Salt-Induced Switching of Microdomain Morphology of Ionically Functionalized Diblock Copolymers

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Introduction. Block copolymers exhibit a variety of ordered morphologies in the microphase separated state.[1,2] For strongly segregated diblock copolymers, the symmetry of these periodic microstructures strongly depends on the volume fraction ϕ of the blocks. Spherical microdomains occur for low volume fractions of one of the blocks, i.e., quite asymmetric chains. Cylindrical microdomains occur for less asymmetric chains, and lamellar microphases occur for roughly symmetric diblocks. A gyroid phase is formed in a small window between the cylinder and lamellar microphase.[3] If the molecular architecture is changed, e.g., from a linear diblock to a miktoarm[4] star copolymer (A_nB), additional features have to be taken into account. For these systems Milner[5] calculated a phase diagram on the basis of chain free energy minimizations, predicting the morphology as a function of volume fraction and of an asymmetry parameter ϵ. This parameter describes the effect of both chain architecture and elastic asymmetry in the strong segregation regime. The phase diagram is shifted toward higher volume fractions of the B block for A_nB miktoarm star copolymers compared to linear diblock copolymers. The amount of this shift depends on *n*, the number of A chains connected to the star center. This behavior can be explained in terms of the locally preferred curvature of the A−B interface. Due to overcrowding of *n* A chains, the interface is forced to curve toward the B side. At the same time the A chains have to stretch away from the interface. The resulting morphology is thus determined by a delicate balance between interfacial energy and the stretching energy. Good agreement with the calculated morphology diagram was found in a number of studies on I_2S miktoarm star copolymers (I = polyisoprene, S = polystyrene),[6,7,8] except for one sample.[9] This sample at ϕ(PS) = 0.81 formed a new structure of randomly oriented wormlike micelles.

In this communication we report on a different approach to manipulate the phase behavior of a diblock copolymer, initiated by a study by Schädler and Wiesner.[10] They were able to control the lamellar spacing of a symmetric poly (styrene-*block*-isoprene) diblock copolymer (PS-*b*-PI) by introducing ionic groups with opposite charges at the chain ends. In apolar polymer matrices these ionic groups have a strong tendency to associate into ion aggregates, superimposing an additional self-assembly principle onto the system. The competition between block segregation and ionic aggregation could be controlled by addition of low molecular weight salt which leads to the observed changes in the lamellar spacing. Here, we use this principle of such tandem molecular interactions in an ionically functionalized polymer, which bears one ionic group at the block junction point and another one with opposite charge at one chain end. Addition of low molecular weight salt induces a change of the bulk microphase morphology. This is similar to what is observed by changing the architecture from an AB diblock copolymer to an A_2B miktoarm star copolymer, but without the necessity of a new, demanding polymer synthesis.

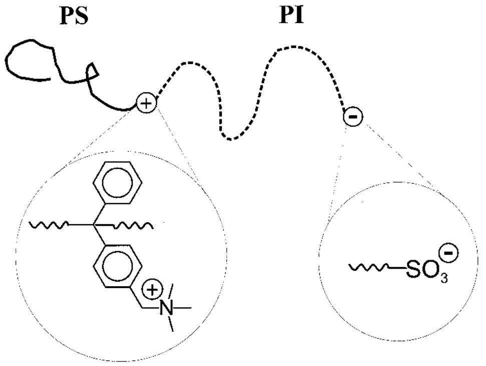

Figure 1. Schematic representation of the μ,ω macrozwitterionic PS-*b*-PI diblock copolymer with its functional groups.

