SUPPORTING INFORMATION

Asymmetrical Self-assembly From Fluorinated and Sulfonated Block Copolymers in Aqueous Media

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CONTENTS:

Experimental Details

Materials

Styrene (Aldrich, 99%), isoprene (Fisher, 98%), cyclohexane (Fisher, 99%) and methanol (Fisher, ACS certified) were purified according to standard procedures[1] for anionic polymerization. *sec*-Butyllithium was synthesized[1] and its concentration was determined by anionically polymerizing styrene and measuring the number-average molecular weight of the product. Hexafluoropropylene oxide (HFPO, Aldrich, 98%), 2,6-di-*tert*-butyl-4-methylphenol (BHT, Aldrich, > 99.0%), 1,2-dichloroethane anhydrous (DCE, Aldrich, 99.8%), acetyl anhydride (Aldrich, 99.5%) concentrated sulfuric acid (Aldrich, ACS regent 95 to 98%), sulfur trioxide (Aldrich, 99%), triethyl phosphate (99.8%, Aldrich) were used as received.

Synthesis of Diblock Copolymer of Styrene and Isoprene

The diblock copolymers of styrene and isoprene were prepared by sequential polymerization of these monomers *via* high vacuum techniques[2]. The main reactor was washed with *n*-butyllithium solution in cyclohexane to remove impurities on the glassware, followed by rinsing with distilled cyclohexane from a purge flask. Solvents were finally collected from purging solution of *n*-butyllithium. A typical procedure for preparation of diblock copolymer PS-*b*-PI is as follows.

All reagents in ampoules, including styrene, isoprene, initiator and methanol, were attached to the reactor and introduced at the appropriate time by breaking a break-seal. Polystyryllithium was generated by reacting *sec*-BuLi with styrene in cyclohexane.

The immediate red color of the solution indicated successful initiation followed by propagation of styrene. This reaction solution was left overnight at room temperature to ensure complete consumption of styrene. Small aliquots of solution were sampled before isoprene was charged for characterization of the polystyrene block. Upon addition of isoprene, the color changed from red to pale yellow indicating the initiation of the isoprene block. Isoprene polymerization was allowed to proceed overnight at room temperature and was quenched by addition of methanol. Finally, diblock copolymer products were recovered by pouring the reaction solution into a 10-fold excess of methanol containing BHT (0.1%, w/v), filtered, dried in vacuo at 50 ºC. Size Exclusion Chromatography (SEC), Figure SI1.

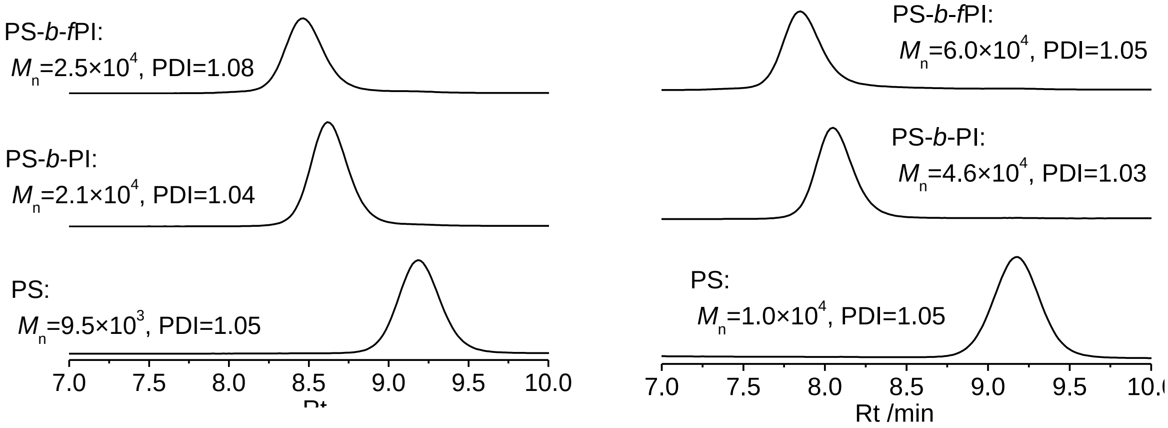

Figure SI1 Size exclusion chromatography of PS, PS-*b*-PI, PS-*b*-*f*PI. Left, samples in Series1; Right, samples in Series 2 in Table SI1.

