

GRAFTING OF POLY(SODIUM STYRENESULFONATE) ONTO GOLD SURFACE FROM NaNO_3 SOLUTION*

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Abstract The chemical grafting of thiol terminated poly(sodium styrenesulfonate) (HS-PSSS) chains from sodium nitrate (NaNO_3) salt solution to a gold surface was investigated with a quartz crystal microbalance with dissipation monitoring (QCM-D) in different salt concentrations. It was found that at low salt concentration grafting density of HS-PSSS was low and the grafted chains adopted a mushroom conformation. With the increase of salt concentration polyelectrolyte chains underwent a transition toward coiled state due to reduction of electrostatic repulsion and as a result more chains were grafted on the surface. When the grafting density reached a certain limit after which further grafting caused repulsion between already grafted HS-PSSS chains and as a result grafted chains adopted a brush conformation.

Keywords: Poly(sodium styrenesulfonate); Quartz crystal microbalance; Kinetics of grafting.

INTRODUCTION

Polyelectrolytes are special class of polymers with ionizable groups^[1, 2]. These groups dissociate in polar solvents leaving charges on polymer chain and releasing counter ions in solution. The presence of different effects such as long range of electrostatic interactions, interaction between counterions and macromolecules, internal configuration due to the flexibility of chains makes polyelectrolyte solutions very complex systems^[3]. In salt free solutions, long range repulsive interactions between neighboring charges on a polyion chain result in expanded conformation of polyion. Addition of salt screens the electrostatic interactions between monomer units on the chain and results in the collapse of the chain. The salt effect is not feeling by polyelectrolyte chain if Debye screening length is much larger than the chain size. At high salt concentration Debye screening length is less than electrostatic globule size and the polyelectrolyte chain has a structure similar to neutral polymer^[4]. On the basis of local chemistry of molecules and balance between electrostatic and solvent induced interactions single polyelectrolyte chains exhibit different conformations *i.e.* globules, rods, pearl necklace structures, torri and helices^[5].

Conformation of free polymer molecules in solutions is quite different from surface grafted polymer chains^[6, 7]. The properties of grafted polyelectrolyte brushes are characterized by the interactions between the grafted chains. Neutral and charged polymer brushes are quite distinct from each other. In neutral polymer brushes the repulsion between the monomer units of grafted chains is of short range nature and described as an excluded volume effect. Neutral polymer chains get stretch only when the grafting density is high enough and chains overlap each other thus exhibit perturbed conformation. In contrast to neutral polymer brushes, charged

* This work was financially supported by the Higher Education Commission (HEC) of Pakistan under the indigenous PhD scholarship program.

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Received September 8, 2010; Revised October 8, 2010; Accepted October 25, 2010

doi: 10.1007/s10118-011-1065-3

polymer brushes have long range columbic forces which are active at much larger distance between the grafted polyelectrolytes.

Formation of brush is determined by the grafting density, structure of the chains, solvent quality and segment surface interaction. Both theoretical and experimental studies on kinetics of grafting are limited. Theoretical studies reveal that kinetics of grafting exhibits two regimes, in the first regime grafted chains form mushrooms while in second regime grafted chains form brushes^[8–11]. In the case of weakly reactive functional groups kinetics obeys mean field theory and for strong reactive functional groups reaction kinetics becomes diffusion controlled. Experimental studies reveal that kinetics of grafting exhibits three regions instead of two predicted by theory. Tetherings in the presence and absence of segmental adsorption (physical adsorption) are quite distinct from each other. The number of chains tethered per unit area is larger and saturation is attaining earlier when segmental adsorption occurs^[12–17]. Most of the work in the past was done on neutral polymers, and limited amount of work was done on polyelectrolytes due to complications in the presence of charged groups.

The formations of the brushes are greatly influenced by pH of surrounding medium and ionic strength^[18]. Liu *et al.* investigated the grafting kinetics of HS-PDMM (poly[(2-dimethylamino)ethyl methacrylate]) at different pH^[19]. Like pH, variation of salt is also a key factor for tuning the structural properties of polyelectrolyte brushes. The aim of the present work is to study grafting kinetics of thiol terminated poly(sodium styrenesulfonate) at different salt concentrations using quartz crystal microbalance with dissipation monitoring (QCM-D).