Experimental Section. The polymer used in this study was synthesized by anionic polymerization following procedures described in ref 11. A slightly asymmetric PS-*b*-PI diblock copolymer architecture was chosen (ϕ (PI) = 0.6), with a tertiary amino group at the block junction point and a sulfonate group at the PI chain end. The resulting structure is schematically shown in Figure 1. The amino group was introduced by using an amino functionalized diphenylethene derivative. The sulfonate group was introduced by termination with 1,3-propansultone.[11] A bifunctional species resulted from the quaternization of the amino group in the sulfonated polymer. For comparison an uncharged diblock of exactly the same structure was obtained by taking a sample just before the sultone termination, quenching it with methanol and without quaternization. Molecular characteristics of the ionically functionalized material are presented in Table 1. Through dialysis,[10] low molecular counterions were removed, resulting in a salt free macrozwitterion. In analogy to the α,ω functionalized polymers described earlier,[10,11] we refer to this polymer as a μ,ω macrozwitterionic PS-*b*-PI. Details of the synthesis and characterization will be described in a forthcoming paper.[12]

Solid films of approximately 2 mm thickness were slowly cast from 5% polymer solutions in toluene. For salt containing samples a 0.05% solution of LiCl in methanol was added. Casting was performed at room temperature, and evaporation of solvent was controlled to form a solid film within 10 days. The samples were subsequently placed in a vacuum oven at room temperature for 1 day to remove residual solvent, and were then annealed for 1 day at 100 °C. For small-angle X-ray scattering (SAXS) measurements a Rigaku Rotaflex X-ray source with λ = 0.154 nm and a beam diameter of 1 mm was employed. Scattering patterns were recorded on a two-dimensional Siemens X-1000 area detector with a sample-to-detector distance of 118 cm.

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Table 1. Molecular Characteristics of the μ,ω Macrozwitterionic PS-*b*-PI Diblock Copolymer

sample	M_n (PS block)[a]	M_n (PI block)[b]	1,4 PI content[b,c] (%)	ϕ(PI)[c]	$D = M_w/M_n$ (PS-*b*-PI)[a]	$f(SO_3^-)$[d] (%)	$f(NR_4^+)$[e] (%)
μZ48	21 400	27 000	90	0.6	1.04	>95	95

[a] Obtained by SEC. [b] Obtained by ^{1}H NMR. [c] With respect to total PI content. [d] Obtained by dye extraction.[9] [e] Obtained by HPLC.

