qualify that all the results and discussion to be described hereafter are valid only for a special sample preparation condition and history described in sections III.2 and III.4.

IV.1. Characterization of Pd Nanoparticles. Figure 2a shows the Pd-(P2VP-*b*-PI) particles observed under TEM according to the method as detailed in section III.3. The Pd particles appear dark, but the P2VP-*b*-PI blocks cannot be detected in the micrograph. A total number of about 95 particles are sampled to obtain a histogram of the size of the particle diameters. The results are shown in Figure 2b, and the average diameter was estimated to be 7 nm.

IV.2. Visualization and Characterization of Isolated Single Block Chains. Before presenting results on AFM studies of Pd-(P2VP-*b*-PI), we shall report those of P2VP-*b*-PI chains, free from the Pd particles. Note that those polymers used for this purpose (P2VP-*b*-PI-L) are slightly different from those (P2VP-*b*-PI-S) used to prepare Pd-(P2VP-*b*-PI) (see Table 1). However, this difference is not important in this study. The specimens for the AFM observation were prepared according to the same method as described in section III.4.

Figure 3 presents a typical AFM image on the mica surface (part a), a height profile along the white line of the image (part b), and sketch of the image in part a (part c). The image in part a shows about five chains. Among them, the two chains marked by A and B in part

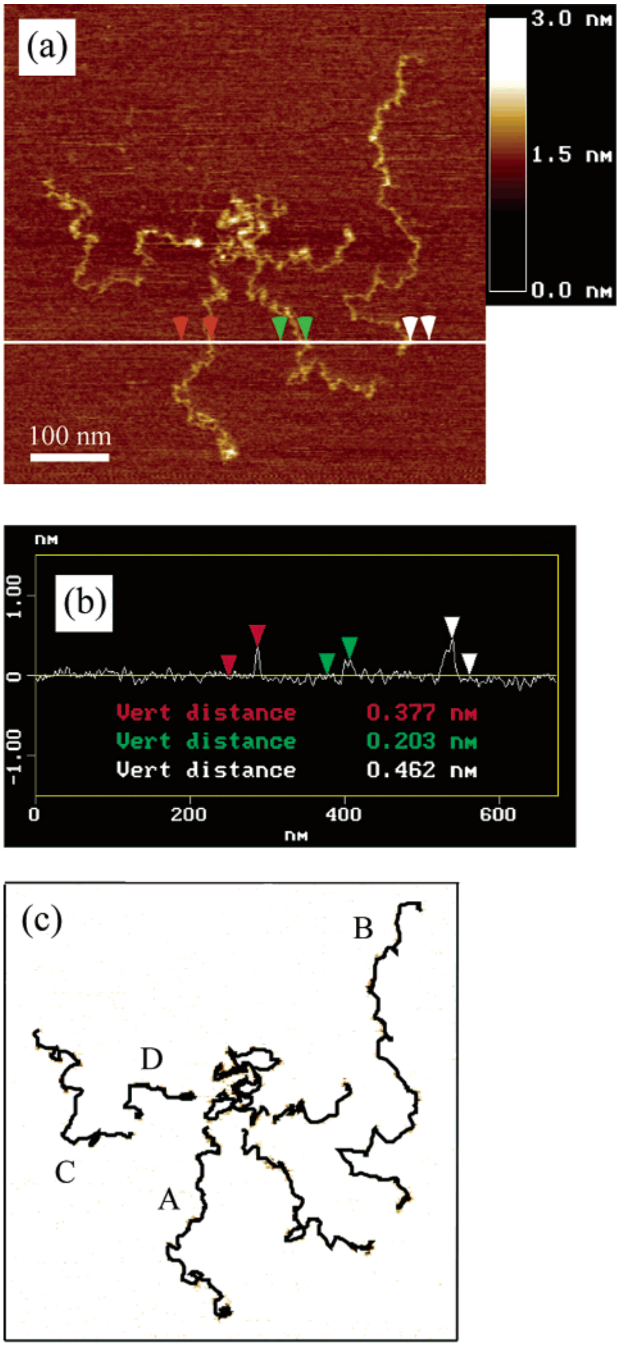

Figure 3. (a) Tapping-mode AFM image of isolated chains of P2VP-*b*-PI-L, (b) height profile across the scanning line shown by the white line in (a), and (c) a sketch of (a).

c are well isolated from others and have clear-cut continuity. The two short chains C and D on the left-hand side of the image are probably those disrupted during the specimen preparation process for the AFM observation. The discontinuity between the two chains was confirmed by the height profile along the appropriate scanning lines.