EXPERIMENTAL

Materials

Sodium styrene sulfonate (SSS) from Aldrich was recrystallized three times in a methanol/water mixture. 4,4'-Azobis(4-cyanovaleric acid) from Fluka was used as received. Poly(sodium styrenesulfonate) (PSSS) was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization in water^[20]. The molar mass ($M_w = 5.32 \times 10^4$ g/mol) and the polydispersity index ($M_w/M_n = 1.25$) of PSSS were measured by size exclusion chromatography (Waters) equipped with 1515 pump and Ultrahydrogel (Waters) 2000, 1000, 500, 250 columns at 40°C. Monodisperse poly (ethylene glycol) was used as the calibration standard. The mobile phase consisted of 80% (V/V) Milli-Q water, 20% (V/V) acetonitrile and 0.1 mol/L NaNO₃ at a flow rate of 1.0 mL/min.

PSSS terminated with thiol end groups (HS-PSSS) was prepared by reduction of trithiocarbonate-terminated PSSS (TTE-PSSS) with NaBH₄. In a typical experiment, 0.061 g TTE-PSSS was dissolved in 30.5 mL deionized water and NaBH₄ aqueous solution with NaBH₄/TTE-PSSS molar ratio of 40/1 was introduced under stirring. The reaction mixture was stirred at room temperature for one week to ensure that trithioester groups were completely reduced to yield HS-PSSS.

QCM-D Measurements

QCM-D and the AT-cut quartz crystal with a fundamental resonant frequency of 5 MHz were purchased from Q-sense AB^[21]. The quartz crystal was mounted in a fluid cell with one side exposed to the solution. By using highly polished crystals with a root-mean-square roughness less than 3 nm, the effects of surface roughness were minimized^[22]. A detailed description of the technique can be found elsewhere^[23]. In brief, the decrease of the resonant frequency of the crystal relates to the mass of thin layer on quartz crystal, whereas the dissipation factor is to the viscoelastic properties of the additional layer. The change in frequency (Δf) and dissipation (ΔD) in the present work give information about the grafting and structural changes of HS-PSSS. The presented frequency and dissipation data were based on the third overtone ($n = 3$). Due to insufficient energy trapping, Δf and ΔD values from the fundamental were usually noisy and hence discarded^[24]. All experiments were conducted at $(25 \pm 0.02)^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1 shows the changes of frequency (Δf) and dissipation (ΔD) of HS-PSSS verses logarithmic time in the

absence of salt. In Fig. 1 the dissipation increases, indicating the increase in thickness of polymer layer on the surface. This figure is just shown for comparison. Figure 2 shows the changes of frequency (Δf) and dissipation (ΔD) of HS-PSSS versus logarithmic time at different NaNO_3 concentrations. For HS-PSSS in 0.01 mol/L NaNO_3 concentration, Δf decreases whereas ΔD increases at 25°C , indicating the deposition of HS-PSSS onto the surface. It is known that the increase in mass on quartz resonator causes the frequency to decrease. The change in dissipation gives information about the structure of the polymer layer formed by the grafted chains. The change in dissipation increases with the increase in thickness and looseness of the polymer layer on quartz resonator^[25]. In both these cases (0.05 mol/L and 0.1 mol/L NaNO_3 concentrations) Δf also decreases but the decrease is more pronounced as compared to 0.01 mol/L NaNO_3 salt concentration. Similarly, ΔD increases with NaNO_3 salt concentration which is also larger as compared to lower salt concentration. This indicates that with the increase in concentration of NaNO_3 gradual collapse of HS-PSSS chains occurs and as a result more and more chains are grafted on the surface. At high salt concentration (1 mol/L) Δf becomes more negative and ΔD becomes more positive as compared to low salt concentration, indicating more deposition or grafting of polymer chains on the surface of quartz resonator.