Fluorination of Block Copolymer of Styrene and Isoprene

Fluorination of polyisoprene blocks of block copolymers was conducted in a high pressure Parr reactor at 180 ºC under magnetic stirring. A typical fluorination reaction is described as follows. 4.06 grams of PS-*b*-PI block copolymers (isoprene units, 1.89g, 0.028 mol) were added into the reactor along with 0.19 grams of BHT (~10 wt % of polyisoprene), both of which were dissolved in 200 ml of purified cyclohexane. The reactor was assembled, purged with pure N_2 for about 0.5 hours to remove oxygen, and then was sealed. After the system was frozen, the reactor was degassed for about half an hour in order to remove residual traces of oxygen, more importantly, to create a vacuum for readily charging the fluorination reagent hexafluoropropylene oxide (HFPO, 51.8g, 0.31mol) through the inlet of the reactor. The amounts of HFPO added were monitored during the process of transferring HFPO into reactor. The accurate mass added into reactor was obtained by weighing the HFPO tank before and after transferring. The solution was thawed using a hot water bath to room temperature, followed by heating to 180 ºC, and was maintained at this temperature for 4 hours. The reaction was quenched by cooling the system with ice water bath to room temperature. The pressure and the excess of HFPO were released by bubbling through a 10 wt % NaOH aqueous solution before the reactor was opened. The reaction solution was filtered, concentrated by rotary evaporation, and precipitated into large amounts of methanol or a mixture of methanol/2-propanol (1/2, v/v). The recovered polymers were dried under vacuo at 50 ºC overnight. Yield, 5.05 g, 92.7 %; SEC, Figure SI1 (left).

Sulfonation of Polystyrene Blocks of Block Copolymers

Two methods were applied for obtaining different degrees of sulfonation. One method, utilizing acetyl sulfate developed by Makowski[3], was applied to sulfonate polystyrene blocks. Low and medium sulfonation degrees (SD, molar percent of sulfonated styrene units, 0 – 60%) were achieved by this method. For high degrees of sulfonation (60% –

100%), the complex of sulfur trioxide and triethyl phosphate was used as sulfonating reagent[4,5]. Typical reactions were run as follows.

Acetyl sulfate method (Series1-SD57.0): A three-necked round flask dried at 80 ºC was equipped with an inlet of high purity nitrogen, a condenser with outlet of N_2 to bubbler, magnetic stirring bar, and the third neck was sealed with a septum and was easy to open for the purpose of sampling the reaction solution. Block copolymers (1.0 g, styrene units: 0.40 g, 3.85 mmol) and 10 ml of 1,2-dichloethane were added into the reactor after the empty reactor was purged with N_2 for about 20 min. The reactor then was immersed into a water bath thermostated to 50 ºC and was stirred for about 30 – 60 min. Acetic anhydride (3.63ml, 38.4 mmol) was injected drop-wise into the solution, which was then stirred for 10 min, followed by drop-wise addition of sulfuric acid (2.0g, 20 mmol) under a slight flow of N_2 over 10 min with strong stirring. After a couple of minutes, the solution changed from colorless to yellow-brownish; no polymer was precipitated out of the solution during the entire period of reaction. After stirring at 50 ºC for 2 – 5 hours, depending on the sulfonation degree desired, the reaction was quenched by cooling the reactor with ice water and by injection of several milliliters of methanol into the solution For each reaction, the solution was sampled and tested by ^{1}H-NMR to confirm the desired SD before quenching. Sulfonation degree was monitored by sampling the solution out over a period of time. Solid polymers for ^{1}H-NMR were recovered by precipitating the sampled solution into hexane, followed by dissolution in *d*-DMSO. Monitoring of SD by ^{1}H-NMR, Figure SI2; yield after purification (see below), 1.01g, 85.1 %.

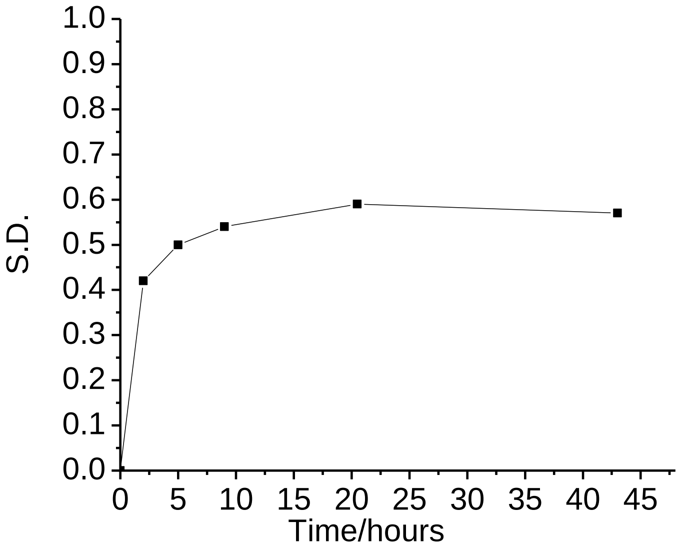

Figure SI2 Sulfonation degree (SD) monitored as a function of time in acetyl sulfate method.

