Micellization of *ω*-Functionalized Poly(styrene-*b*-isoprene) Copolymers in *n*-Decane

Stergios Pispas,* Serena Allorio, and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, Panepistimiopolis, Zografou 157 71, Athens, Greece

Jimmy W. Mays

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294

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ABSTRACT: Results are presented from static low-angle and dynamic light scattering as well as viscometry experiments for *ω*-functionalized diblock copolymers of styrene and isoprene in *n*-decane, a nonpolar selective solvent for the polyisoprene block. The copolymers have dimethylamino and sulfobetaine zwitterionic groups at the end of the polystyrene block. The amine-capped copolymers show moderate aggregation in *n*-decane. Aggregation numbers for the zwitterionic copolymers are larger relative to the amine precursors. There is an enhancement in the degree of association arising from the presence of the highly polar group at the end of the insoluble block. Some differences in the size, shape, and hydrodynamic and thermal behavior of the micelles formed by the different species, reflecting the nature of the end group, are identified by comparing the results from the various techniques used.

Introduction

Over the past few years there has been an increasing interest in determining the structure−properties relationships for ion-containing polymers.[1,2] To date, many studies have dealt with the solution and solid state properties of random ionomers[3−6] (polymers with nonpolar macromolecular chains bearing 1−10 mol % ionic groups, randomly distributed), block ionomers[7,8] (consisting of a neutral block and an ionomer block), ionic block copolymers[9−15] (made up of a nonpolar block and a polyelectrolyte block), and end-functionalized homopolymers[16−23] (nonpolar macromolecules with polar end groups, a limiting case of ionomers).

On the other hand it is a well-established fact that block copolymers consisting of nonpolar dissimilar blocks can form micelles in selective solvents,[24−36] i.e. solvents that are good for one block but are precipitants for the other. These polymeric micelles originate from the association of the insoluble blocks. The micelle structure is usually described as consisting of a more or less compact core containing the insoluble blocks and a corona composed of the soluble sequences which emanate from the core.

End-functionalized block copolymers, e.g., polymers consisting of nonpolar incompatible blocks having highly polar end groups, constitute an interesting area for polymer research because they are expected to demonstrate a combination of properties characteristic of block copolymers and ionomers, or more specifically those of end-functionalized polymers. Such systems can display a large variety of properties depending on the nature of the end groups and the nonpolar blocks, the position of the end group with respect to the block sequences, the polymer concentration, the selectivity and polarity of the solvent, and temperature.

The solution properties of *ω*-functionalized block copolymers of styrene and isoprene with tertiary amine and sulfobetaine end groups on either of the two blocks were studied in detail in CCl_4.[37,38] In this low polarity nonselective solvent aggregates are formed due to the association of the sulfozwitterionic groups and the aggregation number, *N*, depends on the length of the nonpolar copolymer chain. *N* decreases as the molecular weight of the copolymer increases due to excluded volume effects, a behavior that was also observed for zwitterionic linear polyisoprenes, polybutadienes, and polystyrenes.[18] The hydrodynamic behavior of the aggregates, as evidenced by dynamic light scattering and viscometric measurements, resembles that of star polymers. Aggregation numbers decreased as the polarity of the medium increased, by adding small amounts of alcohol, but without changing the solvent quality for the copolymeric tails.[38]

In a previous paper[39] we studied the static and dynamical properties of *ω*-functionalized diblock copolymers of styrene and isoprene in the bulk, by small-angle X-ray scattering (SAXS), rheology, and dielectric spectroscopy. These experiments confirmed the presence of aggregation of the polar zwitterionic groups in the solid and melt state, even at high temperatures above the order−disorder transition temperature of the neutral diblocks, their organization in the polymeric matrix, and their influence on the bulk properties of the material, especially in the case where the zwitterionic group is attached on the polystyrene chain end.