The contour lengths for A and B were estimated to be 460 and 630 nm, respectively. The height of the chains was measured in three places along the horizontal line in part a, and the three values were shown together with the height profile in part b. Among the three values, the smallest value of 0.2 nm is considered to be closest to the value for the single chain. It is difficult to distinguish the P2VP blocks from the PI blocks in this AFM images. However, the globular portions of the chains with the larger heights at the ends of the single chains, as seen partly in parts a and c with height of ~2 nm, might be a part of a PI block chain. This is because PI blocks may less interact with mica compared to P2VP and tend to make intramolecular aggregation to form a globule of a single PI block chain, as in the PS globules found previously for polystyrene-*block*-poly(methyl methacrylate).[22,23] It is also important to note here that the contour length of PI block is much less than that of P2VP block by the factor of about 10, judging from their molecular weights (Table 1). The block chains on other area of mica surface had a feature very similar to those in Figure 3, though the images are not shown here.

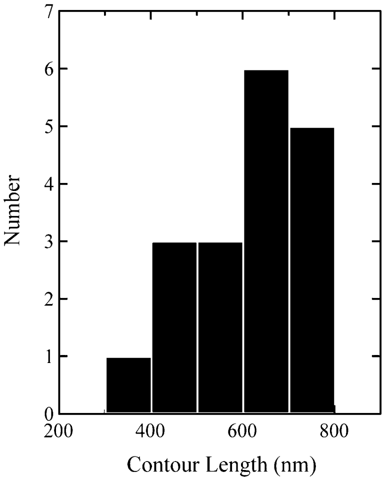

Figure 4. Histogram for contour length of P2VP-*b*-PI-L block chains directly estimated from AFM images.

Figure 4 shows a histogram for the contour (curvilinear) length of the whole block copolymer chains P2VP-*b*-PI-L. The number-averaged contour length was estimated to be ~600 nm for a small sampling number of 18 chains, slightly shorter than but consistent with the contour length (900 nm) calculated from molecular weight. It is reasonable that the measured length is smaller than the calculated length, primarily because small kinks of chains parallel and perpendicular to the substrate at the length scale smaller than the AFM resolution are all ignored. Those 18 chains were selected among many other chains because they are well separated and hence distinguished from other chains. They are free from intramolecular segmental contacts and seemingly free also from chain sissions. Since the sampling number is limited, the statistical accuracy in evaluating contour length is poor. However, it will still give qualitatively correct trend, thus ensuring visualization of single P2VP block chains.

In the literature, single synthetic polymer chains in extended or expanded conformations were observed for flexible polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA),[22,23] very rigid macromolecules,[24-26] and charged P2VP.[27,28] A possible chain-expanding mechanism in the present case may be due to attractive interactions between P2VP blocks and mica surface. In the dipping and pulling-out process of mica using the very dilute solution of P2VP-*b*-PI in benzene and the subsequent gentle washing process of the mica with a few drops of benzene, the block chains are put in a very thin layer of the solvent before the solvent is evaporated. The chains are then expanded in more or less two-dimensional space of the solvent, and the interactions

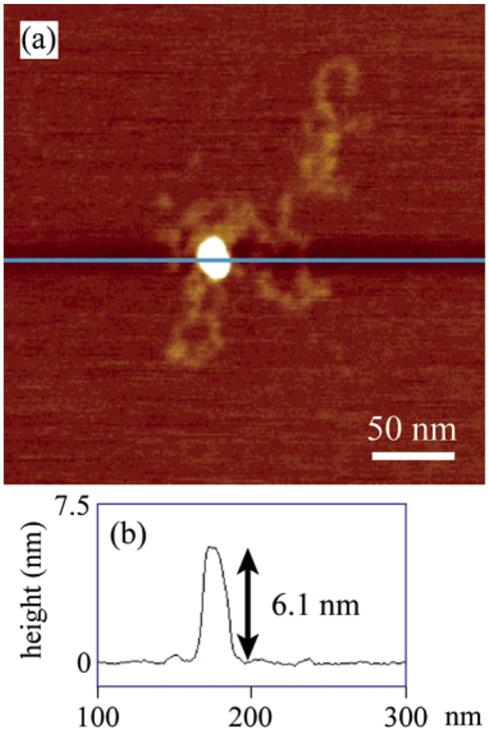

Figure 5. (a) Tapping-mode AFM image of Pd-(P2VP-*b*-PI−S) and (b) height profile across the scanning line shown in (a).

of P2VP blocks with the solvent molecules will be replaced by those with mica, resulting in frozen configurations of P2VP blocks on mica. Thus, we anticipate that P2VP block chains on mica may be more expanded than P2VP block chains in the bulk dilute solution. On the other hand, PI blocks are less interacting with mica so that PI blocks may be collapsed in globules during the solvent evaporation process.