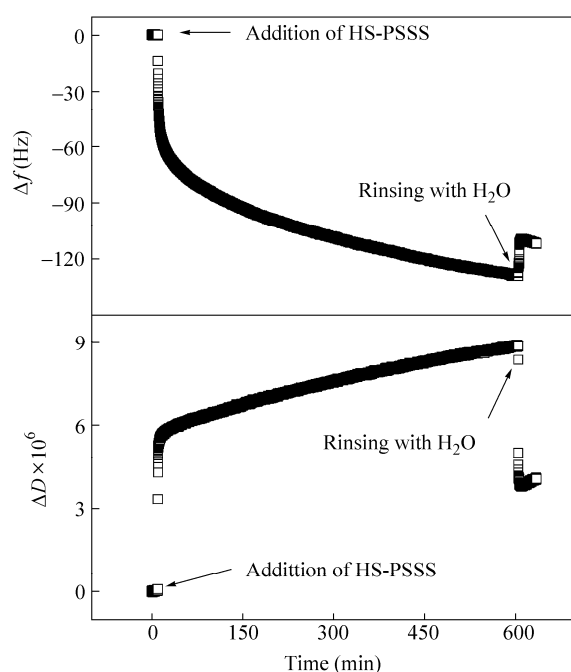


Fig. 1 Change of frequency (Δf) and dissipation (ΔD) of the quartz resonator immersed in HS-PSSS solution as a function of logarithmic time

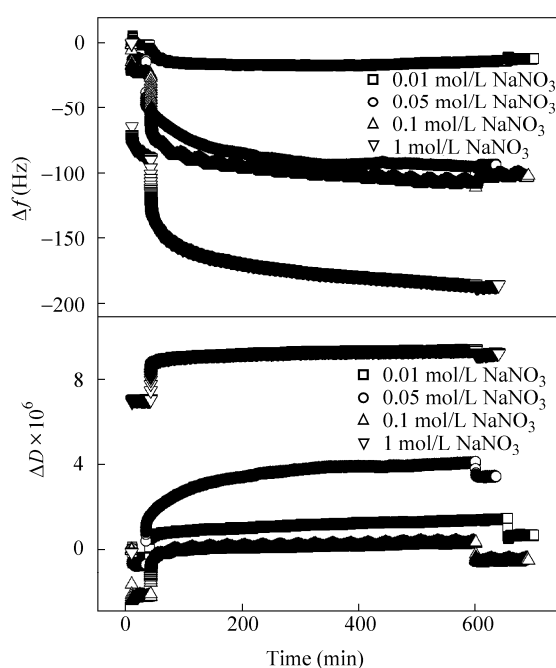


Fig. 2 Change of frequency (Δf) and dissipation (ΔD) of the quartz resonator immersed in HS-PSSS solution with different NaNO_3 concentrations

In the absence of salt HS-PSSS chains in solution has extended conformation due to electrostatic repulsion between monomer units^[26]. Also in the absence of salt a large decrease in frequency and increase in dissipation are observed because the HS-PSSS chains are rod like so large number of chains are grafted on the surface, as a result of which the grafting density increases. When salt is added the chains become coiled and few chains are grafted and grafting density becomes low as compared to salt free case. With the addition of salt, electrostatic repulsion between charged polyelectrolyte segments in solution decreases. The strong coulombic repulsion between nearby charges on polyelectrolyte, which tend to stretch polyelectrolyte chain, is screened by rearrangement of counter ions of salt in solution. The screened polyelectrolyte adopts a coiled conformation and as a result more chains are grafted onto the surface. When the chains are grafted to surface through end groups some chains are attached to surface through weak physical adsorption. With the increase of salt concentration,

grafting density increases and the chains which are initially adsorb through physical adsorption are replaced by the chains that have thiol end group, because thiolate group strongly interacts with the gold surface. The reason of increasing thickness of the polymer chains on quartz resonator is due to the conformational change of HS-PSSS in higher salt concentration.

