Salt-Controlled Lamellar Spacing in Ionically End-Capped Symmetric Diblock Copolymers

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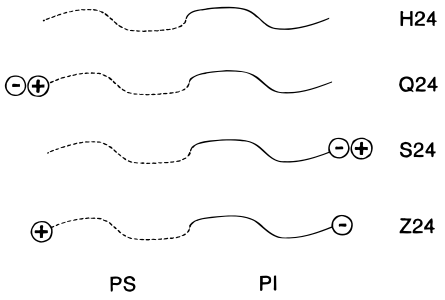
Introduction. Block copolymers are fascinating compounds of great commercial and scientific interest. The intriguing properties of these materials arise from their ability to self-assemble spontaneously into ordered structures below a critical temperature.[1] For diblock copolymers, in strong analogy to lipids and surfactants,[2] the composition, expressed, *e.g.*, as the volume fraction f of one block, largely dictates the supramolecular structure in the ordered state. A full description of the phase behavior of poly(styrene-*b*-isoprene) diblock copolymers (PS-*b*-PI), experimentally the most studied material, has been elucidated only recently by Bates and co-workers.[3,4] In this material, because of fluctuations, significant differences are found from the behavior predicted by the classical mean-field model, in which only the product χN and f determine the thermodynamic equilibrium,[5] where χ is the Flory−Huggins segment−segment interaction parameter and N the overall degree of polymerization. By manipulation of the molecular architecture of the block copolymers, the equilibrium state can be further controlled: In general, triblock, star, graft, and so-called miktoarm star block copolymers (stars with distinct arms) have a smaller tendency to separate into microphases than diblocks of the same N, reflecting a higher fraction of interfacial junction points for the former species.[6,7] For simple graft copolymers the observed morphology diagram is indeed shifted with respect to the classical one, in agreement with theoretical predictions.[8,9]

In this communication we report on an entirely different approach to manipulate the block copolymer phase behavior: By introducing ionic groups at one or both chain ends of a symmetric PS-*b*-PI diblock copolymer, we are able to control stabilization *or* destabilization of the microphase separation. In polymer matrices these ionic groups have a strong tendency to associate into ion aggregates[10] which superimposes an additional principle of self-assembly onto the system. As a first step toward a manipulation of the phase behavior, we examine how the competition between block segregation and ionic aggregation induces changes in the lamellar spacing. In addition we show how the periodicity can effectively be fine-tuned by the concentration of added salt.

Experimental Section. SAXS measurements were performed with a Kratky compact camera (Anton Paar KG) equipped with a one-dimensional position-sensitive detector (M. Braun). The Ni-filtered Cu Kα radiation ($\lambda = 0.154$ nm) was used from a Siemens generator (Kristalloflex 710 H) operating at 35 kV and 30 mA. The samples were kept in the camera under vacuum in a special brass furnace at room temperature. The data were collected in a multichannel analyzer and transferred to a VAX station for further analysis. Smeared intensity data were corrected for absorption, background scattering, and slit-length smearing following the Strobl procedure.[11] Intensities in absolute units were determined by using the moving slit method.

Results and Discussion. We synthesized a series of end-capped symmetric PS-*b*-PI diblock copolymers of varying molecular weights (MW), with quaternized ammonium (Q) at the PS and/or sulfonate (S) groups at the PI chain ends.[12] The four species with different endfunctionalities and MW of 24 000 g/mol, on which we will concentrate in the present study, are shown schematically as follows together with their code names.



All four samples were derived from *one* anionic polymerization batch, thus guaranteeing identical MW and a narrow MW distribution. The functionality of both endgroups is of the order of 99%. The synthetic route as well as the characterization of the products is described in detail in ref 12. The monofunctional species Q24 and S24 with their counterions can be viewed as a polymer with a strong dipole at one chain end, whereas Z24 represents an α,ω-macrozwitterion, which is obtained in a salt-free state by dialysis.

