Atomic Force Microscopy Visualization of Single Star Copolymer Molecules.

Anton Kiriy[1], Ganna Gorodyska[1], Sergiy Minko[1], Constantinos Tsitsilianis[2] and Manfred Stamm[1]

[1]*Institut für Polymerforschung Dresden, Hohe Straße 6, 01069 Dresden, Germany*

[2]*Department of Chemical Ingineering, University of Patras, 26500 Patras, Greece*

INTRODUCTION

Since the outstanding innovation of Binnig and Rohrer[1] scanning probe microscopy (SPM) has been used as an important analytical tool in biology,[2] supramolecular chemistry,[3] polymer[4] and material science[5]. SPM was successfully used to resolve fine structure of some biopolymers[2, 6] and synthetic polymers with bulky side groups such as dendronized polymers[7] and molecular brushes[8]. Recently, we reported on visualization of polyelectrolyte (PE) single molecules in different conformation.[9] Those investigations provide possibility to improve resolution without a considerable distortion of solution's conformations of PE. Here we present the SPM visualization of polystyrene/poly(2-vinylpyridine) hetero-arm star copolymer[10] (PS_7-$P2VP_7$, where 7 is number of arms) as single molecule entities. Metallization of the P2VP part of the star copolymer allows to improve resolution and to visualize single PS_7-$P2VP_7$ molecules even on silica-wafers.

EXPERIMENTAL

The sample of PS_7-$P2VP_7$ (Table 1) was prepared via three-step sequential "living" anionic polymerization using divinylbenzene linkage (DVB).[10]

Table 1. Characteristic of the PS_7-$P2VP_7$ Sample.

$M_w(PS_{arm})$/number of arms (by SEC)	20000 / 6.9
$M_w(P2VP_{arm})$/number of arms by LS/calculated	56500 / 6.9
W_{P2VP}, fraction of P2VP (by NMR)	66 (%)
$M_w(PS_7\text{-}P2VP_7)$ (by LS)	544000

Solution of PS_7-$P2VP_7$ in tetrahydrofurane (THF) (0.01 g/l) was diluted by slow addition of the 10-fold excess of acidic water (pH 2, HCl) or toluene. After stirring during 2 h we set a drop of the solution onto the surface of freshly cleaved mica for 1 minute and afterwards removed the rest of the drop with centrifugal force and investigated the dry sample with SPM.

Metallized PS_7-$P2VP_7$ was prepared on Si-wafer. In the first step, PS_7-$P2VP_7$ was deposited on the cleaned Si-wafer from THF - acidic aqueous solution (0.001 g/l PS_7-$P2VP_7$) for 1 min. In the second step, the Si-wafer was placed into the palladium acetate solution (pH 2)[11] for 1 min for the formation of the Pd...PS_7-$P2VP_7$ composite. In the third step the silica wafer was rinsed with water, placed for 15 sec into reduction solution which contained 1.0 mg/ml of dimethylamine borane (DMB). Finally, the Si-wafer was cleaned with water and dried with argon. The Pd-PS_7-$P2VP_7$ nanocomposite on Si-wafers was investigated in the dry state with AFM.

Multimode SPM instrument (Digital Instruments, Santa Barbara) was operating in the tapping mode. Silicon tips with radius of 10-20 nm, spring constant of 30 N/m and resonance frequency of 250-300 KHz were used after calibration with gold nanoparticles (diameter 5 nm) to evaluate the tip radius. The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius.[12]