At low salt concentration *i.e.* 0.001 mol/L, Δf and ΔD curves do not level off which indicates that saturation is not reached as shown in Fig. 2 where Δf and ΔD are plotted against the time on logarithmic scale. At low salt concentration physical adsorption plays an important role as adsorption equilibrium is not reached due to adsorption barrier^[27]. At high salt concentration Δf and ΔD curves level off, indicating the saturation of the gold surface. The time needed to attain saturation strongly depends on salt concentration. In high salt concentration saturation of the gold surface reaches rapidly because screened polyelectrolyte chains attain more coiled conformation and as a result large number of chains are grafted on the surface quickly. In case of 1 mol/L salt concentration Δf and ΔD reach to the constant value quickly, indicating that saturation of the gold surface reaches very rapidly as compared to low salt concentration. ΔD drops after rinsing with NaNO_3 ; the reason is that when we add NaNO_3 , it will remove some chains of HS-PSS which are attached to the surface by physical adsorption.

For studying the conformational change of macromolecules, the plot of ΔD versus Δf has proven a helpful relationship^[28]. Liu *et al.* has done experiment on HS-PDMM at different pH and observed three regime kinetics characters^[19] which were akin to experimental observation of Penn *et al.*^[12]. However, in our case of HS-PSSS at different salt concentrations, results are somewhat different. Figure 3 shows ΔD versus Δf plot of HS-PSSS at different NaNO_3 concentrations. At the lowest salt concentration (0.01 mol/L NaNO_3) grafting involves two types of kinetic process. Region I shows grafting process where as region II shows dehydration of the grafted chains. In region II with the increase of grafting density of polymer chains, grafted chains lose their water of hydration and get dehydrated. At low salt concentration saturation of gold surface is not attained that's why we observe increase of Δf with ΔD in the second regime. In case of 0.05 mol/L and 0.1 mol/L NaNO_3 concentrations grafting involves one type of kinetic process. At high salt concentration chains are only attached through their end through "grafting to process". With the increase of salt concentration, chains become more collapsed due to which grafting density increases and as a result all the available space is occupied by the grafted chains and the chains are at the verge of repulsion and thus adopt mushroom conformation. At high salt concentration the HS-PSSS behaves like a neutral polymer and the concentration of NaNO_3 has marked

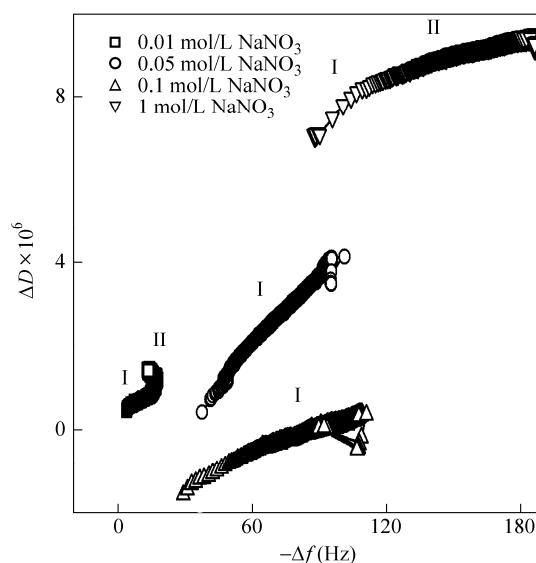


Fig. 3 Plot of ΔD versus Δf for a HS-PSSS with different NaNO_3 concentrations

influence on the conformation of the polymer chains. The grafting in the case of 1 mol/L NaNO₃ concentration also involves two types of kinetic process. In Region I, the grafting density is low so grafted chains adopt mushroom conformation. In region II grafting density increases with the increase in salt concentration and as a result the electrostatic repulsion between the chains becomes stronger and the chains tend to be stretched and adopt brush conformation^[19].

CONCLUSIONS

Grafting kinetics of thiol terminated poly(sodium styrenesulfonate) is strongly influenced by the NaNO₃ concentration. Our results show that at low salt concentrations the chains adopt mushroom conformation. At high salt concentration, the grafting density increases, which in turn change the conformation of grafted chains from mushroom to brush.