In this paper we report results of studies of the association behavior of dimethylamino- and sulfozwitterion-capped diblocks of styrene and isoprene, having the polar groups at the end of the polystyrene block, in *n*-decane, a nonpolar selective solvent for the polyisoprene block. Static low-angle laser light scattering is used to probe the changes in aggregation number with concentration and to investigate the influence of the end groups on this fundamental parameter of an associating system. Hydrodynamic properties, size and shape, of the micelles formed by these polymers are studied by the aid of dynamic light scattering and viscometry. Conclusions about the overall behavior of the systems under investigation are deduced by comparing the experimental data from the three techniques. Some results on the thermal stability of the micelles are also presented and discussed.

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Table 1. Molecular Characteristics of Amine-Capped Diblock Copolymers

sample	10^{-4} M_w	10^{-4} M_n	10^{-4} M_n(PS)	wt % PS	% 3,4 PI	% 1,2 PI
NSI-5F	4.26	3.75	1.01	27	58	16
NSI-4F	1.88	1.70	0.51	30	59	13
NSI-2F	1.14	1.04	0.33	32	57	6

Table 2. LALLS Results for *ω*-Functionalized Diblock Copolymers in *n*-Decane at 25 °C

sample	10^{-5} $M_{w,app}$	10^4 A_2	N_w
NSI-5F	6.55	−1.49	15
NSI-4F	2.49	−2.17	13
NSI-2F	1.11	−5.8	10
ZwSI-5F	35.1	−0.94	82
ZwSI-4F	9.61	0.15	51
ZwSI-2F	10.3	2.0	90

Experimental Section

The functionalized diblock copolymers were prepared by a two-step anionic polymerization procedure under high-vacuum conditions in all-glass reactors. Benzene was the main polymerization solvent. Styrene was polymerized first using [3-(dimethylamino)propyl]lithium as the initiator. In this way the tertiary amine functionality was introduced on the end of the polystyrene block. A small amount of purified tetrahydrofuran (THF) was added to the styrene−benzene mixture before introducing the initiator's solution in order to accelerate the initiation reaction. Isoprene was added after the complete polymerization of styrene, and finally, the living polymers were terminated with degassed methanol. The terminal tertiary amine groups were converted to sulfobetaine groups by reaction with excess cyclopropanesultone.[37]

The synthesis of the samples was monitored by size exclusion chromatography (SEC). Copolymer composition and polyisoprene microstructure were determined by ^{1}H-NMR spectroscopy. The addition of THF to the polymerization mixture results in polyisoprene blocks having high vinyl content (3,4 and 1,2 units). More details regarding the synthesis and the molecular characterization of the samples are given elsewhere.[37,38] The molecular characteristics of the amine-capped precursors (NSI) used in this study are given in Table 1.

Apparent weight average molecular weights, $M_{w,app}$, and second virial coefficients, A_2, were obtained from the concentration dependence of the excess Rayleigh ratio, ΔR_θ, determined at 25 °C with a Chromatix KMX-6 low-angle laser light scattering photometer operating at $\lambda = 633$ nm

$$Kc/\Delta R_\theta = 1/M_{w,app} + 2A_2c + ... \qquad (1)$$

where K is a combination of known optical constants, including dn/dc the refractive index increment, and c is the concentration. n-Decane (analytical grade) refluxed over CaH_2 and fractionally distilled just prior to use was the solvent for the measurements. Stock solutions were prepared for each sample, and lower concentration solutions were obtained by succesive dilutions. The amine-capped samples were easily dissolved after standing overnight with occasional stirring. Zwitterion-capped samples formed macroscopic dispersions of swollen particles during the same treatment. Heating for 0.5−1 h at 70 °C was required in order to achieve complete dissolution, depending on the molecular weight of the polymeric tail, with longer periods needed for the lower molecular weight samples. No precipitation was observed in the stock solutions after returning to room temperature for weeks. The same stock solution preparation protocol was followed for the other methods used in this study in order to ensure consistency of the results. All measurements were performed in freshly prepared solutions (less than 1 week old) optically clarified by filtration through 0.45 μm pore size Nylon filters. LALLS measurements were made on the most extended concentration range allowed by instrumental accuracy. For the measurements of the scattered intensity as a function of temperature the same low-angle photometer was utilized, equipped with a laboratory-built variable temperature control system adapted on the standard measuring cell. The temperature range was from ambient to ca. 65 °C.

