

# Multifunctional Double Hydrophilic Triblock Copolymer in Solution and on Surface

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## INTRODUCTION

Block copolymers with specific architecture and functionality constitute versatile building blocks for fabricating thin films and/or responsive surfaces<sup>1</sup>. Double-hydrophilic block copolymers are a new class of functional polymers of rapidly increasing importance with unique and fascinating properties<sup>2</sup>. A simple synthetic route to prepare such polymeric species is to include in the macromolecular chain at least two different hydrosoluble monomers. More precisely, the combination of ionogenic monomers leads to block copolymers bearing oppositely charged blocks namely block polyampholytes<sup>3</sup>. In this communication we present the various possibilities of an asymmetric ABA polyampholyte to form a variety of transient macromolecular assemblies by switching the solution pH, temperature, ionic strength and dielectric constant. This multifunctional behavior may be proved useful for design and development of "smart" surfaces.

## EXPERIMENTAL PART

**Synthesis and Characterization.** A three-step synthetic procedure was followed to prepare the PAA-P2VP-PAA triblock polyampholyte. In the first and second steps a PtBA-P2VP-PtBA block copolymer was synthesized by "living" anionic polymerization using a bifunctional initiator and sequential addition of the monomers. 2VP was polymerized first by using sodium tetraphenyl diisobutane as the initiator at  $-75^{\circ}\text{C}$ . After the consumption of the 2VP monomer a small amount was sampled out and tBA was added and allowed to be polymerized at  $-65^{\circ}\text{C}$ . To ensure "living" conditions for the tBA polymerization a 5-fold LiCl to the initiator was present in the medium. The reaction was terminated with methanol and the polymer was precipitated in heptane, redissolved in benzene filtered and freeze-dried.

Size exclusion chromatography, Static light scattering and  $^1\text{H-NMR}$  were employed to characterize molecular weight and composition of the PtBA-P2VP-PtBA precursor copolymer.

At the third step the PtBA<sub>134</sub>-P2VP<sub>628</sub>-PtBA<sub>134</sub> precursor was subjected to acid-catalyzed hydrolysis in dioxane at  $80^{\circ}\text{C}$  in order to modify the PtBA end-blocks to poly(acrylic acid), PAA. The obtained PAA-P2VP-PAA copolymer was finally dissolved in water, purified by dialysis and freeze-dried. The degree of hydrolysis of the copolymer was determined by  $^1\text{H-NMR}$  and potentiometric titration and found to be 95% and 93,3%, respectively. Here after the final product will be designated as PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub>.

**AFM Measurements.** Multimode AFM 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 (5 nm in diameter).

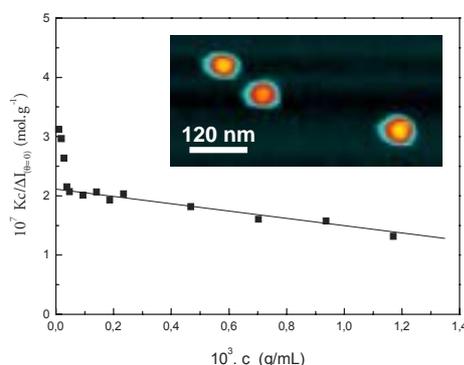
**Rheology.** The linear and non-linear rheological properties of the polymer solutions were studied using a stress controlled Rheometric Scientific SR 200, equipped with either a cone and plate geometry (diameter = 25 mm, cone angle =  $5.7^{\circ}$ , truncation = 56  $\mu\text{m}$ ) or a Couette geometry (gap = 1.1 mm)

## RESULTS AND DISCUSSION

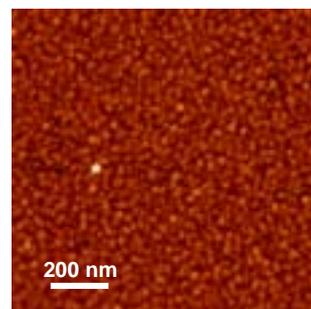
A well-defined asymmetric polyampholyte with a long P2VP central block end-capped with relative short PAA blocks was synthesized by anionic polymerization and investigated in aqueous solutions by the means of electroforesis, static and dynamic light scattering, (SLS, DLS) Rheology and Atomic Force Microscopy.

This double hydrophilic triblock copolymer undergoes various phase transitions by switching the solution pH, Temperature, ionic strength, and dielectric constant.

**High pH Regime.** At  $\text{pH} > 7$ , P2VP is hydrophobic while PAA is in positively charged state exhibiting an amphiphilic character. As Figure 1 shows the PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> copolymer is associated forming compact micelles with an aggregation number  $N=55$ , and hydrodynamic radius 37nm, as determined by SLS and DLS.



**Figure 1.** Concentration dependence of  $(Kc/DI)_{O=0}$  for PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> in water at the high pH regime at  $25^{\circ}\text{C}$ ; inset: shows the spherical micelles isolated on mica substrate. The images were obtained by AFM.

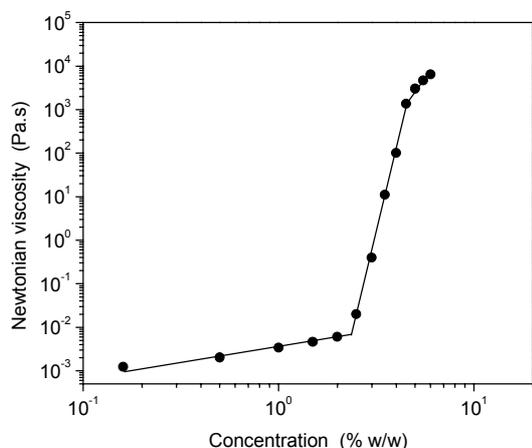


**Figure 2.** AFM image of nearly spherical particles deposited on mica from aqueous solutions of PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> at pH 5.

