

Supporting Information to

“pH Responsive self assemblies from A_n -core-(B-*b*-C)_n heteroarm star block terpolymer bearing oppositely charged segments”

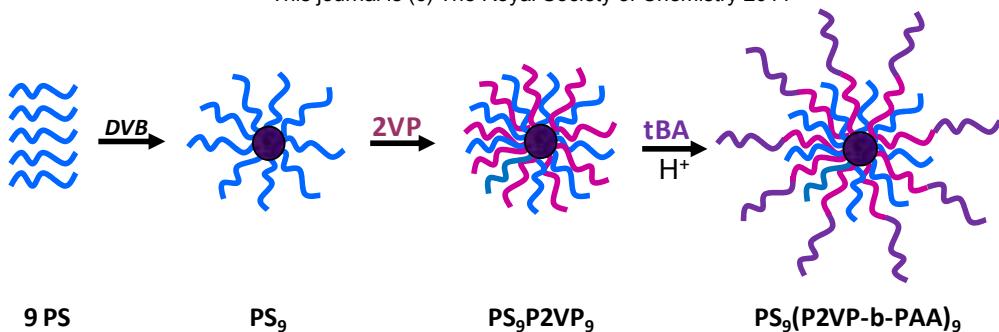
Zacharoula Iatridi^a and Constantinos Tsitsilianis*^{a,b}

^a Department of Chemical Engineering, University of Patras, 26504 Patras, Greece. Fax: +30 2610 997266; Tel: +30 2610 969531; E-mail: ct@chemeng.upatras.gr

^b Institute of Chemical Engineering and High Temperature Chemical Processes ICE/HT-FORTH, P.O. Box 1414, 26504 Patras, Greece.

Materials

An extended “in-out” method was followed for the synthesis of the $(PS_{33})_9$ -PDVB-(P2VP₁₂₆-*b*-PAA₆₉)₉ heteroarm star block terpolymer as reported elsewhere.¹ Briefly, the star terpolymer was prepared by “living” anionic polymerization in a one-pot/four-step reaction and subsequently easy deprotection of the t-butyl-acrylate moieties of the third block by acidic hydrolysis (Scheme S1). In the first step, the PS arms were prepared in THF, using s-BuLi as the initiator. After the consumption of styrene, the ‘living’ PS chains were used to polymerize a small quantity of DVB (crosslinking agent), resulting in a ‘living’ star-shaped polystyrene precursor (PS_n) bearing active sites in its PDVB core. In a next step, the ‘living’ star was used to polymerize 2VP, leading to the formation of a second generation of P2VP arms. The sites located at the end of P2VP arms were used to polymerize tBA. The final $(PS_{33})_9$ (P2VP₁₂₆-*b*-PAA₆₉)₉ terpolymer was obtained after acidic hydrolysis of the PtBA blocks in 1,4-dioxane with a 6 fold excess of hydrochloric acid at 80 °C. The terpolymer was characterized by means of size exclusion chromatography (SEC) and static light scattering (SLS). The results are presented in Table S1.



Scheme S1. Schematic representation of the multistep synthetic procedure for the synthesis of $A_n(B-C)_n$ heteroarm star block terpolymer.¹

Table S1. Molecular characteristics of the $PS_9(P2VP-*b*-PAA)₉$ star block terpolymer.¹

Polymer	Number of arms (average)	M_w	Degree of polymerization
$PS_{(arm)}$		3400 ^a	33
PS_9	9	31500 ^b	
PS_9P2VP_9	18	153000 ^b	
$P2VP_{(block, arm)}$		13200 ^c	126
$(PS)_9(P2VP-b-PtBA)9$	18	235000 ^b	
$(PS)_9(P2VP-b-PAA)9$	18	199000 ^d	
$PAA_{(block, arm)}$		5000 ^e	69

^a Determined by SEC. ^b Determined by SLS. ^c Calculated by subtracting the M_w of the PS_9 from that of PS_9P2VP_9 and dividing by the number of arms (9.2). ^d Calculated from the M_w of the $(PS)_9(P2VP-*b*-PtBA)₉$ precursor assuming quantitative hydrolysis of the tBA moieties. ^e Calculated by subtracting the M_w of the PS_9P2VP_9 from that of $(PS)_9(P2VP-*b*-PAA)₉$ and dividing by the number of arms (9.2).