The dn/dc values were obtained by measurements in n-decane at 25 °C with a Chromatix KMX-16 laser differential refractometer at $\lambda = 633$ nm. The instrument was calibrated with aqueous NaCl solutions.

Dynamic light scattering measurements were performed using a Brookhaven BI200SM goniometer and a ca. 28 mW Ar^+ laser operating at $\lambda = 488$ nm. Correlation functions were analyzed to second order by the method of cumulants using a Brookhaven BI2030AT correlator with 72 channels. Temperature was controlled to 25 ± 0.1 °C. Measurements were confined to an angle of 45° since preliminary experiments showed no angular dependence of the ratio Γ/q^2, where Γ is the decay rate of the correlation function and q is the scattering vector, for all the samples studied, except sample ZwSI-5F, a result that is consistent with the calculated small values for the average hydrodynamic radius, R_h, of the micelles. Translational diffusion coefficients, D_0, at infinite dilution were determined from the concentration dependence of the apparent diffusion coefficient

$$D_{app} = D_0(1 + k_Dc + ...) \qquad (2)$$

where k_D is the coefficient of the concentration dependence of the diffusion coefficient ($k_D = 2A_2M - k_f - u_2$, where A_2 is the second virial coefficient, M is the molecular weight, k_f is the coefficient of the concentration dependence of the friction coefficient, and u_2 is the partial specific volume of the polymer). The average hydrodynamic radius at infinite dilution was calculated from

$$R_h = kT/6\pi\eta_sD_0 \qquad (3)$$

where k is Boltzmann's constant and η_s is the viscosity of the solvent. Second moment, μ_2/Γ^2, where μ_2 is the second cumulant, values were between 0.1 and 0.2 for the amine-capped polymers, showing a decrease by increasing concentration. For the zwitterionic copolymers μ_2/Γ^2 were around 0.1, becoming lower than this value at higher concentrations.

Intrinsic viscosities, $[\eta]$, and Huggins coefficients, k_H, for the amine- and zwitterion-capped diblocks were obtained from the concentration dependence of the specific viscosity, η_{sp} $(=\eta_r - 1)$, where the relative viscosity η_r is the ratio of the solution to solvent flow times

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + ... \qquad (4)$$

in n-decane at 25 ± 0.02 °C. Kraemer plots

$$\ln \eta_r/c = [\eta] + k_K[\eta]^2c + ... \qquad (5)$$

where k_K is the Kraemer coefficient were also used because Huggins plots exhibited considerable curvature in many cases. Solution and solvent flow times were measured in Cannon−Ubbelohde dilution viscometers with a Schott−Gerate automatic flow timer. Solvent flow times were greater than 200 s, making kinetic energy corrections negligible. The average viscometric radii were calculated by aid of

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M)^{1/3} \qquad (6)$$

where N_A is the Avogadro number and M is the apparent weight average molecular weight from light scattering.

Results and Discussion

The results from static light scattering are given in Table 2 together with the experimentally calculated aggregation numbers for the amine (NSI)- and the zwitterion (ZwSI)-capped species. Representative plots of the dependence of the reduced scattering intensity on concentration are given in Figure 1.