**Intermediate pH Regime.** At  $4 < \text{pH} < 7$  the z-potential for the colloidal solution passes from positive to negative sign (isoelectric region) and the isoelectric point (zero charge density) of the polyampholyte was determined to be at pH 5.5. At pH 5 and from dilute solution ( $c=2$  mg/ml) a uniform cover of mica with nearly spherical particles was observed (Fig 2).

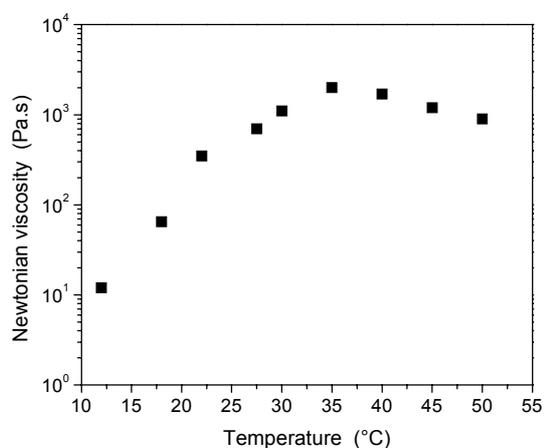
**Low pH Regime.** At  $\text{pH} < 4$  the P2VP central block is positively charged since 2-vinyl pyridine units are protonated and the copolymer exhibits a double hydrophilic character. At low concentration and at pH 3.4 the polyampholyte seems to be in

molecularly dissolved state. At higher concentrations a physical gel is formed as revealed by rheological measurements. In Figure 3 the Newtonian viscosity is plotted as a function of concentration. The viscosity rises abruptly about 6 orders of magnitude above  $C_{gel}=2.4$  wt%. This novel behavior is attributed to the formation of a transient network through electrostatic interactions.



**Figure 3** Double logarithmic plot of the zero shear viscosity,  $\eta_0$ , as a function of concentration for the PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> in water at pH 3.4 and 25°C.

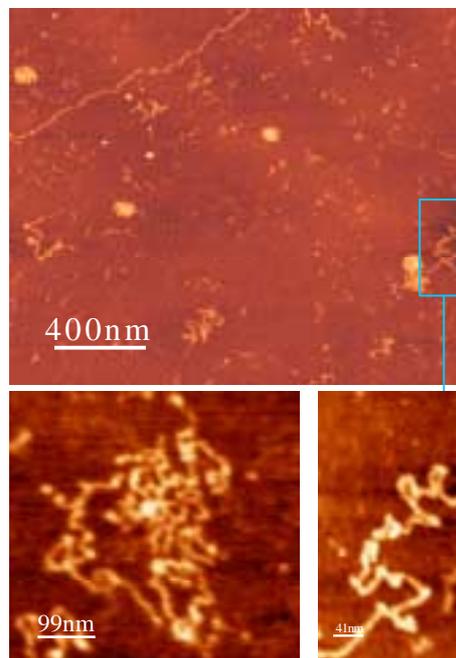
The system also exhibits a very interesting thermo sensitive behavior of different nature from that observed by copolymers bearing polymeric blocks with LCST<sup>4</sup>. As it is shown in Figure 4 the Newtonian viscosity increases about 2 orders of magnitude from 15 to 35 °C and then decreases smoothly with T.



**Figure 4.** Zero shear viscosity,  $\eta_0$  as a function of temperature of the PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> in water (c=4 wt%) at pH 3.4.

This behavior should be attributed mainly to the PAA units which exhibits UCST close to room temperature (Theta temperature 15 °C). At low T, PAA is in the unperturbed coil conformation that prevents the development of the electrostatic interactions. As T rises PAA expands giving rise to the formation of physical electrostatic cross-links. In other words transitions from dangling ends to elastically active chains occur. This network strengthening is completed at 35 °C beyond of which the thermal motion effect predominates.

Another unusual self-organization of the copolymer was observed by AFM imaging analysis at very low concentration and at pH 2. At these conditions P2VP is fully protonated behaving as polyelectrolyte (adopting a stretched conformation<sup>5</sup>) while PAA is in uncharged state close to the theta temperature with hydrogen bonding capability. The AFM images revealed for the first time an unusual *head to tail* association. As one can observe in Figure 5, long linear associates in extended and/or coiling mode have been isolated on a mica surface.



**Figure 5.** AFM images of single molecules and associates deposited on mica from dilute aqueous solution of PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> at pH 2.

We currently investigate another possibility by switching the dielectric constant of the solvent. At high pH and passing from water to methanol the micellar hydrophobic P2VP core will swell while counter ion condensation will occur on the charged PAA end-blocks (ionomer) imposing the transformation of the structure.

## CONCLUSIONS

We have demonstrated that PAA<sub>134</sub>-P2VP<sub>628</sub>-PAA<sub>134</sub> exhibits a variety of different transient nano assemblies in water such as spherical particles surrounding by negatively charged moieties, a stimuli responsive physical network and *head to tail* associates. All these assemblies are reversible adapting their structure by switching the environment conditions and could be used as building blocks to fabricate functional surfaces.

## ACKNOWLEDGEMENTS

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