The structures formed by these end-capped polymers were elucidated by small-angle X-ray scattering (SAXS) on annealed samples. Before being annealed, all block copolymers were precipitated from THF in methanol and pressed into disks. In Figure 1 the scattered intensity $I(q)$ vs q for H24, Q24, S24, and Z24 are presented in a stack plot with a constant offset factor. For all samples, using transmission electron microscopy (TEM), a lamellar morphology was observed, as expected for diblock copolymers with $f \approx 0.5$ (data not shown). The SAXS results, however, show significant structural differences between the different end-functionalized species. In agreement with results of the TEM micrographs, the diffractograms for H24, Q24, and S24 show the characteristic Bragg-peaks of higher order, typical for a lamellar morphology, at integer multiples of q^*, where q^* is the position of the first order maximum. Since q^* reflects the periodicity, $L = 2\pi/q^*$, of the lamellar structure, the data in Figure 1 show that the two monofunctional species Q24 and S24 have a slightly *larger* lamellar spacing than the unfunctionalized H24. This is schematically depicted on the right-hand side of Figure 1 in the form of a composition profile in real space. Similar results have been reported for asymmetric PS-*b*-PI diblock copolymers, ω-functionalized with a sulfobetaine group.[13] The data for the macrozwitterion Z24 show a significantly *shorter* periodicity than the unfunctionalized H24, as also schematically depicted in Figure 1. Another prominent feature of sample Z24 is the lack of higher order reflections which is due to the small correlation length of the lamellar microstructure (as also seen in the corresponding TEM micrographs) as well as possibly an increase in interface thickness.[14]

The same tendency in the shift of periodicity is also observed for the other samples with MW in the range between 11 000 and 49 000 g/mol: $L_Z/L_H \approx 0.75$ for the

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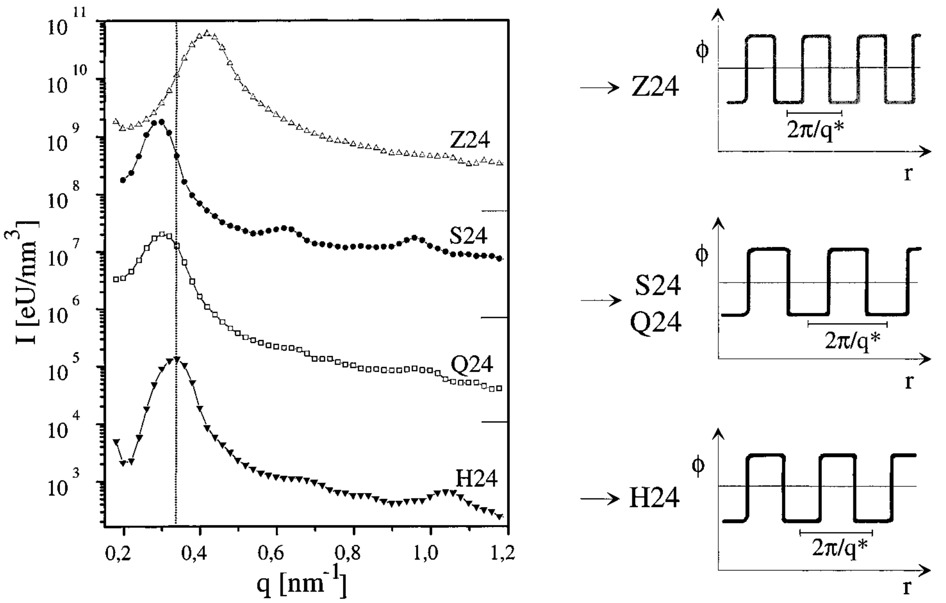

Figure 1. SAXS patterns for the different end-capped block copolymers obtained from pressed and annealed samples as described in the text. They are depicted in a stack plot obtained by multiplying the different data sets with a constant offset factor. The unity intensity points are indicated for Q24, S24, and Z24 on the right-hand side by a horizontal line. The vertical line corresponds to the peak maximum of the unfunctionalized block copolymer H24. On the right-hand side the differences in lamellar spacing as obtained from the peak maximum of the corresponding SAXS patterns are schematically depicted in form of a composition profile $\Phi(r)$ in real space for samples H24, S24 (Q24), and Z24.