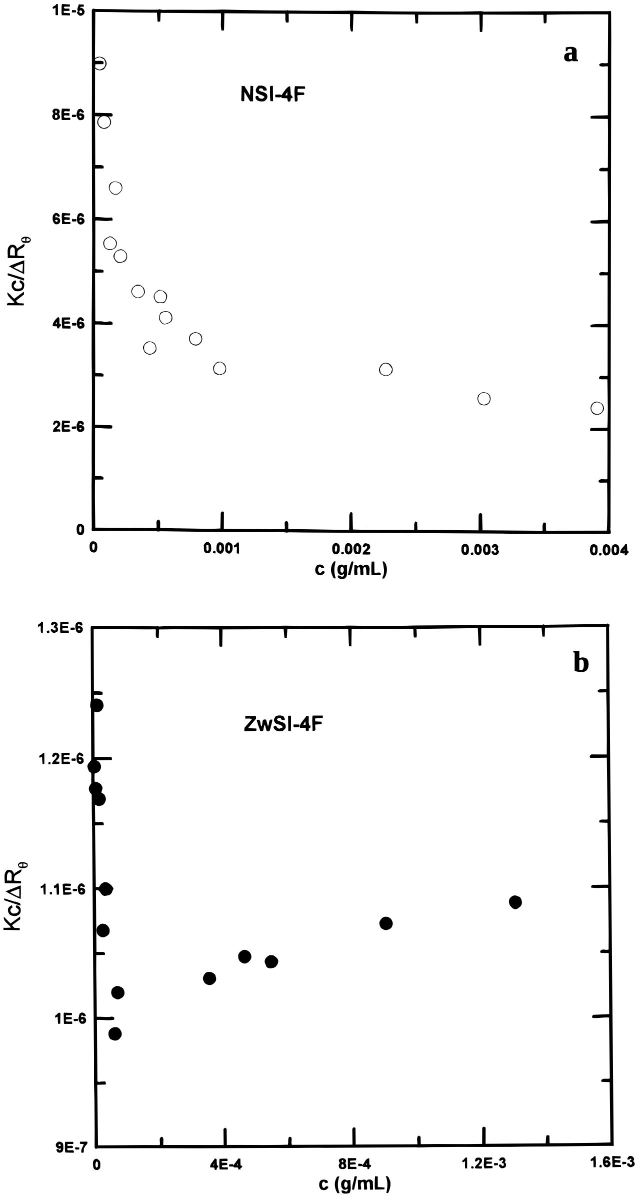

Figure 1. $Kc/\Delta R_\theta$ vs concentration plots for (a) sample NSI-4F and (b) sample ZwSI-4F in *n*-decane at 25 °C.

Aggregation numbers, N_w, obtained from LALLS for the amine-capped polymers are definitely much lower than the ones derived for the zwitterionic samples. N_w for the amine precursors is of the order of 10−15 chains per micelle but in the case of the zwitterion-capped samples lies between 50 and 90, judging from the apparent values of M_w. In both cases the $Kc/\Delta R_\theta$ vs c plots are curved, but the critical micelle concentration (cmc) cannot be observed in either case. Apparently, the cmc is very low for both kinds of systems and out of the experimentally accessible range. However, the decrease in the $Kc/\Delta R_\theta$ values, as well as the attainment of the plateau, occurs at a lower concentration range for the zwitterionic copolymers than for the amine-capped ones. This may also imply a shift of the cmc to lower values in the case of the zwitterion-capped samples. The negative second virial coefficients for the amine-capped samples indicate that the equilibrium is not completely shifted toward the micelles, a result that agrees with previous studies on similar systems,[27] but their low absolute values show that the calculated, by extrapolation at $c = 0$ from the higher concentration range, apparent molecular weights are not far from the true molecular weights of the micelles.

Table 3. DLS Results for ω-Functionalized Block Copolymers in *n*-Decane at 25 °C

sample	$10^7 D_0$ (cm^2/s)	k_D (mL/g)	R_h (nm)
NSI-5F	1.72	−214	14.7
NSI-4F	2.61	−166	9.7
NSI-2F	4.09	−198	6.2
ZwSI-5F	0.694	69	36.6
ZwSI-4F	1.37	9.0	18.4
ZwSI-2F	1.26	335	20.1

The differences in behavior must arise from the presence of the highly polar sulfobetaine group at the end of the insoluble block in the zwitterionic samples, which are incompatible with *n*-decane and tend to associate, introducing another factor that enhances the segregation of the polystyrene blocks. Apparently, the tertiary amine groups are not polar enough to produce an additional effect in the whole process, as can be seen from previous studies in nonpolar solvents.[37,38] A probable structure for the micelles can be visualized as a polar inner core formed by the aggregating polar groups surrounded by a hydrocarbon core of more or less collapsed polystyrene blocks and an outer corona of well-solvated polyisoprene chains.

