Large structures in diblock copolymer micellar solution

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The association properties in water solution of poly(dimethylsiloxane)-b-poly(ethyleneoxide) diblock copolymer was investigated by static and dynamic light scattering in a wide range of concentrations and temperatures. The presence of a long hydrophilic poly(ethyleneoxide) (PEO) chain causes a weak tendency to microphase separation of the system which is responsible for some relevant effects. First of all we observe a late micellization process which is characterized by an unusually high value of the critical micellar concentration ($c_{cmc}=0.007$ g/cm^3) and by an unusually small aggregation number (≈ 6) of the generated micelles. Moreover, the composition of the highly hydrated micelles has been found to change sensitively with temperature. On increasing temperature dehydration of micelles has been observed together with a contemporaneous increase in the aggregation number, whereas the hydrodynamic radius remains constant in the whole range investigated. The long hydrophilic chains also stimulate an efficient entanglement process between micelles. The interpenetrating PEO chains belonging to different micelles causes the depletion of the solvent in the outer layer of micelles. The result is the formation, just after the micellization process takes place, of thermodynamically stable clusters of entangled micelles. These large structures, which are present in the system in small concentrations, maintain their structural properties unchanged in a wide range of concentrations and temperatures, and provide indirect evidence of a weak attractive component to the intermicellar interaction potential.

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I. INTRODUCTION

Self-assembly of block copolymers in selective solvents is a phenomenon of considerable interest in many field of science. It can be viewed in strong analogy to low molecular weight surfactant in water [1]. On the other hand, since a block copolymer chain may consist of more than 300 monomeric units, the free energy per micelles is much larger for block copolymers than for traditional surfactants in water. Moreover, the possibility of molecular control by tuning the desired polymer composition and architecture makes these systems a versatile tool to study, in a convenient way, the rich and complex phenomenology in the field of colloidal science [2], as well as stimulates the route for the rational design and engineering of materials with desired properties [3]. Among these classes of systems particularly representative are amphiphilic block copolymers having poly(ethyleneoxide) (PEO) as the water soluble block. Despite the wide range of promising applications in the field of biotechnology (biomimetics), material science, and environment technologies, PEO-based aggregates has attracted the interest of scientists due to the complex properties of PEO in water solution [4–6].

In some structural investigations of water solution of PEO-based block copolymers it has been found that the regular micelles coexist with the presence of bigger aggregates [7–13]. In most cases the bigger clusters have been interpreted as loose structures and have been detected at the higher concentrations, or in a well defined temperature range. Although similar observations has been recently reported by several groups, up to now no unifying understanding of the origin of these phenomena has emerged.

In this work we give experimental evidence that in water solutions of polydimethylsiloxane-b-polyethyleneoxide diblock copolymer large supramolecular structures, thermodynamically stable, coexist with the smaller regular micelles, just after micellization process takes place. From the experimental point of view the observation of these objects is complicated by the limited sensitivity of measurements carried out in the diluted regime [i.e., near to the critical micellar concentration (cmc)]. The situation can be even more complex because of the fact that often these clusters are present in very small populations. This is probably the reason why in previous investigations this phenomenon has been observed only in limited regions of the concentration-temperature phase diagram [10,11,13]. In our study this problem is overcome by the proper choice of a weak amphiphile, characterized by a long hydrophilic component. The presence of a long hydrophilic PEO chain produces, in fact, some relevant effects in the system. First of all we observe a late micellization characterized by an unusually high value of the critical micellar concentration. The weak tendency to microphase separation of the system is also responsible of the small aggregation number of generated micelles. Moreover, the long PEO chain stimulates an entanglement between micelles due to the depletion of the solvent between the surface of different micelles. The result is the association of micelles into large clusters.

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II. SAMPLES AND DATA ANALYSIS

The system studied in this work is composed of water solutions of polydimethylsiloxane-b-polyethyleneoxide (PDMS-b-PEO) diblock copolymer of molecular weight M_w=5000. It is composed of 82 wt% of PEO (obtained from SP2 Polymer Canada, and further purified). The polydispersity, after purification, is M_w/M_n=1.15.