Sample Preparation

The experiments in aqueous solutions were conducted in H_2O using distilled Millipore MILLI-Q water. The $(PS_{33})_9-PDVB-(P2VP_{126}-*b*-PAA_{69})_9$ star terpolymer was firstly dissolved in DMF. Afterwards, enough quantity of 0.01 M aqueous HCl solution was slowly added into the DMF solution so as to achieve a 3/7 volume ratio of DMF/ H_2O . The prepared solution was then dialyzed against 0.01 M HCl solution for 6 days to remove DMF, using a dialysis membrane (cutoff 12.000). The resultant mother solution, having pH 2 and a polymer concentration of 0.658 wt%, was again dialyzed against aqueous solutions of different pH values, varying from pH 1.4 to 11.8.

Zeta potential

Zeta-potential measurements were carried out at 25 °C by means of a NanoZetasizer, Nano ZS Malvern apparatus. The excitation light source was a 4 mW He-Ne laser at 633 nm and the intensity of the scattered light was measured at 173°. A series of $(\text{PS}_{33})_9(\text{P2VP}_{126}-b-\text{PAA}_{69})_9$ solutions of different pH values ranging from 1 to 12 and at a concentration of 0.3 wt% were prepared in H₂O in order to determine the phase behavior and the *iep*.

Transmission Electron Microscopy (TEM)

High Resolution Transmission Electron Microscopy (TEM) experiments were carried out using a JEM 2100 microscope operating at 200 kV. For TEM, very dilute aqueous solutions (0.007 wt%) were used. A drop of the dilute solution was deposited onto a Formvar-coated copper grid and allowed to evaporate at room temperature.

In order to ensure that the preparation procedure does not affect the observed morphologies, a drop of a 0.07 wt% $(\text{PS}_{33})_9(\text{P2VP}_{126}-b-\text{PAA}_{69})_9$ aqueous solution at pH 2.0 was deposited onto a Formvar-coated copper grid and the excess liquid was removed by blotting. The TEM images i.e. patchy multicore micelles of c.a. 150 nm in radius, obtained from this procedure (Fig. S1b) is similar to those obtained by evaporation (Fig. S1a). Similar images were obtained from stars of the same nature but of different number of arms, i.e. $(\text{PS}_{34})_{22}-PDVB-(\text{P2VP}_{136}-b-\text{PAA}_{119})_{22}$ (Fig. S1c), which support further our TEM results. Thus, the presented morphologies are reproducible and seem to be independent on the method of preparation.