ACKNOWLEDGEMENT Miss Iram Bibi wishes to acknowledge Third World Academy of Science and Chinese Academy of Science (TWAS-CAS) for one year fellowship to work in the University of Science and technology, Hefei, China. We are also thankful to Professor Guangzhao Zhang for the helpful discussion.

REFERENCES

- 1 Forster, S. and Schmidt, M., *Adv. Polym. Sci.*, 1995, 120: 51
- 2 Barrat, J.L. and Joanny, J.F., *Adv. Chem. Phys.*, 1996, 94: 1
- 3 Kuhn, P.S., *Physica A*, 2004, 337: 481
- 4 Dobrynin, A.V. and Rubinstein, M., *Prog. Polym. Sci.*, 2005, 30: 1049
- 5 Yethiraj, A.J., *Phys. Chem. B*, 2009, 113: 1539
- 6 Alexander, S.J., *Phys. France*, 1977, 38: 983
- 7 Halperin, A., Tirrell, M. and Lodge, T.P., *Adv. Polym. Sci.*, 1991, 100: 31
- 8 Hasegawa, R. and Doi, M., *Macromolecules*, 1997, 30: 5490
- 9 Fredrickson, G.H. and Milner, S.T., *Macromolecules*, 1996, 29: 7386
- 10 O'Shaughnessy, B. and Sawhney, U., *Macromolecules*, 1996, 29: 7230
- 11 Kramer, E.J., *Isr. J. Chem.*, 1995, 35: 49
- 12 Huang, H., Rankin, S.E., Penn, L.S., Quirk, R.P. and Cheong, T.H., *Langmuir*, 2004, 20: 5770
- 13 Tokumitsu, S., Liebich, A., Herrwerth, S., Eck, W., Himmelhaus, M. and Grunze, M., *Langmuir*, 2002, 8: 8862
- 14 Stamm, M., Motschmann, H. and Toprakcioglu, C., *Macromolecules*, 1991, 24: 3681
- 15 Abraham, T., Giasson, S., Gohy, J.F., Jerome, R., Müller, B. and Stamm, M., *Macromolecules*, 2000, 33: 6051
- 16 Huguenard, C., Varoqui, R. and Pefferkorn, E., *Macromolecules*, 1991, 24: 2226
- 17 Tao, J., Guo, A., Stewart, S., Birss, V.I. and Liu, G., *Macromolecules*, 1998, 31: 172
- 18 Ruhe, J., Ballauff, M., Biesalski, M., Dziezok, P., Grohn, F. and Johannsmann, D., *Adv. Polym. Sci.*, 2004, 165: 79
- 19 Liu, G., Yan, L., Chen, X. and Zhang, G., *Polymer*, 2006, 47: 3157
- 20 Chiefari, J., Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, G., Rizzardo, E. and Thangs, S.H., *Macromolecules*, 1998, 31(16): 5559
- 21 Rodahl, M., Höök, F., Krozer, A., Kasemo, B. and Breszinsky, P., *Rev. Sci. Instrum.*, 1995, 66: 3924
- 22 Daikhin, L. and Urbakh, M., *Faraday Discuss.*, 1997, 107: 27
- 23 Sauerbrey, G., *Z. Phys. A*, 1959, 155: 206
- 24 Bottom, V.E., "Introduction to quartz crystal unit design", van Nostrand Reinhold Co, New York, 1982, p. 50
- 25 Voinova, M.V., Rodahl, M., Jonson, M. and Kasemo, B., *Phys. Scr*, 1999, 59: 391
- 26 Zhang, P., Qian, J.W., Xuan, L.J., Bai, Y. X., An, Q.F. and Choi, P., *Chinese J. Polym. Sci.*, 2009, 27(3): 297
- 27 Sturat, M.A.C., Hoogendam, C.W. and Keizer, A.De., *J. Phys. Condens. Matter.*, 1997, 9: 7767
- 28 Liu, G.M. and Zhang, G.Z., *J. Phys. Chem. B*, 2005, 109: 743