The use of siloxane polymers has recently attracted increasing interest in the field of colloidal science. The high flexibility and high hydrophobicity of the PDMS segments produce, in fact, an enhanced stability of the generated supramolecular aggregates. These properties, together with their biocompatibility, make PDMS-based block copolymers also a good candidate for drug delivery applications.

Each solution was prepared by weight using pure distilled water and the phase diagram was constructed by reproducible visible observation following warming and cooling cycles. All measurements were done after a stabilization time of a week.

Density measurements were carried out in order to obtain concentration value in g/cm^3 units and to evaluate the specific volume occupied by the block copolymer in the solvent. An Anton-Paar densimeter DMA5000, having a reproducibility of 5×10^{-6} g/cm^3, was used. All solutions are clear in the temperature range below 55°C. The upper cloud consolute point (UCCP) varies in the range 58–65°C for concentration values between 0.01 and 0.3 g/cm^3.

For the static and dynamic light scattering experiments we used a homemade computer controlled goniometric light scattering apparatus with a duplicate Nd:yttrium-aluminum–garnet (532 nm) laser at a power of 200 mW. The laser beam is linearly polarized orthogonally to the scattering plane. The angular range explored is 20°–150°. For the correlation function measurements we used a MALVERN correlator in a homodyne (self-beating) detection mode and a cooled Hamamatsu photomultiplier R943-02, which guarantees few dark counts.

The involved quantity in the static measurements is the absolute excess scattered intensity, R, a function of the exchanged wave vector $|Q| = (4\pi n/\lambda_0)\sin(\theta/2)$ [14–16]:

$$R(Q) = KM_w cP(Q)S(Q), \tag{1}$$

where $P(Q)$ and $S(Q)$ are the normalized form factor and the structure factor respectively, M_w the molecular weight, c the mass concentration and K the optical constant defined as

$$K = \frac{4\pi n^2}{\lambda_0^4 N_A}\left(\frac{dn}{dc}\right)^2, \tag{2}$$

θ being the scattering angle, n is the refractive index of the solution, λ_0 is the wavelength of light in vacuum. The refractive index increment dn/dc=0.13 cm^3/g has been measured using a homemade differential refractometer at temperatures below the UCCP and it does not depend on temperature.

It is known that the molecular weight, for a chemically heterogeneous copolymer, as measured by static light scattering, is an apparent value depending on the refractive index of the solvent [14,17,18]:

$$M_w^{app}\left[\frac{dn}{dc}\right]^2 = M_w\left(\frac{dn_A}{dc}\right)\left(\frac{dn_B}{dc}\right) + \left[\left(\frac{dn_A}{dc}\right)^2 - \left(\frac{dn_A}{dc}\right)\right.$$
$$\left.\times\left(\frac{dn_B}{dc}\right)\right]w_A M_A + \left[\left(\frac{dn_B}{dc}\right)^2 - \left(\frac{dn_A}{dc}\right)\right.$$
$$\left.\times\left(\frac{dn_B}{dc}\right)\right]w_B M_B. \tag{3}$$

The indices A and B refer to the refractive index increments and the molecular weights of the two copolymer blocks. In order to obtain M_w it is necessary to measure M_w^{app} in three different solvents at least. In our case, however, the two components PEO and PDMS have very close refractive indices[19] and the measured refractive index increment of the block copolymer-water solution is very close to that of PEO-water solution (dn_{PEO}/dc=0.135 cm^3/g [20]). Therefore, the apparent and the weight average molecular weight are therefore not distinguished in this work.

As far as the dynamic light scattering experiment is concerned the measured quantity is the normalized intensity autocorrelation function [16]:

$$g_2(Q,t) = \frac{\langle I(Q,0)I(Q,t)\rangle}{\langle I(Q,0)\rangle^2}. \tag{4}$$

If the scattered field obeys a Gaussian statistic, $g_2(Q,t)$ is related to the normalized field autocorrelation function, $g_1(Q,t)=\langle E^*(Q,0)E(Q,t)\rangle/\langle I(Q,0)\rangle$, through the Siegert's relation

$$g_2(Q,t) = 1 + |\alpha g_1(Q,t)|^2, \tag{5}$$

α being a constant depending on the experimental setup (coherence area). For diffusing monodisperse spherical scatterers, the normalized field autocorrelation function takes a simple exponential form: $g_1(Q,t)=\exp[-\Gamma(Q)t]$. For $QR_H < 1$, $\Gamma(Q)$ is related to the collective diffusion coefficient, D, by the relation $\Gamma = DQ^2$.