macrozwitterionic and $L_{Q,S}/L_H \approx 1.05$ for the monofunctional species. This demonstrates the general impact of ionic end groups on the self-assembly of diblock copolymers. Since, as a consequence of the synthesis, the composition and degree of polymerization are identical for all species within one set of H, Q, S, and Z samples, differences in the periodicity can only be a result of changes in chain conformation due to ionic aggregation. In order to better understand the structural differences between the unfunctionalized and ionically end-capped block copolymers, it is necessary to characterize the ionic aggregates. This can be achieved using an EPR spin-probe technique, as described in a separate publication.[15] There we show that in case of the monofunctional species Q and S, association of ionic chain ends occurs within the pure homopolymer domains, stabilizing the microphase separation and leading to a weak stretching of chains. In contrast, for an α,ω-macrozwitterionic chain structure, under the boundary condition of phase separation, as found in the EPR study oppositely charged chain ends *must* associate near the styrene–isoprene interface in order to achieve charge compensation. Hence, by forcing the chain ends close to or even into “foreign” domains, the microphase separation becomes heavily frustrated due to an increase of unfavorable segment–segment contacts. The associated backfolding of the polymer chains leads to a significant decrease of the lamellar spacing as observed for Z24 in Figure 1. For a quantitative comparison of the lamellar spacings observed for the present systems with that in cyclic diblock and linear triblock copolymers,[16] the reader is refered to ref 15.

The difference in lamellar spacing as a result of changes in chain conformation due to ionic aggregation of chain ends leads to the question of control of the strength of this perturbation. In order to achieve this, the intermolecular Coulomb forces must somehow be tuned. In polyelectrolyte studies, adding a low molecular weight salt is a very common tool by which ionic interactions can effectively be screened. In the present case of a bulk polymer, adding salt requires modifying the solvent casting technique. This can be done by mixing a solution of the end-capped polymers in toluene with the calculated amount of a 0.05% methanolic LiCl solution. Up to a critical salt content of about 6–8 equiv of salt per polymer, the resulting films were optically transparent, indicating quite homogeneous solubilization of the LiCl in the block copolymer. Subsequently, the films were dried thoroughly and annealed in order to obtain equilibrium conditions. Indeed, no significant differences in TEM-micrographs or SAXS patterns were found by comparing annealed samples which were either solvent cast or precipitated from THF in methanol as described above.[17] In order to avoid effects arising from macroscopic order, measurements were performed on powder samples of the solvent cast material.

Representative results of the effect of salt on the SAXS-diffractograms are shown for Z24 in Figure 2 in form of a stack plot. The results for H24 (top) and salt-free Z24 (bottom) are included as references. The most prominent difference in the diffraction patterns of samples Z24 with 1 and 5 equiv of salt and these references is a shift of the peak maximum. Increasing salt concentration moves the maximum toward smaller q values. In fact, the position of the structure factor peak (q^*) turns out to be highly sensitive with respect to salt concentration. Values for the lamellar spacing L derived from these data are plotted as a function of salt concentration in Figure 3. The result for H24, i.e., $L \approx 18$ nm, is depicted as a horizontal line. At $c_{\mathrm{LiCl}} = 0$ the first data point for Z24 corresponds to $L \approx 14$ nm and reflects the situation described above, namely strong destabilization of the microphase separation for salt free species Z24. The difference in L between H24 and Z24 continuously diminishes when the salt concentration is increased until at about 5–6 equiv, within experimental error, the two measured lamellar spacings become the same. Results for the behavior of the monofunctional species Q24 are also depicted in Figure 3 and are equivalent to what is observed for Z24, with

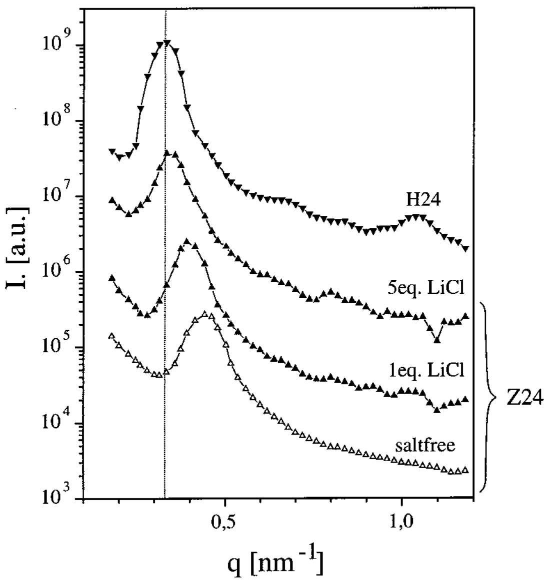

Figure 2. SAXS patterns of sample Z24 as a function of concentration of added salt. All patterns were obtained from solvent-cast material as described in the text. The patterns of salt-free Z24 (bottom) as well as of the unfunctionalized sample H24 (top) are also depicted as references.