Sulfur trioxide/triethyl phosphate complex method (Series 1-SD98.0): TEP (0.2 equiv, 0.14g) in DCE (7 ml) was placed in a flask equipped with two addition funnels (one of them was connected to N_2 outlet to bubbler), a condenser with N_2 inlet, and a magnetic stirring bar and was cooled to 0 °C using an ice bath. Copolymer (1.0 g, 1.0 equiv and 0.4g of PS) was dissolved in DCE (20 ml) and placed in one addition funnel. SO_3 (1.5 equiv. 0.45g) in DCE (7 ml) was placed in the other addition funnel. The SO_3 solution was added first at about 1 to 2 drops per second. Polymer solution was added a few seconds later at the same rate with stirring. Then both solutions were alternatively added, while keeping the solution at 0 °C. After completing addition of reagents, the solution was kept at 0 °C and stirred for another hour, followed by injecting several milliliters of methanol to quench the reaction. Yield after purification, 1.23g, 100%; SD: 98% by ^{1}H-NMR.

Purification: Dialysis of Polymer Solution

After the reaction was quenched, the dichloroethane solvent was removed by rotary evaporation until residuals in flask stopped bubbling, followed by dissolving the residuals in about 5 to 10 ml of THF, forming a clear transparent solution. About an equal volume of distilled water was added into this solution (or the THF solution was slowly dropped into water). If the solution formed in this way was milky and opaque, it was subjected to rotary evaporation again to remove possible traces of DCE until either cloudiness disappeared or the solution stopped boiling. In the case of the latter situation, about an equivalent amount of THF was added into the solution in order to cause the milky solution to become clear and transparent. The polymer solutions in water/THF mixtures were dialyzed against deionized water over 72 hours with regular changes of water in order to remove small molecules such as sulfuric acid. As the dialysis proceeded slowly, it was observed that the solution in the dialysis tubing became clearer and clearer, in some cases solutions undergoing gel formation, followed by reverting back to a readily flowing solution. Finally, polymers were recovered by lyophilization. The yield was obtained basing on SD which was measured by ^{1}H-NMR prior to calculation.

Self-assembly of Block Copolymer in water

Solutions of 0.5 – 1% (w/v) concentration were made using HPLC grade THF. Deionized water was slowly added at 0.3 ml/min by a syringe pump into the polymer solution with vigorous stirring until 50% by volume of water was added. The entire process of addition of water was monitored by shining a laser (lecture use laser point) through the solution in order to observe the Tyndall Effect which is a good indication if colloidal particles were present in the solution, block copolymer aggregates in our case. The Tyndall effect was always found for all of samples investigated, which means that no molecularly dissolved state was achieved over the entire range of solvent composition. After addition of water, the solution was dialyzed against deionized water to remove THF for three days. The concentration of the polymer was calculated from the volume of dialyzed solution and mass of polymers initially added.

Characterization

Number-average molecular weight M_n, polydisperstiy index M_w/M_n (PDI) of all samples before sulfonation were determined by size exclusion chromatography using a Tosoh EcoSEC instrument which was equipped with two TSKgel Super Multipore HZ-V columns calibrated using standard polystyrenes with M_n from 580 to 7.5×10^6 g/mol. The polymer was eluted in THF at 40 ºC at a flow rate of 0.35 ml/min.

^{1}H-NMR spectroscopy was performed on Varian Mercury 300 MHz spectrometer with deuterated dimethylsulfoxide (DMSO-d_6) as solvent. Element analysis (EA) was conducted by Galbraith Laboratories Inc for sulfur content (Table SI2).