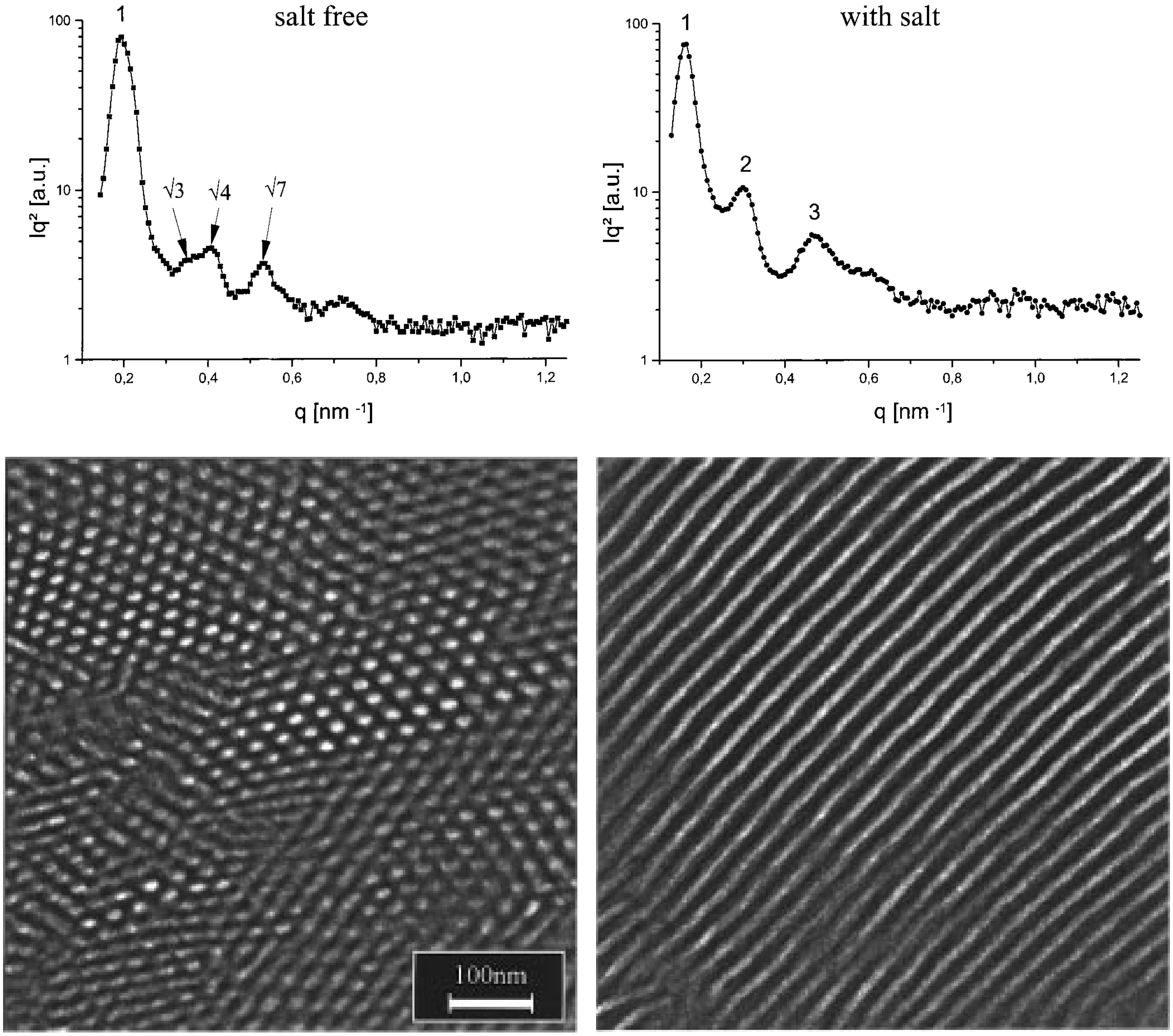

Figure 2. SAXS patterns and TEM images obtained for the sample with added low molecular weight salt (right) and for the salt-free sample (left). The length scale is the same for both TEM images (see bar on the left).

Results are displayed as a one-dimensional plot of Iq^2 vs scattering vector q (I: intensity), radially integrated from a two-dimensional scattering pattern. Transmission electron microscopy (TEM) was performed on a LEO 912Ω operated at 120 kV. Prior to sectioning the bulk samples were hardened by 48 h exposure to gaseous OsO_4. Ultrathin sections were produced at −55 °C using a Reichert ultramicrotome (UCS, 0.1 mm/s, nominal thickness 40 nm). Sections were floated off the diamond knife onto aqueous DMSO solution, transferred to Au grids and left for 6 h under vacuum. The dry specimens were stained with OsO_4 vapor for 15 h.

Results and Discussion. The structures formed by the present μ,ω macrozwitterionic polymers with and without low molecular weight salt were elucidated by SAXS and TEM. Representative results for the salt free samples and samples containing 6 equiv of salt per chain are shown in Figure 2. Significant structural differences are observed. The diffractogram of the salt free μ,ω macrozwitterion (Figure 2, left) shows Bragg peaks of higher order appearing at values $\sqrt{3}q^*$, $\sqrt{4}q^*$and $\sqrt{7}q^*$, where q^* is the position of the first-order maximum. This is indicative of a hexagonal structure. Indeed, with help of the TEM image it is confirmed that the morphology consists of hexagonally packed PS cylinders in a PI matrix. In the SAXS diffractogram of the sample with 6 equiv of salt (Figure 2, right) only peaks at integer multiples of the position of the first-order maximum, typical of a lamellar phase,

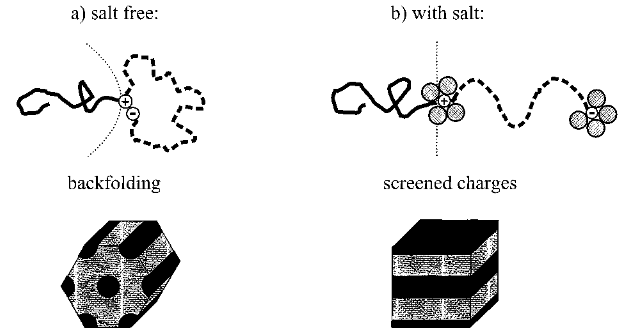

Figure 3. Schematic drawing of the expected chain conformation of a μ,ω macrozwitterionic chain: (a) without salt; (b) with salt.