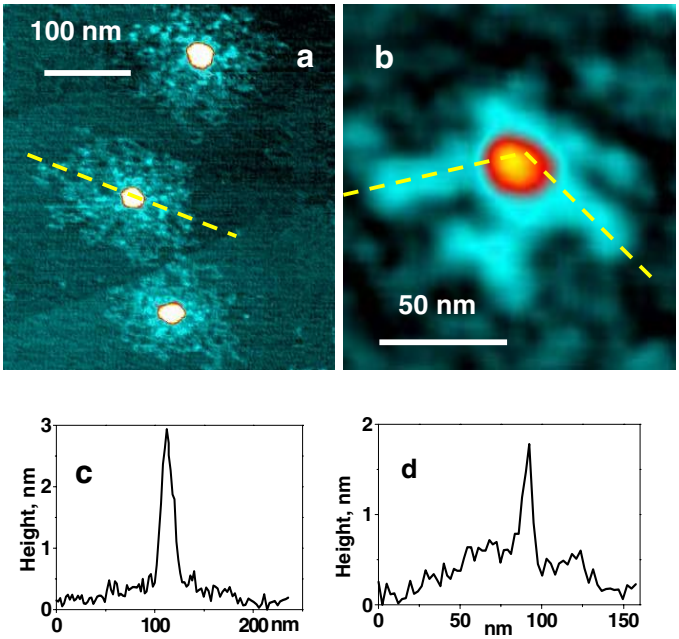

Figure 1. Representative SPM images (a-b) and cross-sections (c-d) of PS_7-$P2VP_7$ molecules adsorbed onto the mica from THF-acid water solution (a, c) and from toluene (b, d).

DISCUSSION

Tetrahydrofurane (THF) is solvent of *moderate* quality for both P2VP and PS components and PS_7-$P2VP_7$ molecules are molecularly dissolved. In this solvent P2VP and PS arms adopt strongly coiled conformation.[13] Upon adsorption onto the mica surface and evaporation of the solvent PS_7-$P2VP_7$ molecules undergo additional collapse and resulting structures appears in AFM images in near spherical poorly resolved conformation. On the other hand, in acid water protonated P2VP chains adopt an extended conformation due to long range Coulomb repulsion between similarly charged monomer units. This effect became even more pronounced for star-shaped block copolymers due to additional inter-chain repulsions (excluded volume interaction).[14] At the same time water insoluble PS blocks of PS_7-$P2VP_7$ molecules collapse and form a dense core. We found that addition of acid water (pH 2) into the THF solution of PS_7-$P2VP_7$ and adsorption onto the mica surface results in uniform star-like core-shell structures (Figure 1a; Table 2). The diameter and the thickness of outer shell of observed particles was found to be about 126±35 and 0.3±0.1 nm, respectively. Collapsed PS blocks appears in globule conformation (3 nm in height and 16 nm in diameter).

Table 2. Average dimensions of the PS_7-$P2VP_7$ (on the base of at least 50 structures taken from 3-5 AFM images for each conditions).

Conditions	Shell, nm		Core, nm	
	Diameter	Height	Diameter	Height
THF	28±5	2.4±0.5	28±5	2.4±0.5
pH 2	126±35	0.3±0.1	16±7	2.9±0.3
Toluene	49±10	0.5±0.2	12±3	2.4±0.3

Upon addition of toluene which is selective solvent for PS block we induce reverse intrasegregation. In this case in final state P2VP arms adopt a collapsed conformation but PS blocks - an extended