Dynamic light scattering (DLS) was used to characterize hydrodynamic diameter (D_h) of the aggregates of the fluorinated and sulfonated polymer solution in THF and water (Table SI3). D_h of the polymers at 25 °C was measured on a PD Expert instrument (Precision Detectors) at a scattering angle of 45° or 95°. The diameters and polydispersity indices (PDIs) were averaged over 10 repetitive measurements. The concentration of the solutions used for DLS was about 0.05–1.2 mg/ml and 8.7 mg/ml (initial concentration for self-assembly before water was added) in water and THF, respectively. It was found that D_h is essentially independent of concentration of polymers in aqueous solution, giving quite close D_h values. All the samples were filtered using a 0.45 µm Millipore nylon membrane. For the freshly made solution of sample Series 2-SD 29.6, the concentration dependence of D_h was measured with concentrations ranging from 5 µg/ml – 0.5 mg/ml after aging 4 days. Multiple populations of micelles existed through the whole range of concentrations (Figure SI8).

Transmission electron microscopy (TEM) was performed using a Hitachi H-800 instrument with 75 Kev voltage. TEM samples were prepared by depositing a droplet (1-4 µl, 0.5 or 1.2mg/ml) of aqueous solution of polymer on copper grid which was coated by a carbon film, then dried overnight. Atomic force microscopy (AFM) experiments were performed using a Nanoscope IIIa Microscope with Multimode Controller (Veeco Intrument) at ambient temperature and humidity. The tapping mode was employed with an antimony-doped Si tip (radius < 10 nm) at a line scanning frequency of 1 Hz. The set point of amplitude of the cantilever was set to just capture the real morphology of the aggregates and avoid applying excess force to the objects which might lead to squeezing between scanning target and substrate. After the TEM observation, the same grid was taped to a metal disk substrate, and then was applied for AFM scanning.

Table SI1 Characteristics of Block Copolymers: PS-*b*-PI, PS-*b*-*f*PI, and *s*PS-*b*-*f*PI

Series[a]	PS-*b*-PI			PS-*b*-*f*PI		*s*PS-*b*-*f*PI
	M_n(SEC)	PDI	f[b]	M_n(SEC)	PDI	SD
1	2.1×10^4	1.04	0.50	2.5×10^4	1.08	13.4
						38.8
						98.0
2	4.6×10^4	1.03	0.23	6.0×10^4	1.05	29.6
						45.4
						80.0

[a], series1 in acid form; series2 in Na form. [b], f, volume fraction of polystyrene in PS-*b*-PI

Table SI2 Sulfur content analysis by HNMR and EA (%)

Analysis / Sample	Series-SD17.8	Series-SD57.0	Series-SD98.0
^{1}H-NMR	2.09	6.00	9.09
EA	2.55	6.16	8.22

Table SI3 D_h of aggregates in THF and Water at 25 ºC

Solvent / Sample	Hydrodynamic diameter (nm)		
	Series1-SD13.4	Series1-SD38.8	Series1-SD98.0
THF	6.0	7.5/150.6	20.6
Water	231	252	260

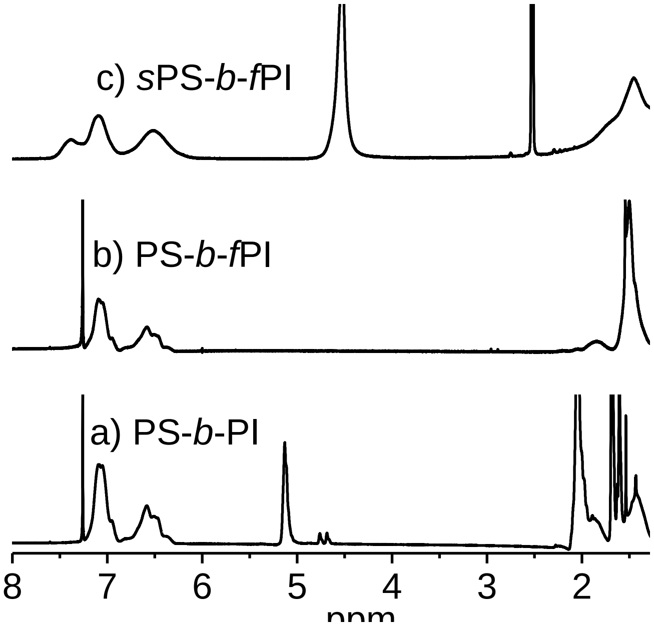

Figure SI3 ^{1}HNMR spectra of (a) precursor PS-*b*-PI, in CDCl$_3$, (b) fluorinated PS-*b*-PI: PS-*b*-*f*PI, in CDCl$_3$, (c) fluorinated and sulfonated PS-*b*-PI: *s*PS-*b*-*f*PI, in *d*$_6$-DMSO