III. RESULTS AND DISCUSSION

The first characterization of the PDMS-PEO copolymer investigated in the present work involves the determination of the cmc value. The absolute intensity as a function of concentration at the scattering angle of 90° was measured. In Fig. 1 the quantity $Kc/R^{90°}$ displays a minimum at $c = c_{cmc} \approx 0.007$ g/cm^3, indicating that a micellization process takes place. This value does not depend markedly on temperature, as found also in the case of poly(dimethylsiloxane)-graft-polyether copolymers [21,22]. Thus, the decrease of the solvent quality of water (and, hence, hydrophilicity) for the PEO blocks with increasing temperature has comparatively little effect on the cmc value.

Dynamic light scattering measurements showed that the field autocorrelation functions (an example is reported in Fig. 2) are composed of two distinguishable relaxations, well represented by two exponential decays

$$g_1(t) = A_F\exp[-\Gamma_F t] + A_S\exp[-\Gamma_S t]. \tag{6}$$

There are many works in literature (see for example Refs. [14,23,24]) about the different relaxation rates of a field au-
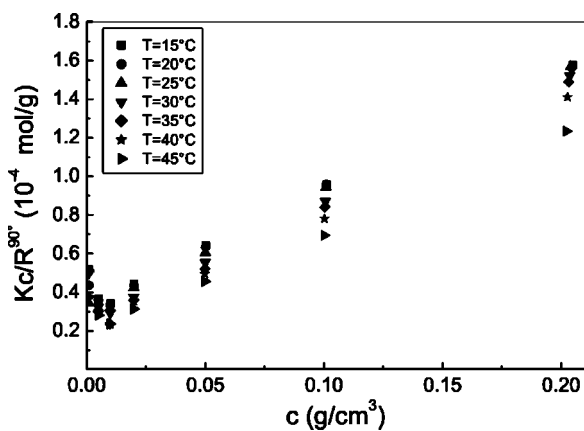
FIG. 1. Normalized inverse excess scattered intensity at 90° as a function of concentration for different temperature values.

tocorrelation function of colloidal solutions. In principle, the fast mode can be related to the Q^2-dependent collective diffusion of micelles or of unimers; the interpretation of the slow mode, on the other hand, is not always straightforward. Depending on the investigated system, in fact, it can be attributed to the self-diffusion process (which is an heterogeneity or polydispersity mode dependent on the inverse of the solution viscosity) [24,25], or to larger clusters diffusion [26–28]. Moreover, internal motions can be detected [29].

In recent investigations of water solution of PEO-based amphiphilic block copolymers, the presence of large aggregates has been found to coexist with smaller micelles in a well defined temperature and concentration range [10,11,13].

In the present study, even just above the cmc, the scattered intensity is mainly due to micelles, so that light scattering does not contain information on the dynamic of unimers. Moreover, internal motions relative to the center of mass are not detected.