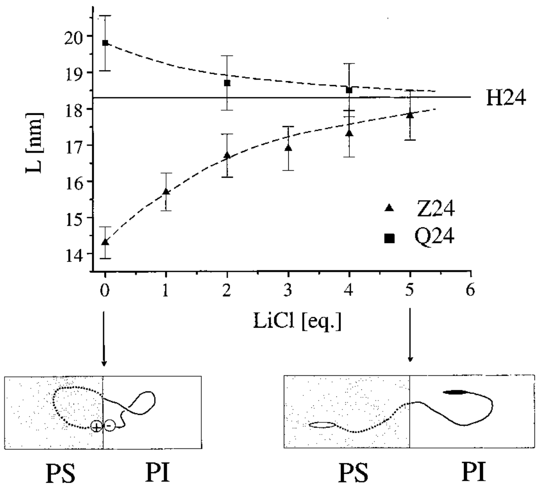

Figure 3. Lamellar spacings as obtained from the peak maximum of the corresponding SAXS patterns as a function of salt concentration for Q24 (upper data set) and Z24 (lower data set). The curves through the data points serve as guides for the eye. The lamellar spacing of the unfunctionalized H24 is shown as a horizontal line. In the bottom part possible chain conformations of the diblock copolymer chains in the absence (backfolding) and presence of salt are shown as discussed in the text.

a reversed sign. Note that for both species Q and Z, the assimilation of the periodicity occurs rather continuously within the given concentration range.

These results indicate that the additional impact of ionic chain ends on the self-assembly of lamellar diblock copolymers can effectively be suppressed by adding salt. This system serves as an example of how the concept of "tandem interactions" can be employed to fine-tune morphological parameters. The observed changes can only be accounted for by the weakening of Coulomb interactions via added salt. Though this phenomenon is well-known from solution studies of polyelectrolytes,[18] it is not well investigated for ionomers in solution, let alone in the bulk. In contrast to polyelectrolyte solutions, the uptake of salt in the present ionomeric system, which consists of a nonpolar polymer matrix, can only occur at the locus of the polar chain ends which form so-called multiplets[19] (e.g., LiCl does not dissolve in styrene, isoprene, or toluene). In order to accommodate the added salt, the ionic domains either "swell", keeping the total number of aggregates constant, or they dissociate, ultimately to form structures with free chain ends, surrounded by low molecular salt. Our data strongly suggest that in the ionomers we have examined, salt can disrupt ion aggregates in the bulk very efficiently. This scenario is schematically depicted for sample Z24 at the bottom of Figure 3. The screening process can then gradually "switch off" the perturbation initially superimposed on the block copolymer chain conformations and allow the periodicity to relax to the value observed for the unfunctionalized species. Similarly, in an NMR study on end-capped PS in toluene, Vanhoorne *et al.* showed that polar solvents (methanol) disrupt ion aggregates above a critical molar ratio of about 10 000 equiv of solvent per ion pair.[20] They thus demonstrated that electrostatic effects in ionomeric systems are screened by polar solvents in much the same way as salt reduces long-range interactions in the case of a polyelectrolyte in solution. These concepts obviously also hold for the present bulk materials.

In conclusion, ionically end-capped diblock copolymers represent an interesting example of a model macromolecular system in which the effect of the superposition of two distinct and partly opposing self-assembly mechanisms can be studied. By introducing quaternized ammonium and/or sulfonate groups at the chain ends of lamellar PS-*b*-PI diblock copolymers, we have shown how the competition between block segregation and ionic aggregation induces changes in the lamellar spacing that can effectively be fine-tuned by the concentration of added salt. Beside the variation of the periodicity, it should in principle be possible to also achieve salt-induced changes in the phase morphology of such functionalized block copolymers. Work along these lines is now in progress in our laboratory.

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