can be found. The TEM image clearly shows the lamellar morphology. To the best of our knowledge, this is the first time that such a salt induced switching of microdomain morphology is reported for bulk diblock copolymers. For a conventional PS-*b*-PI diblock copolymer of this molecular weight and composition a lamellar morphology is expected.[13] In fact, for our uncharged polymer species this is the observed morphology (data not shown). Since the composition and degree of polymerization are identical for charged species with and without salt, the salt-driven transition from hexagonally packed cylinders for the salt free μ,ω macrozwitterions to a lamellar morphology for the salt-containing polymer must be due to differences in the aggregation behavior of the ionic groups. As in the case of the salt-controlled lamellar spacing,[10] these differences are expected to translate into changes of the chain conformations triggering the transition.

Ionic Coulomb forces are the strongest interaction in the salt-free samples. To achieve charge compensation, a charged chain end can either stretch to the oppositely charged group in the next interface, or it can fold back to its own interface. Our results strongly suggest that, due to the entropic penalty of stretching,[14] the latter is more favorable. A sketch of such a single chain is shown in Figure 3a. As a consequence, in this picture twice as many PI chains as in a conventional diblock copolymer are connected to one PS chain. This resembles the situation in I_2S miktoarm star copolymers, where two PI arms are grafted on a PS chain. As described before, this crowding of PI chains leads to a curving of the interface toward the PS phase. The picture of a PI loop drawn in Figure 3a is of course oversimplifying the real situation. From studies on ionomers,[15] α,ω macrozwitterions,[16] and ω-functionalized diblock copolymers,[17] it is well-established that in an apolar matrix several ionic groups aggregate into so-called multiplets.[18] The probability that a PI chain end folds back to a neighboring aggregate is high, leading to a network structure. Nevertheless, also for this scenario the average ratio of PI chains connected to a PS chain remains 2. Thus, the effect of curving the interface by overcrowding on the PI side is similar to the simplified picture of a single chain shown in Figure 3a.

The situation dramatically changes upon addition of salt, which screens the Coulomb interactions between the opposite charges along the chains. The uptake of salt in the present system, which consists of an apolar polymer matrix, can only occur at the locus of the polar ionic groups which form multiplets (i.e., LiCl does not dissolve in styrene, isoprene, or toluene). To accommodate the added salt, these ionic domains either swell, keeping the total number of aggregates constant, or they dissociate. As found for α,ω macrozwitterionic polymers,[10] and also suggested by the present results, the preferred structure consists of free chain ends surrounded by low molecular weight salt. A schematic drawing of such a single chain is shown in Figure 3b. This situation is similar to uncharged PS-*b*-PI diblock copolymers, and indicates that the additional impact of ionic groups on the self-assembly of μ,ω macrozwitterions can effectively be suppressed by the addition of salt.

In conclusion, the self-assembly of a diblock copolymer, functionalized with a quaternized amino group at the block junction point and a sulfonate group at one chain end, referred to as a μ,ω macrozwitterion, was elucidated. This system represents an interesting novel model macromolecular surfactant system[19,20] in which the effect of superposition of two distinct self-assembly mechanisms can be studied. It was shown that a salt-induced transition from hexagonally packed cylinders for a salt-free sample to a lamellar morphology for a sample with salt takes place due to differences in ionic aggregation. The structure of the salt-free sample is expected to be reminiscent of I_2S miktoarm star copolymers. The ionic aggregation effects on chain conformation can be effectively suppressed by low molecular weight salt. Since in the phase diagrams of block copolymers the gyroid phase occurs between the cylinder and the lamellar phase we expect more interesting morphological changes for this new polymer system at different salt concentrations. Work along these lines is now in progress in our laboratory.

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