This picture can be supported by the experimental fact that the amine samples were soluble in *n*-decane at room temperature whereas heating was required for the zwitterionic samples. Additionally, more time was required for the low molecular weight sample, which has the higher relative content of dipolar groups, to dissolve. It seems that a certain activation energy is required for the large intermolecular associations of the polar groups, in the solid state, to be broken and the chains to be separated and transported (unimolecularly or in the form of smaller clusters) into the solution. Once the chains find themselves in the environment of the solvent, the micelle structure is stabilized, because of the soluble corona, and no precipitation occurs.

Another point to be mentioned here concerns an attempt made to dissolve (in *n*-decane) diblock samples that have the zwitterion group at the end of the polyisoprene block in order to study their behavior in solution. These latter polymers are virtually insoluble in *n*-decane. Even after the stock solutions were heated at 70 °C for 48 h, a dispersion of particles visible to the naked eye resulted. Lowering the temperature to 25 °C caused the polymer to precipitate in a swollen state. This cycle of cooling and heating could be repeated many times. A final addition of a small amount of THF to the inhomogeneous mixture of polymer, at room temperature, resulted in a homogeneous solution. Obviously, the presence of insoluble segments, which are incompatible with each other, on both sides of the soluble block does not allow the polymer molecules to dissolve, e.g. by screening of the ends via loop formation by the polyisoprene blocks as in the case of triblock copolymers.[25,33,36] The separate segregation of polystyrene chains on one side and the zwitterions on the other results in some kind of gelation.

Results for the amine- and zwitterion-capped copolymers from dynamic light scattering (DLS) are shown in Table 3. The concentration dependence of the apparent diffusion coefficient was in most cases linear. An exception is sample NSI-5F (Figure 2) where the plot shows curvature with a negative initial slope and a plateau at higher concentrations corresponding to an R_h value of 20.9 nm. The k_D values are negative for

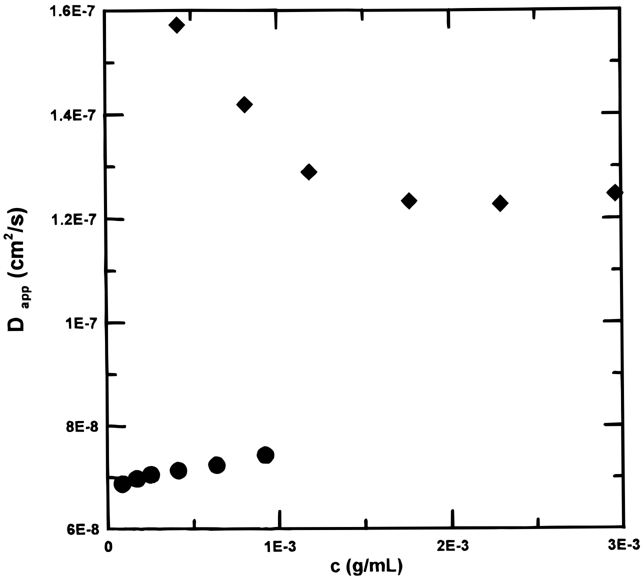

Figure 2. Apparent diffusion coefficient vs concentration for samples NSI-5F (◆) and ZwSI-5F (●) in *n*-decane at 25 °C.

Table 4. Viscometric Results for ω-Functionalized Diblock Copolymers in *n*-Decane at 25 °C

sample	$[\eta]$ (mL/g)	k_H	R_v (nm)	$[\eta]_{ZW}/[\eta]_N$
NSI-5F	34.1	1.1	15.2	
NSI-4F	20.3	0.77	9.3	
NSI-2F	11.6	0.62	5.9	
ZwSI-5F	34.3	1.1	26.7	1.01
ZwSI-4F	26.2	1.1	15.8	1.29
ZwSI-2F	17.6	1.2	14.2	1.52

the amine-capped copolymers, reflecting the negative second virial coefficient values found from static light scattering. For the zwitterionic samples k_D is positive, reflecting the shift of the equilibrium completely in favor of the micelles. R_h values for the zwitterion-capped polymers are larger than the ones calculated for the amine precursors, confirming the conclusion drawn from LALLS that the former species form larger micelles.