Before closing this section, we like to stress that the present AFM resolution is not enough to follow every detail of the coil conformation. The very small loops and kinks in the chains cannot be resolved as noted already by a piece of evidence of finding always a lower contour length than the predicted one. This qualification is applied also for the conformation of chains adsorbed by palladium particles to be discussed immediately below.

IV.3. Visualization and Characterization of Isolated Single Pd-(P2VP-*b*-PI). Figure 5 shows an AFM image of an isolated Pd-(P2VP-*b*-PI−S) on mica (a) and a height profile (b) along the horizontal blue scanning line shown on the image in part a. The bright object has a height of 6.1 nm and diameter of 21 nm. The height is very close to the average diameter (7 nm) of the Pd nanoparticles as observed under TEM (Figure 2), suggesting that the object is a single Pd particle. The width is much larger than 6.1 nm, which is well-known to be due to a smearing effect induced by the finite size of the probe tip. The stringlike object observed around the particle is believed to be the adhered block chain(s). The height analysis of the string shows the height value of 0.2 nm, consistent with the single block chain. It should be noted that the image was highlighted on a large bright particle at the center of the image. Consequently, the single chain image is less clear than the image shown in Figure 3.

To further confirm that the bright circular object in the image corresponds to the single Pd particles, we obtained a histogram for the height of the objects. Figure 6 shows a histogram obtained for 83 particles in total. The average height estimated is 8 nm, consistent with the average diameter (7 nm) measured by TEM.

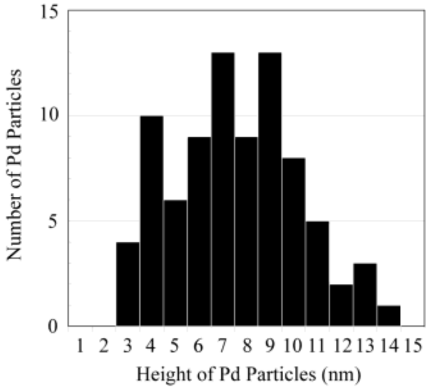

Figure 6. Histogram for height distribution of Pd particles for Pd-(P2VP-*b*-PI-S).

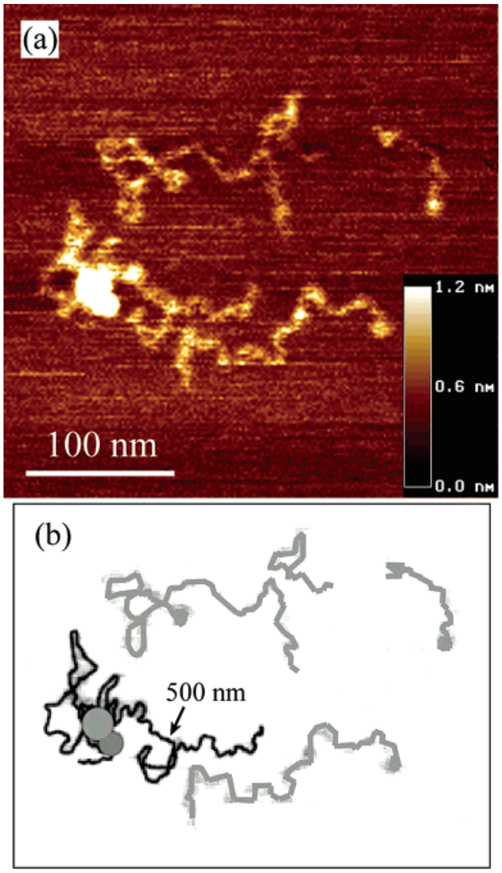

Figure 7. (a) Tapping-mode AFM images for Pd-(P2VP-*b*-PI-S) and (b) its sketch.