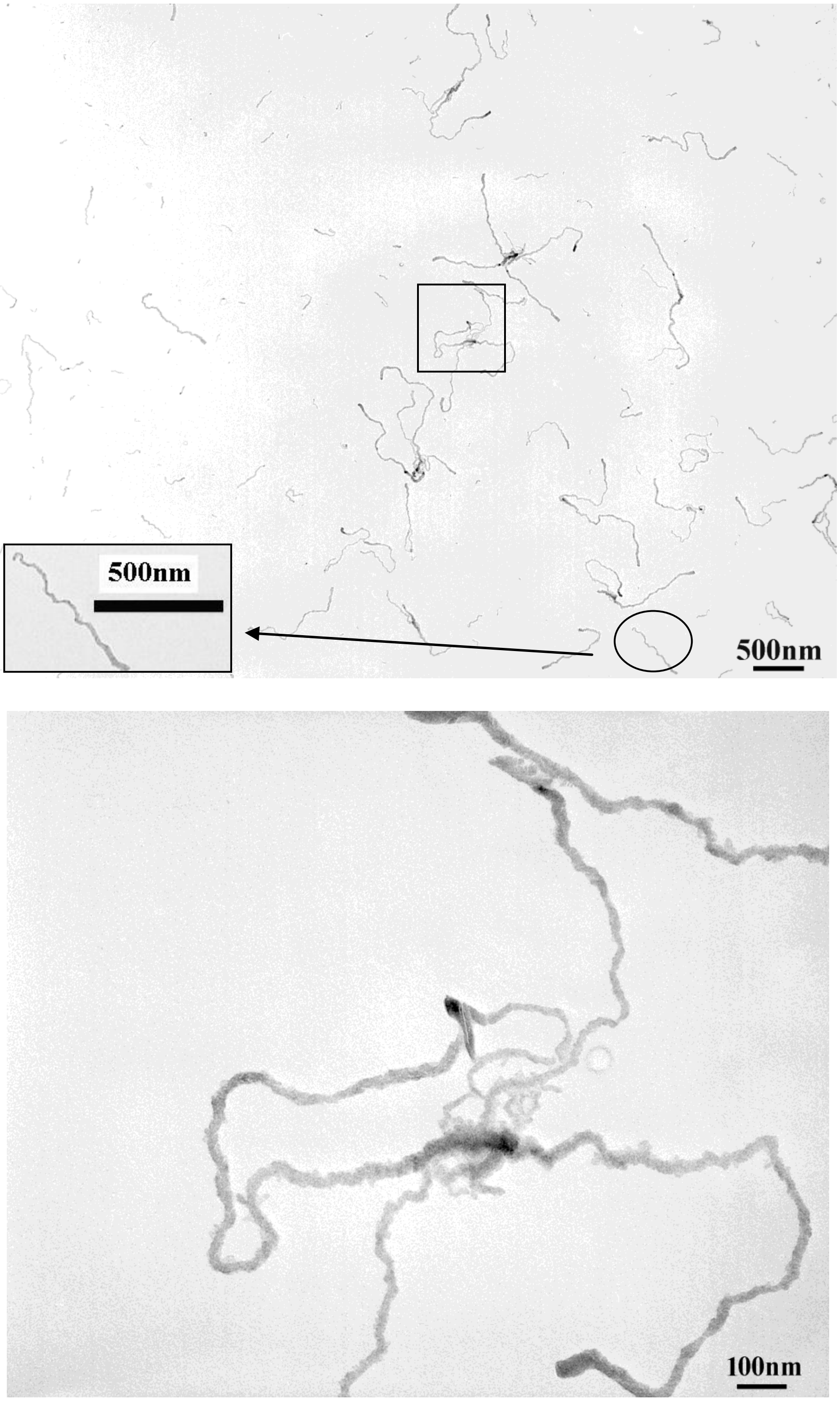

Figure SI4 Large area TEM image same as the one shown in main text(Figure 1(b)) and TEM image of the postion squared with high high magnification.