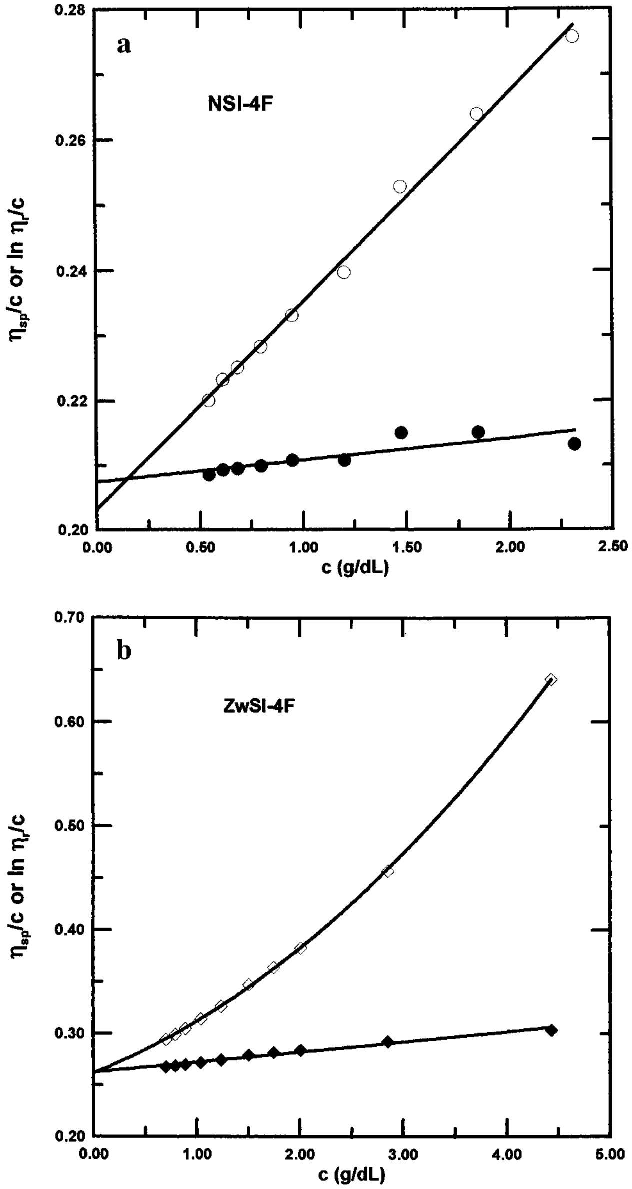

Figure 3. (a) Huggins (○) and Kraemer (●) plots for sample NSI-4F. (b) Huggins (◇) and Kraemer (◆) plots for sample ZwSI-4F. Solvent: *n*-decane. Temperature: 25 °C.