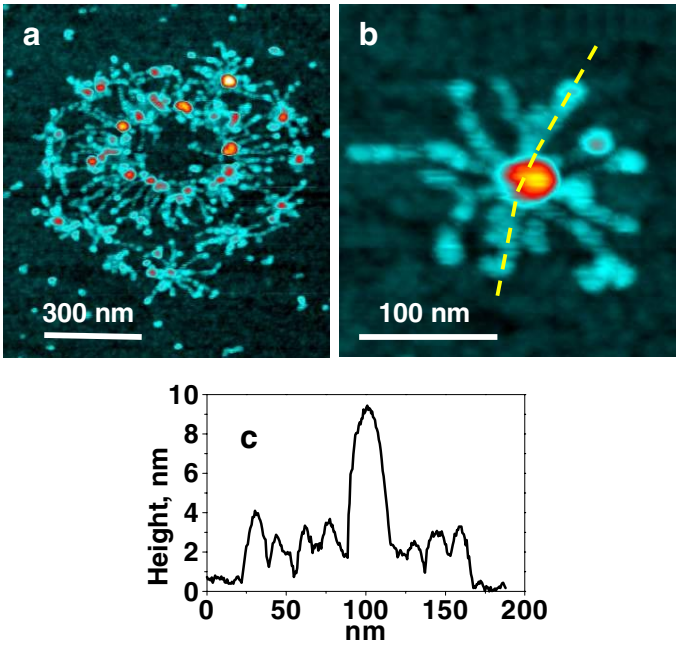

Figure 2. AFM images of single Pd...PS_7-$P2VP_7$ nanocomposite (a) and supramolecular structure of Pd...PS_7-$P2VP_7$ (b) on Si-wafer; cross-section of (a) (c).

one. Adsorption of PS_7-$P2VP_7$ molecules results in star-like structures with collapsed core (D=16nm) and well-definite arms about 30 nm in length and 0.8 nm in height (Fig. 1b, d; Table 2). To metallize PS_7-$P2VP_7$ on Si-wafer surface we employed recently developed approach which is based on the ion exchange reaction between protonated $(P2VPH^+)Cl^-$ and $(2H^+)PdCl_4^{2-}$ (formed from PA and HCl) followed by reduction with DMB.[10] Due to the reduction Pd atoms localized along the P2VP chain and form clusters.

$$\mathrm{P2VP + nHCl} \rightleftharpoons \mathrm{P2VP \cdot nHCl}$$

$$\mathrm{Pd(OAc)_2 + 4HCl} \rightleftharpoons \mathrm{H_2PdCl_4 + 2HOAc}$$

$$\mathrm{P2VP \cdot nHCl + n/2\ H_2PdCl_4} \longrightarrow \mathrm{P2VP \cdot n/2\ H_2PdCl_4 + nHCl}$$

$$\mathrm{2\ (P2VP \cdot n/2\ H_2PdCl_4) + n\ (CH_3)_2NH\ \ BH_3 + 3n\ H_2O} \longrightarrow$$

$$\longrightarrow \mathrm{2(P2VP \cdot nHCl) + nPd^0 + nB(OH)_3 + n(CH_3)_2NH\ \ HCl + nHCl + 2nH_2}$$

After metallization[11] of PS_7-$P2VP_7$ with fully extended P2VP arms the Pd...PS_7-$P2VP_7$ nanocomposite appears in the good resolved star-shaped conformation (Fig. 2b-c). P2VP arms as well as Pd clusters are clearly observed in the SPM images and can be calculated (Table 3).

Table 3. Dimensions of Pd-PS_7-$P2VP_7$ nanocomposite (averaged from 52 structures in 6 AFM images).

Length (L), height (H) and number (N) of P2VP arms			Diameter (D) and height (H) of PS core		Diameter (D), height (H), and number (N) of Pd clusters per arm		
L, nm	H, nm	N	D, nm	H, nm	D, nm	H, nm	N
61±15	1±0.2	3±1	9±3	7.2±2	3±1	2.2±1	3±1

As it is seen from the SPM image (Figure 2a), sometimes PS_7-$P2VP_7$ molecules adsorbed from acid water can form complicated circular superstructures. It is not clear either such structures are formed during sample preparation (upon adsorption of PS_7-$P2VP_7$ and solvent evaporation) or due to aggregation in solution.

In conclusions, polystyrene/poly(2-vinylpyridine) star copolymer have been visualized with molecular. At concentrations below 0.01mg/ml PS_7-$P2VP_7$ exists in molecularly dissolved state in both selective (acid water, toluene) and non-selective (tetrahydrofurane) solvents. Adsorbed from acid water (pH 2) PS_7-$P2VP_7$ single molecules form core-shell nanoparticles with extended P2VP arms and collapsed PS blocks. It was found that upon addition of toluene PS_7-$P2VP_7$ undergoes reverse intramolecular segregation resulted in star-shaped nanoparticles with extended PS arms. Metallization of P2VP arms leads to the organic-inorganic nanocomposite of an star-shaped morphology. The approach presented in this paper is a useful route to single-molecule devices of dedicated structure from properly designed single polymer molecules of a complicated architecture.