Figure 7 shows another AFM image of Pd-(P2VP-*b*-PI−S) (a) and its sketch (b). In preparing the sketches for the isolated chains, we judged continuity and discontinuity of given chains from the height profiles along appropriate scanning lines. The figure shows the two particles adhered to a single block chain as well as two block chains free form the particles and seemingly disrupted chains. It is very rare to observe the two particles being coalesced and adhered by a single chain in our experimental condition. The contour length of 500 nm measured for the block chain adhered to the particles is consistent with that of 700 nm calculated from molecular weight of P2VP-*b*-PI-S. We can estimate

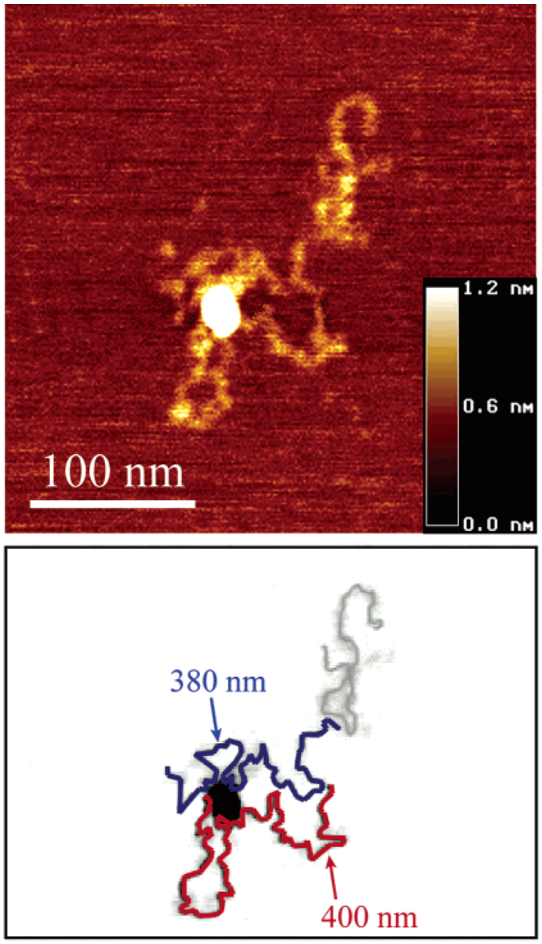

Figure 8. Tapping-mode AFM images for Pd-(P2VP-*b*-PI-S) (top) and its sketch (bottom). The Pd particle is adhered by two block chains.

an approximate number of chains adsorbed on the particle because the AFM images have a resolution just enough to estimate the contour length of the adsorbed chains. When the estimated length is consistent with the length calculated from its molecular weight, we counted the observed chain as one of the adsorbed chains. Figure 8 shows an AFM image and corresponding sketches for Pd-(P2VP-*b*-PI−S), representing two chains with contour length of 380 and 400 nm adhered to a single Pd particle.

We should note a possibility that the structures of the polymers adsorbed on the Pd particles, as observed by the AFM images shown in Figures 5, 7, and 8, may differ significantly from those in the special solution prepared after the purification processes of Pd-(P2VP-*b*-PI) and the dilution process as described in sections III.2 and III.4. For example, the observed polymer tails and loops on the AFM images might emerge upon adsorption of polymers to mica. Such studies to clarify the changes in the structures should be open future works. Nevertheless, let us consider below possible changes that might occur in the transfer process of the Pd-(P2VP-*b*-PI)'s from the bulk solution onto the mica substrate.

As we already discussed in section IV.2 in conjunction with the chain expanding mechanism of P2VP-*b*-PI on mica surface, the block chains adhered on the nanoparticles are also put in a very thin layer of the solvent in a very rapid solvent evaporation process encountered in the transfer process. Thus, loops and tails of adsorbed chains may be also expanded in more or less two-dimensional space where the adsorbed polymers are interacting with the palladium particles and solvents. After solvent evaporation, palladium−polymer−solvent interactions are replaced by palladium−polymer−mica interactions, and polymer−mica interactions will freeze conformations of the polymer chains adhered on the particle. The conformation of the chains (loops and tails) adsorbed on the particle will be certainly different before and after the transfer process.

However, we think that a more important issue here is how many interacting sites between polymer and palladium are replaced by interacting sites between polymer and mica during the very rapid freezing-in process of the chain conformation on the mica. If the replacement of the interactions are moderate, we may be able to anticipate that the characterstics of the adhered chains such as an average number of chains adsorbed on the particle, an average number of tails and loops per adsorbed chain or their contour lengths, and adhering positions of the particle along the P2VP block chain are *statistically* unaltered before and after the transfer process. Under this situation the AFM images are anticipated to replicate or maintain important memories of structures of the chains adsorbed on the particles in the bulk solution. This anticipation is well supported by the experimental evidence discussed in section II; i.e., the Pd particles are distributed more or less uniformly in P2VP lamellae across the interface.[20,21] To confirm the possibility that an average number of chains adhered to the particles in solution is unaltered after the transferring them on mica, it may be useful to measure molecular weight of the Pd-(P2VP-*b*-PI) in solution. This deserves future work.