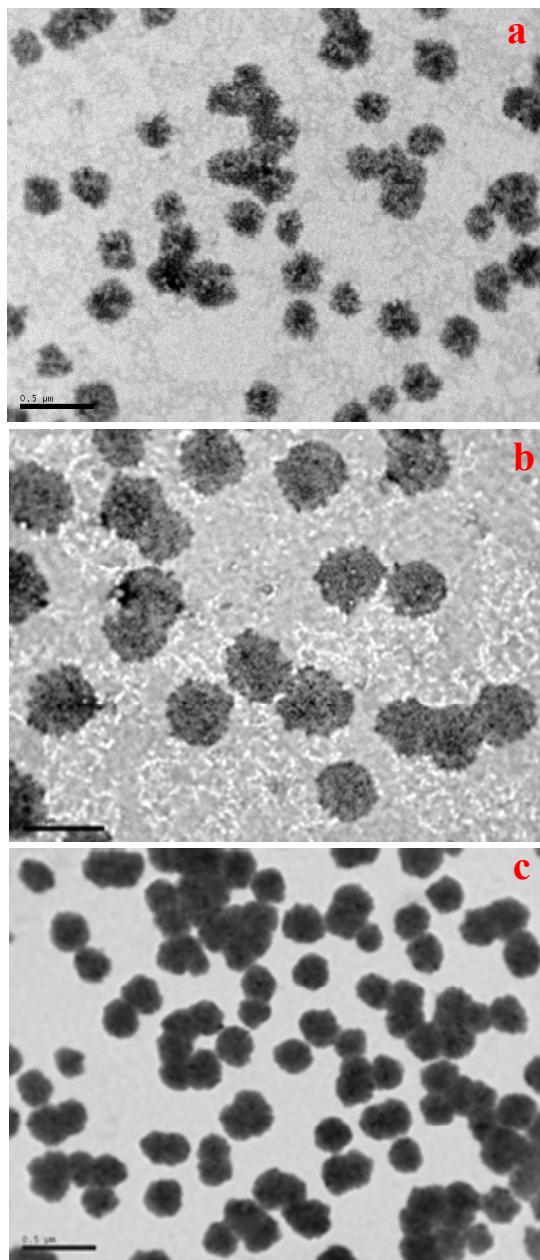


Fig. S1. TEM images of $(PS_{33})_9-PDVB-(P2VP_{126}-b-PAA_{69})_9$ (a,b) and $(PS_{34})_{22}-PDVB-(P2VP_{136}-b-PAA_{119})_{22}$ (c) aqueous solutions at pH 2.0. The samples were prepared: by evaporation (a,c) or by blotting (b). Scale bars indicate 500nm.

Additional images demonstrating the worm like structures observed at pH 1.6 are presented in Fig. S2.

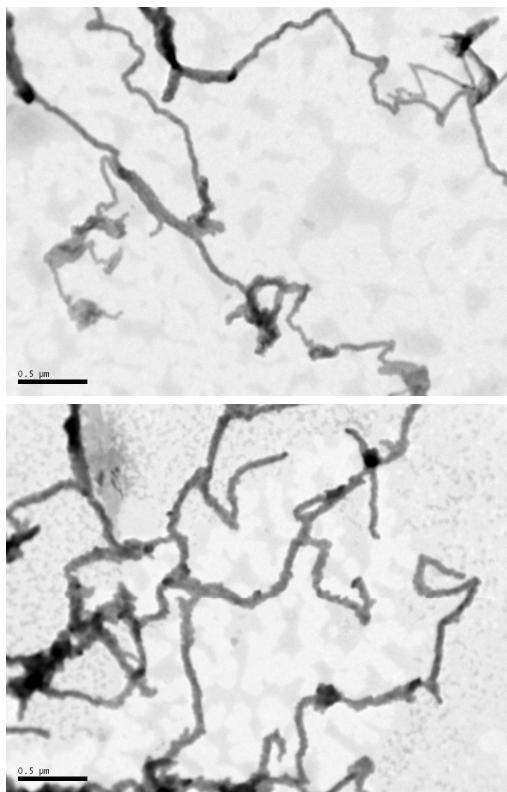


Fig. S2. TEM images of 0.007 wt% star terpolymer aqueous solution at pH 1.6

Dynamic Light Scattering (DLS)

Autocorrelation functions $g(q,t)$ were measured with a Brookhaven BI-9000AT/Turbocorr digital correlator from a light source of He-Ne laser (632.8 nm). CONTIN analysis was performed through BI-DLSW software. The apparent hydrodynamic radius was determined via the Stokes-Einstein equation:

$$R_H = k_B T / 6\pi\eta D_{app}$$

where D_{app} is the diffusion coefficient, k_B is the Boltzmann constant and η is the viscosity of the solvent at absolute temperature T .