The results from viscometry are given in Table 4, and representative plots, in Figure 3. The intrinsic viscosity values depend primarily on the molecular weight of the unimer in each series of samples (amine- and zwitterion-capped) and increase as the molecular weight of the individual chain increases. Huggins coefficients also increase as the molecular weight of the unimer increases, at least for the amine-capped samples. This can be attributed to the more or less starlike structure of the corresponding micelles due to the small aggregation number. However, in the case of the zwitterion-capped copolymers k_H remains constant with a value around 1.1, due to the more compact structure and increased hydrodynamic interactions as a result of the higher aggregation number. Comparison between samples with the same molecular weight which carry different polar end groups shows that the largest increase in $[\eta]$ occurs for the lowest molecular weight sample, while for the largest molecular weight sample the values are identical, irrespective of the end group and in contrast to the fact that the increase in N_w is also significant in this case. The ratio $[\eta]_{ZW}/[\eta]_N$ decreases with increasing molecular weight of the unimer. For star block copolymers[40] and homopolymers[41] with many arms, which can be regarded as models of spherical micelles, it has been shown that when the number of arms is larger than 6, the intrinsic viscosity is almost independent of the number of arms and depends only on the molecular weight of arms. For spherical micelles the same is true.[24] Taking into account that the relative increase in N_w, when the tertiary amine group is changed to a sulfozwitterionic one, is of the same order of magnitude for the samples under investigation, the dependence of the ratio may indicate a change in the shape of the micelles by increasing the molecular weight of the unimer and consequently by decreasing the ionic content in the sample. This change can originate from different structures in the nonsoluble core of the zwitterion- and amino-capped samples. This assumption is supported by the large increase of the hydrodynamic radius, R_h, for the zwitterionic polymers. Its value for the zwitterionic micelles is more than twice that of the micelles formed by the amine-capped precursors in most cases. For spherical micelles a large increase in the association number usually results in a small increase in the radius of the micelles.[24] Having in mind that the environment in the core resembles that of the bulk polystyrene it can be assumed that a linear packing of the zwitterion head groups takes place in the core,[42] analogous to the structure observed in bulk zwitterionic polyisoprenes of low molecular weight.[43] This packing yields a core more extended[44] than the spherical compact one usually encountered in micelles of nonpolar block copolymers. The phenomenon is expected to have greater importance for low molecular weight unimers in the present case. Another point that deserves attention is that the values of R_v and R_h are identical, within experimental error, for the amine-capped samples where for the zwitterion end-functionalized copolymers R_h is much higher than R_v. The result for the amine-capped polymers agrees with a spherical (starlike) shape of their micelles. The discrepancy in the case of the zwitterionic polymers may be due to the higher sensitivity of DLS to the larger micelles (*D* is a *z*-average quantity) and/or the development of shear forces in the capillary viscometer which may disrupt the larger aggregates.[14,45] Judging from the relatively narrow polydispersity estimated from dynamic light scattering, and from the results of our previous investigation in CCl_4,[38] the latter possibility seems closer to the truth.

In order to gain information on the thermal behavior of the micellar solutions of the end-functionalized polymers, the intensity of scattered light at small angles (6−7°) was measured as a function of temperature. Representative plots are given in Figure 4. The behavior also depends on the molecular weight of the precursor diblock (or in other words on the ionic content). Sample NSI-5F, with the highest chain molecular weight, seems to have a critical micelle temperature around 60 °C (Figure 4a) in accordance with results on similar systems.[27] Its dipolar analog, sample ZwSI-5F, shows at almost the same concentration a decrease in the intensity analogous to sample NSI-5F, but at the nominal cmt the plateau intensity is much higher than the amine precursor. Apparently, some kind of association persists at high temperatures for the zwitterion-capped sample. Judging from the ratio of the intensities at the plateau region (corrected for solvent scattering and differences in concentration), it can be calculated that the zwitterion-capped polymer exhibits a degree of association equal to 6 unimers per aggregate. This value compares well with the value of 4 chains per aggregate found for the same sample in carbon tetrachloride,[38] a nonpolar good solvent for the polymeric tails. At that temperature range solvent quality has been improved and aggregation of the polystyrene blocks does not take place, but the ionic groups are still in a hostile environment and the situation resembles that of a good nonpolar solvent. It can also be deduced that at this elevated temperature ionic interactions are still strong enough to keep the molecules together.

For the pair of samples NSI-4F and ZwSI-4F (Figure 4b) the intensity drops monotonically for the amine precursor where for the zwitterion analog the intensity remains almost constant until the temperature reaches ~53 °C, when it begins to decrease, remaining, however, much higher than the amine-capped sample. It seems that the presence of the zwitterionic group on the polystyrene chain end acts as to stabilize the polystyrene cores of the micelles. The phenomenon is analogous to the behavior observed in the bulk state[39] for this kind of zwitterion-capped samples, where at high temperatures a transformation of polystyrene cylinders to polystyrene spheres was noted by SAXS, the spherical micelles being stable even at the highest temperature studied.