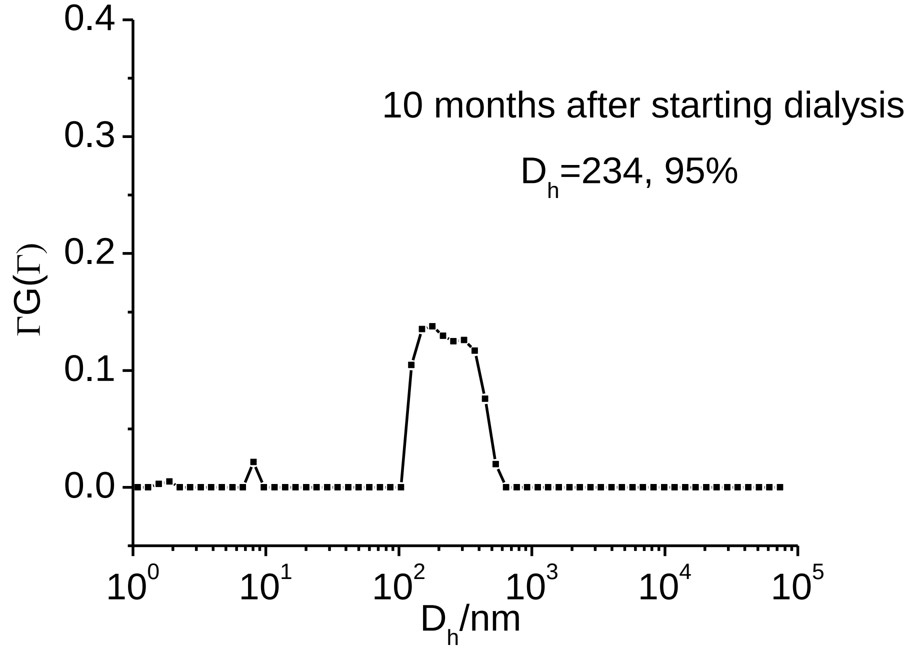

Figure SI5. 10 months after starting dialysis for sample Series1-SD38.8 in aqueous solution.

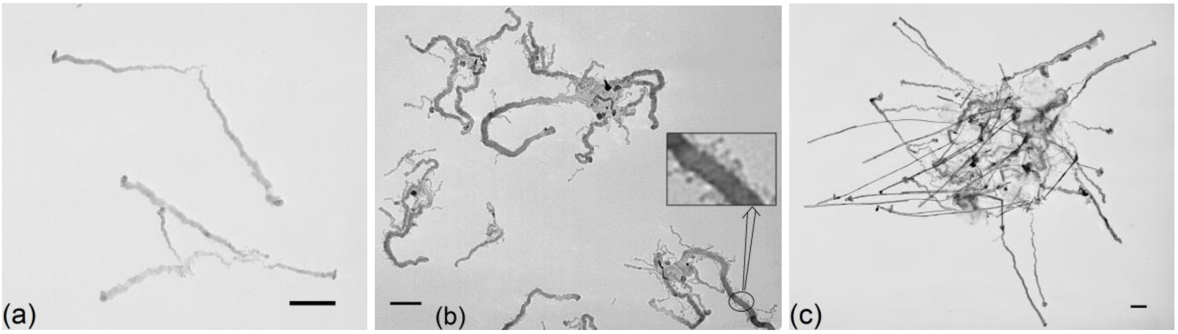

Figure SI6. TEM images of Series 2-SD29.6, three different morphologies were observed after aging 60 days: a) extended tapered rods; b) hairy worms; c) smooth rigid “fibers”. Scale bar 250 nm