For the DLS measurements, samples of 0.007 wt% $(\text{PS}_{33})_9(\text{P}2\text{VP}_{126}-b-\text{PAA}_{69})_9$ aqueous solutions at pH 2.0 and 8.5 were used after having been filtered through 0.45 μm hydrophilic filters. The characteristic autocorrelation functions, along with the apparent micelle size distributions (through CONTIN analysis) are presented in Figures S3 and S4. At pH 2.0 and at room temperature (25°C), the formed micelles

demonstrated broad size distribution (inset of Fig. S3a). The high R_H values were in good agreement with the sizes of the micelles observed by TEM in Fig. 2c,d. Upon heating at 45°C the size distribution was shrunk significantly and the mean size determined was similar to that of the unimolecular micelles. This effect is reversible (i.e. returning to 25°C the distribution becomes again broad), confirming our assumption that the driving force for the formation of the large compound micelles (LCM) is H-bonding coronal interactions.

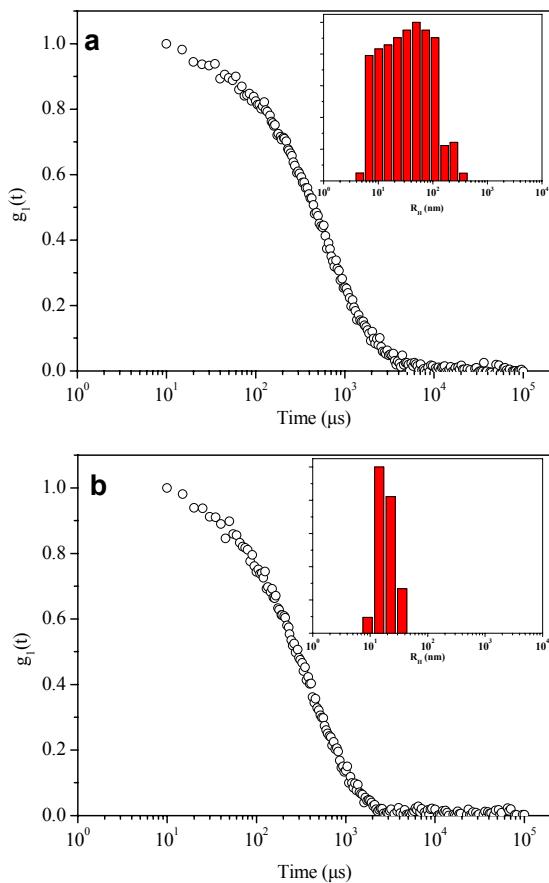


Fig. S3. Autocorrelation function of 0.007 wt% star terpolymer aqueous solution at pH 2.0 at 25°C (a) and at 45°C (b). Inset: Distribution of the hydrodynamic radius, R_H .

In Fig. S4, DLS results obtained at pH 8.5 shows broad size distribution which is consistent with the TEM image (Fig. 3b), indicating the tendency of the star terpolymer to form a network-like structure.

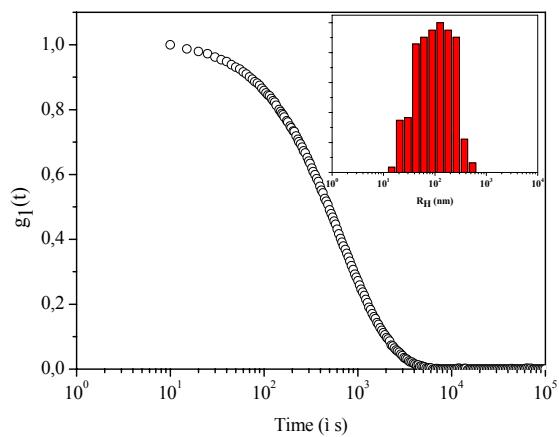


Fig. S4. Autocorrelation function of 0.007 wt% star terpolymer aqueous solution at pH 8.5. Inset: Distribution of the hydrodynamic radius, R_H .

References

1. N. Stavrouli, A. Kyriazis, C. Tsitsilianis, *Macromol. Chem. Phys.*, 2008, **209**, 2241.