The images show the three important features for the chain adhered to a single Pd particle. (1) Only a small fraction of segments in a single chain is adhered to the particle, but the majority of segments are free from the particle. The free subchains are long enough to effectively protect a given Pd particle for a coalescence with others to grow or aggregate into a larger particle. This finding rules out the possible models given by (a) to (c) in Figure 1. (2) Only a few chains (up to about three) were observed to adhere to single particles, though the absolute number itself is not important. (3) A majority of the surface sites of the particle may therefore be still free from the polymer segments, promoting an efficiency of surface activity of the nanosized Pd particles. This is because the efficiency depends on a spatiotemporal average of the surface fraction of the particles occupied by polymer segments in the dynamical process of physical adsorption.

Let us compare these results obtained by the single-particle and single-polymer experiments with what is know about polymer adsorption on solid surfaces. For example, excellent classical works by Killmann[18] revealed the following points:

(i) At low surface coverage by polymers, site fraction, p, occupied by the adhered polymer segments on the silica surface is 0.5; the polymers adsorb unhindered by each other with highest possible contact points and hence an extremely flat conformation. This picture seems close to the one shown schematically in Figure 1b,c but not the one shown in Figure 1d.

(ii) At high surface coverage, the new adsorbing polymer segments are in contact not only with silica surface but also with already adsorbed polymer segments, giving $p = 0.2-0.25$. This picture seems to close to the one shown in Figure 1a.

However, we should note that these two systems are quite different in not only polymers, their molecular weights, particles, and particle size but also the conditions employed for adsorption experiments. Consequently, detailed and quantitative comparisons of these two kinds of experiments should be open to the public for future work.

V. Concluding Remarks

The Pd nanoparticles, prepared by reducing Pd^{2+} ions at 85 °C for 45 h in a dilute solution of P2VP-*b*-PI and palladium acetylacetonate with benzene as a solvent and 1-propanol as a reductant and a subsequent purificantion process as described in sections III.2 and III.4, were stabilized by P2VP-*b*-PI chains adhered to them. The particles stabilized had average diameter of 7 nm. The stabilizing mechanism of the particles was investigated by a direct observation of the particles, transferred onto a mica sheet by dipping the sheet into their very dilute solutions with benzene followed by a gentle pulling-out of the sheet from the solution and washing of the sheet with drops of the solvent, under atomic force microscopy (AFM). The AFM images revealed the following: (a) Only a few chains (up to about three P2VP-*b*-PI chains) are adhering to the single Pd particle, though the absolute number itself is not important at all. (b) Only a small fraction of segments of a single chain are adhered to the particle, and a majority of segments are free from the particle, yielding sufficiently long free subchains effective for the steric or entropic stabilization of the particle against coalescence-driven aggregation and growth. (c) The majority of surface sites of the particle may remain free from the polymers, thus promoting an efficiency of surface activity. The result (a) given above is consistent with our previous analytical evaluation of the numbers of the chains adhered to a single Pd particle (less than five chains),[19] although one should note a difference in composition and P2VP block length in Pd-P2VP-*b*-PI between the previous system[19] and the present system. The trend that only a few chains adhere to the block copolymers would be qualitatively valid at least for these particular systems.

VI. Some Remarks for Future Studies

As already stated repeatedly, the results obtained in this work are legitimate only for the particular block copolymers and the particular sample history employed for preparing Pd-(P2VP-*b*-PI) and the purification processes employed. For example, the molecular weight of the P2VP block employed in this work is large such that its radius of gyration in solution is larger than the Pd particles formed by the chemical reduction method of Pd ions. The molecular weight and composition of P2VP-*b*-PI block copolymers should affect configurations of the copolymer chains adsorbed on the particle. For a given block copolymers and ions adsorption characteristics such as average number of chains adsorbed per particle and average number of adsorbed segments per chain generally depend on the reduction process (time, temperature, solvent, etc.), the purification process (each step of which may change the adsorption), and a storage duration of the solution prepared with the purified Pd-(P2VP-*b*-PI). The most crucial but difficult problem to be solved in the future is, how extensive is the reconstruction of the adsorption characteristics described above before and after the transfer of the Pd-(P2VP-*b*-PI) solution on mica, besides the conformational reconstruction of the adsorbed chains? We consider that the conformational reconstruction itself is natural as discussed in sections IV.2 and IV.3 and is not very important for the controlled alignment of the nanoparticles in the domain space of the block copolymers. However, the reconstruction of the adsorption characteristics is believed to be very important for the controlled alignment.

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