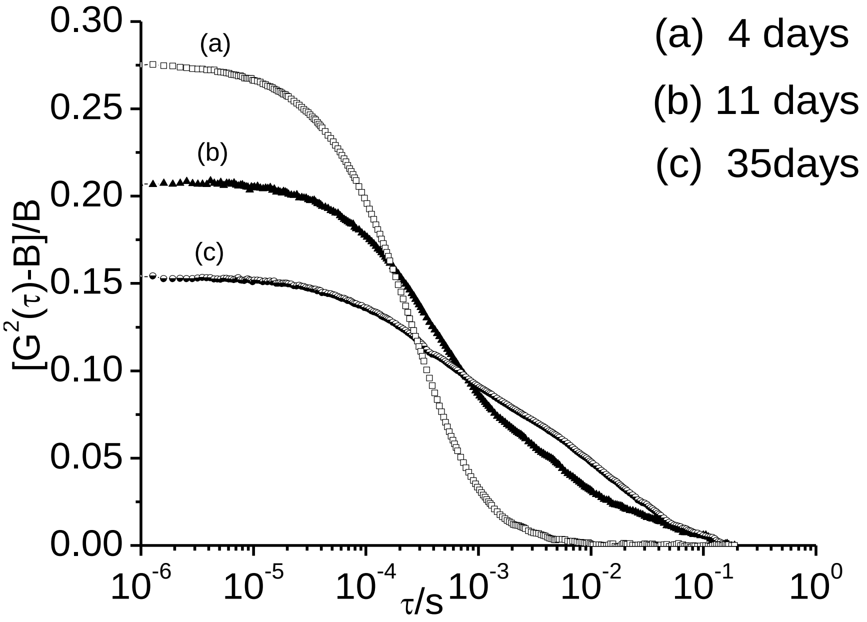

Figure SI7. Intensity-intensity time correlation functions by DLS at 45° scattering angle as a function of time: (a) 4 days;(b) 11days; (c) 35 days of sample Series 2-SD29.6 at 0.5 mg/ml.

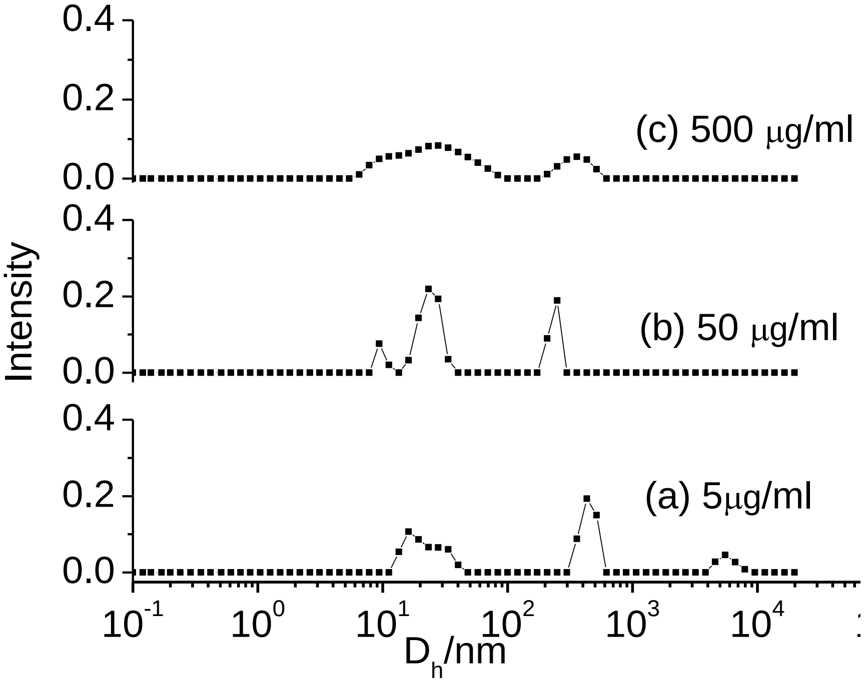

Figure SI8. Concentration dependence of D_h distributuions of freshly made sample Series 2-SD29.6 at a) 5 ug/ml; b) 50 ug/ml, c) 500ug/ml after aging 4 days.