As reported in Fig. 3 the quantities Γ_F/Q^2 (fast mode) and Γ_S/Q^2 (slow mode) are not dependent on the scattering wave vector, Q, at all the investigated concentration, thus indicating the diffusive nature of the detected modes. The fast mode is related to the collective diffusion of micelles whereas the
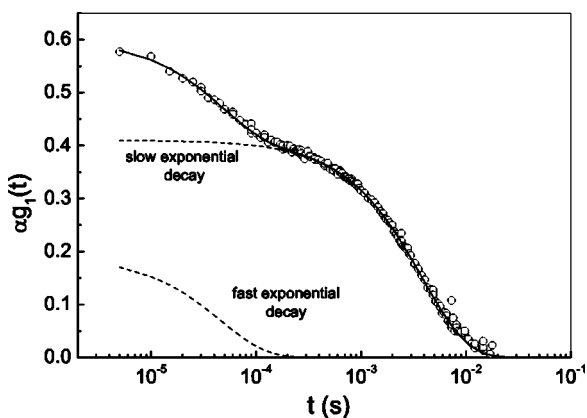
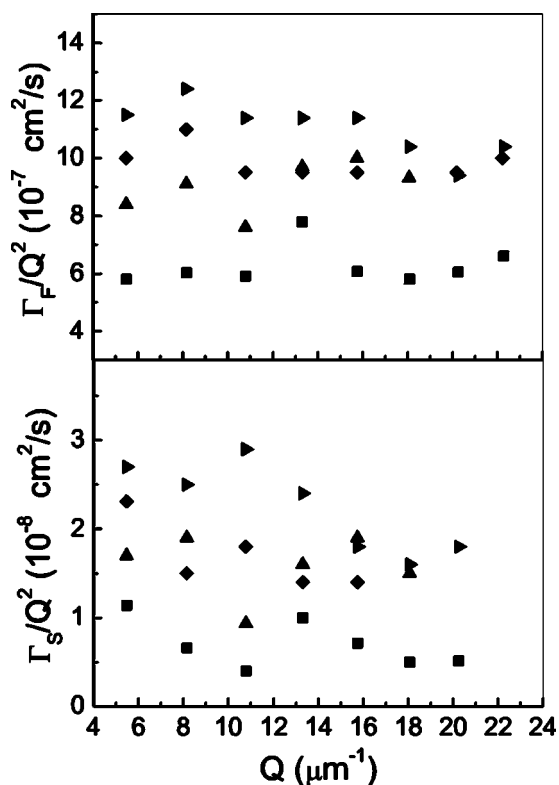

FIG. 3. Dependence of the fast and slow relaxation modes on the scattering wave vector for $c=0.02$ g/cm³, as an example. The symbols are the same as in Fig. 1.

slow one to that of clusters of micelles. The presence of clusters is confirmed by a microscopy image of a droplet of solution, as shown in Fig. 4. Submicrometric particles were seen to undergo a Brownian diffusion.

Considering, therefore, that two different species are present in solution, the amplitude of the two components of the correlation function can be written as [14]:
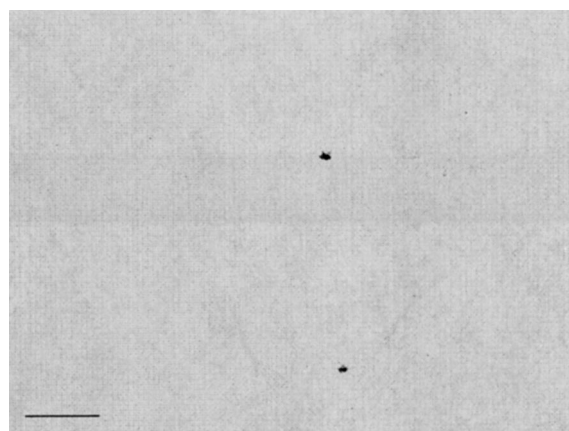
$$a_F(Q) = P_F(Q)S_F(Q)M_{wF}c_F,$$

FIG. 2. Example of field autocorrelation function measured for $c=0.1$ g/cm³ and $T=25\,°$C at a scattering angle of 60°. The dashed lines are the two exponential contributions (see text for details) to the fit.

FIG. 4. Image of clusters in solution obtained by an inverted Zeiss microscope (Axiovert S100 with an objective $100\times$NA$=1.4$). Technique for enhancing contrast has been used (Sobel and low-pass algorithms) [30]. The solid line represents 10 μm.
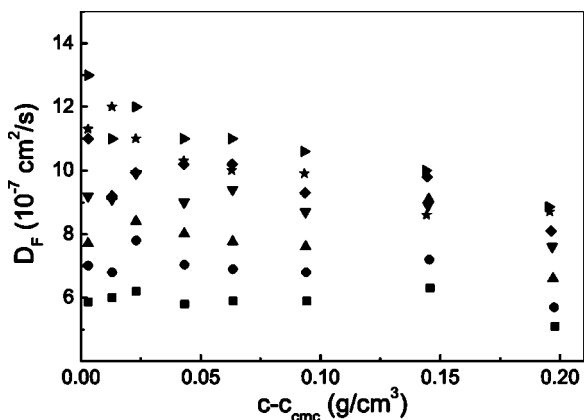
FIG. 5. Collective diffusion coefficient of micelles as a function of micelles concentration at different temperature values. The symbols are the same as in Fig. 1.

$$a_S(Q) = P_S(Q)S_S(Q)M_{wS}c_S, \tag{7}$$

where indexes F and S refer to micelles and clusters, respectively, and $A_F = a_F/(a_F + a_S)$ and $A_S = a_S/(a_F + a_S)$.