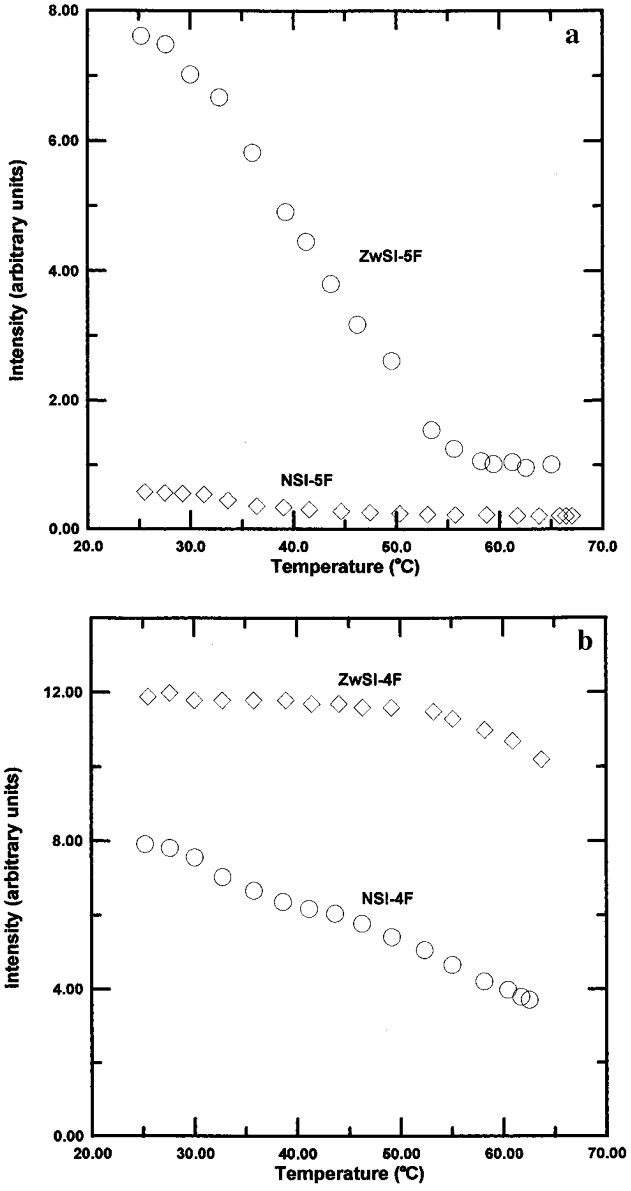

Figure 4. (a) Intensity vs temperature plots for samples ZwSI-5F (○) ($c = 1.262 \times 10^{-3}$ g/mL) and NSI-5F (◇) ($c = 1.147 \times 10^{-3}$ g/mL). (b) Same plots for samples ZwSI-4F (◇) ($c = 1.629 \times 10^{-3}$ g/mL) and NSI-4F (○) ($c = 2.800 \times 10^{-3}$ g/mL).

It should also be mentioned that for this last experiment concentrations were chosen so that the equilibrium is shifted appreciably toward the micelles for both polymers. As a result the concentration of the dimethylamino-terminated diblock is almost double that of the sulfobetaine-terminated copolymer. The behavior of the pair NSI-2F/ZwSI-2F resembles that mentioned for the pair NSI-4F/ZwSI-4F. Clearly, not only do the zwitterion samples have higher association numbers than the amine precursors at lower concentrations but also their micelles seem to be stable at higher temperatures. This last property may have significant importance for potential applications of the dipolar polymers as viscosity modifiers of fluids at high temperatures.

Conclusions

The static low-angle light scattering measurements on amine- and zwitterion-capped diblock copolymers, having the functional groups at the end of the polystyrene block, in *n*-decane, showed that the latter species have larger aggregation numbers and the equilibrium is shifted in favor of the micelles at lower concentrations, due to the presence of the highly polar sulfobetaine groups. Dynamic light scattering and viscometry results confirm that the size of the micelles formed by the zwitterionic copolymers is larger and implies that they exhibit a more extended shape. Light scattering intensity measurements as a function of temperature showed that the zwitterionic micelles are stable over a more extended temperature range than the micelles from the amine-capped precursors even at lower polymer concentrations.

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