ACKNOWLEDGEMENTS

We are grateful for the financial support provided by DFG.

REFERENCS

1. Binnig, G.; Rohrer, H.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57-61. Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, *56*, 930-933.
2. Rivetti, C.; Guthold, M.; Bustamante, C. *J. Mol. Biol.* **1996**, *264*, 919.
3. Schenning, A. P. H. J.; Kilbinger, A. F. M.; Biscarini, F.; Cavallini, M.; Cooper, H. J.; Derrick, P. J.; Feast, W. J.; Lazzaroni, R.; Leclere, Ph.; McDonell, L. A.; Meijer, E. W.; Meskers, S. C. J. *J. Am. Chem. Soc.* **2002**, *124*, 1269-1275.
4. Sheiko, S. S.; Möller, M. *Chem. Rev.* **2001**, *101*, 4099-4123.
5. Magonov, S. N.; Whangbo, M.-H. *Surface Analysis with STM and AFM: Experimental and Theoretical Aspects of Image Analysis.* VCH: New York. 1996.
6. Camesano, T. A.; Wilkinson, K. J. *Biomacromolecules* **2001**; *2*, 1184-1191.
7. Shu, L.; Schlüter, A. D.; Ecker, C.; Severin, N.; Rabe, J.P. Angew. Chem. 2001, 113, 4802-4805. *7*, 549. Prokhorova, S. A.; Sheiko, S. S.; Mourran, A.; Semenov, A. E.; Möller, M.; Beginn, U.; Zipp, G.; Ahn, C.-H.; Percec, V. *Langmuir* **2000**, *16*, 6862.
8. Khalatur, P. G.; Khokhlov, A. R.; Prokhorova, S. A.; Sheiko, S. S.; Möller, M.; Reineker, P.; Shirvanyanz, D. G.; Starovoitova, N. *Eur. Phys. J.* **2000**, *1*, 99.
9. Minko, S.; Kiriy, A.; Gorodyska, G.; Stamm M. *J. Am. Chem. Soc.* **2002**, *124*, 3218-3219. Kiriy, A.; Gorodyska, A.; Minko, S.; Jaeger, W., Štěpánek, P.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 13454-13462.
10. Tsitsilianis, C.; Voulgaris, D.;M. Štěpánek, Podhájecká , K.; Procházka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2000,** *16,* 6868-6876. Tsitsilianis, C.; Voulgaris D. *Macromol. Chem. Phys.* **1997**, *198*, 997.Voulgaris, D.; Tsitsilianis, C.; Grayer, V.; Esselink, F.; Hadziioannou,; G. Polymer **1999**, 40, 5879. Voulgaris, D.; Tsitsilianis, C.; Esselink, F.; Hadziioannou, G. Polymer **1998**, *39*, 6429.
11. Kiriy, A.; Minko, S.; Gorodyska, A.; Stamm, M.; Jaeger, W. *Nano Letters* **2002**, *2,* 881-885. Minko, S.; Kiriy, A.; Gorodyska, A.; Stamm, M. *J. Am. Chem. Soc.***2002**, *124,* 10192-10197.
12. Xu, S.; Arnsdorf, M. F. *J. Microscopy* **1994**, *173*, 199-210. Vesenka, J.; Manne, S.; Giberson, R.; Marsh, T.; Henderson, E. *Biophys. J.* **1993**, *65*, 992-997.
13. Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1993**, *15*, 1. Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168-3181. Liu, S.; Armes, S. *Angew. Chem.* **2002**, *114*, 1471-1474. Moffitt, M.; Khougaz, K.; Eisenberg, A. *Acc. Chem. Res.* **1996,** *29,* 95-102.
14. Wolterink, J.; Leermakers, F.; Fleer, G.; Koopal, L.; Zhulina, E.; Borisov, O. *Macromolecules* **1999**, *32,* 2365-2377.