Simulation studies: In order to develop a better understanding of the underlying mechanisms responsible for the morphology, we examined the structural evolution of the charged copolymer systems using Stochastic Molecular Dynamics (MD) simulation in the canonical ensemble (constant NVT). The MD simulations are carried out for a diblock copolymer melt system of chain length 64 with A and B blocks having 32 monomers each. The second block is charged with 28.1% and 46.9% charges respectively. The initial configurations are randomly generated with a number density of monomers $\rho\sigma^3 = 0.5$ (in solution) with equal number of counterions distributed in the system. All the monomers of the system have mass m_i and diameter σ. Polymer chains are modeled following the Kremer-Grest bead spring polymer model[6] in which bonded beads are connected by finitely extensible non-linear elastic (FENE) springs represented by $U^{FENE}_{ij}(r_{ij}) = -0.5\kappa R_0^2 \ln[1-(r_{ij}/R_0)^2]$, where $R_0 = 1.5\sigma$ is the finite extensibility and $\kappa = 37.5\varepsilon/\sigma^2$ is the spring constant. The energetic interaction between any pair of uncharged monomers beads is modeled by a truncated shifted Lennard-Jones potential, $U^{LJ}_{ij}(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + 1]$. Where ε is specific to two different blocks, ε_{AA} and ε_{BB} are 2.0 and 4.0 respectively with the Lorentz-Berthelot mixing rules applied for cross interactions. For the charged sites, explicit Coulomb interactions have been considered for which Ewald summation techniques are used. The electrostatic interactions are modeled via Coulomb potentials: $U_{ij}^{C}(r) = q_iq_j/Dr$, where D is the dielectric constant. Temperature is the first energy parameter of the system. We introduce a second energy parameter, $\xi_B = q^2/(D\varepsilon\sigma)$, which is also the strength of Coulomb interaction and inversely proportional to dielectric constant. This interaction strength is directly proportional to the Bjerrum length which is the ratio between electrical energy and kinetic energy of a charged monomer. The motions of the particles are governed by classical Newton-Langevin equation: $m_i d\mathbf{v}_i/dt = - U_i(r) - \Gamma d\mathbf{r}_i/dt + \mathbf{W}_i(t)$, where U_i is the potential, Γ is the friction coefficient between the chain monomer and background solvent and $\mathbf{W}_i(t)$ represents a Gaussian ‘white noise’ with zero mean acting on each particle. The last two terms couple the system to a heat bath where the friction term acts as a ‘heat sink’ and the noise term acts as a heat source. The advantages of this scheme, is that the natural MD integration time steps are larger, thereby permitting simulation at a longer time scales. On this time scale, only the mean effect of the stochastic forces acting on the system needs to be considered, leading to a first order temperature relaxation which in tern reduces the need of an external thermostat. The dimensionless units are defined as follows, $t^* = t/\sqrt(m_i\sigma 2/\varepsilon)$, $r^* = r\sigma^3$, $T^* = k_BT/\varepsilon$, $U^* = U/k_BT$ and $r^* = r/\sigma$.

For high dielectric constant, snapshots of the simulation are shown in Figure SI 8 at the end of the run. The figures show preferential formation of flat interface demonstrating chain stretching away from the interface caused by increasing interfacial tension between the blocks.

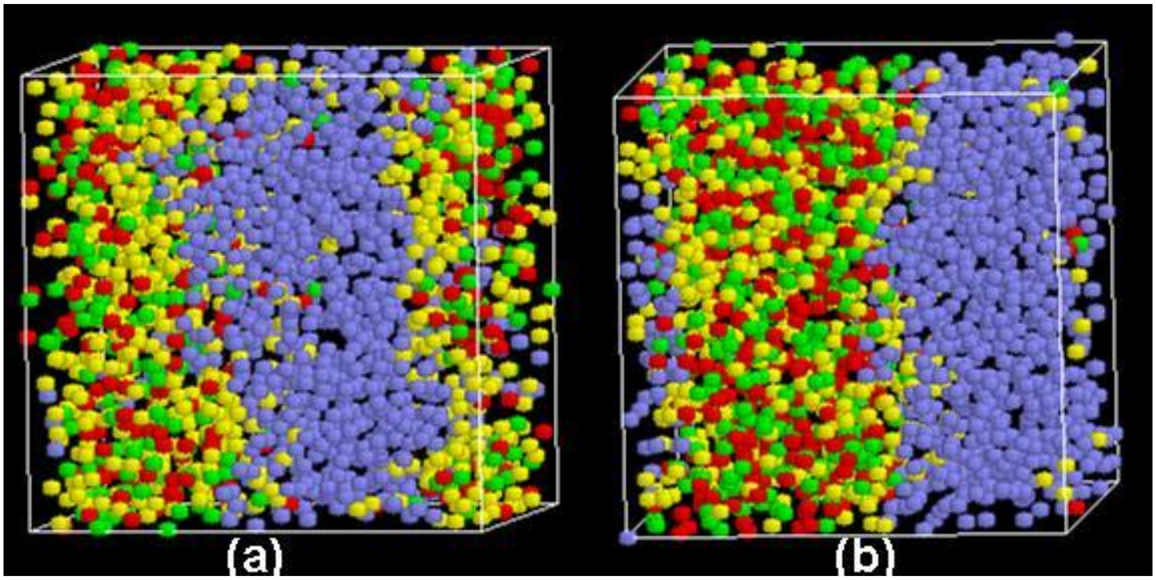

Figure SI9: Snapshot of the system at the end of the simulation run for (a) 28.1% and (b) 46.9% of charges on the charged block. The diblock consists of 50-50 uncharged and charged blocks. The blue dots are uncharged block, red dots are the counterions and the yellow and green dots are the uncharged and charged monomeric sites of the charged block. A comparatively flat interface are seen to be formed preferentially with micro phase separated charged and uncharged block. The higher charged states on the charged block forms flatter interface.

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