As it will be shown in the following, the clusters concentration is negligible with respect to that of micelles; micelles concentration can be considered, therefore, $c - c_{cmc}$. The plot of the fast diffusion coefficient $D_F = \Gamma_F/Q^2$ as a function of micelles concentration, at different temperatures, is shown in Fig. 5.

In the low concentration region $(0 < c - c_{cmc} < 0.075 \text{ g/cm}^3)$ the linear behavior of the diffusion coefficient can be described by the relation $D = D_0[1 + k_D^c(c - cmc)]$. From the extrapolation to zero concentration of the linear fit, the hydrodynamic radius is obtained using the Stokes-Einstein relation $(R_H = K_B T/6\pi\eta D_0, \eta$ being the viscosity of the solvent); the slope, on the other hand, furnishes the dynamic virial coefficient k_D^c.

As reported in Fig. 6, the obtained hydrodynamic radius of micelles remains constant over the explored range of temperatures, whereas the dynamic virial coefficient is approximately close to zero and then slightly decreases on increasing temperature. This indicates the presence of attractive interactions [24], which is compatible with the presence of clusters of micelles.

Neglecting the contribution of clusters to the scattering at 90° (as it will be demonstrated later it is small enough to be neglected), useful information about micellar interactions can be obtained from the scattered intensity at 90°, through the virial expansion [14]:

$$\frac{K(c - c_{cmc})}{R^{90°} - R_{cmc}^{90°}} = \frac{1}{M_{wF}}[1 + 2A_2 M_{wF}(c - c_{cmc})]. \tag{8}$$

In Fig. 7 the Debye plot is reported as a function of the micelles concentration. From a linear fit the molecular weight of micelles, M_{wF}, as well as the virial coefficient A_2, are obtained.

The molecular weight of micelles progressively increases with temperature from about 30 000 to about 55 000 Da. The corresponding mean aggregation number of micelles, N_{aggr},
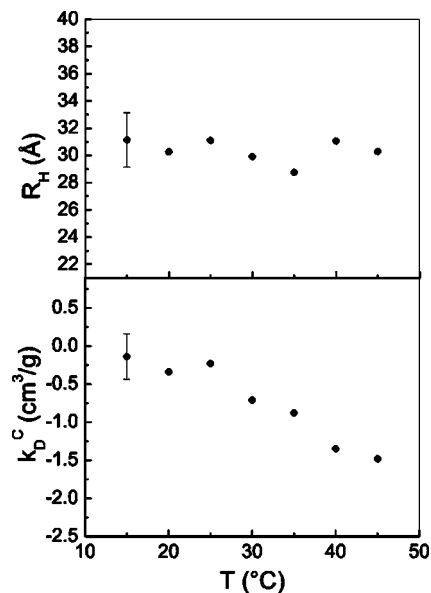

FIG. 6. Temperature dependence of both hydrodynamic radius and dynamic virial coefficient.

increases from about 6 to about 12 (see the inset of Fig. 7) and their volume fraction decreases accordingly. Similar trend has been obtained in water solution of diblock and triblock copolymers [5,22,31].

The aggregation number is very small in comparison with most results reported in literature on block copolymers and it can be explained as a direct consequence of the relatively long PEO chain. The hydrophilic part of the copolymer chain, in fact, constitutes more than 80% of its total mass; the geometrical packing, therefore, requires a low aggregation number to screen the hydrophobic PDMS segments from the contact of water.

The increase in temperature favors dehydration but also interactions between PEO chains (the solvent quality for PEO decreases [20,32,33]); the net effect between dehydration and the increase in the aggregation number is the un-
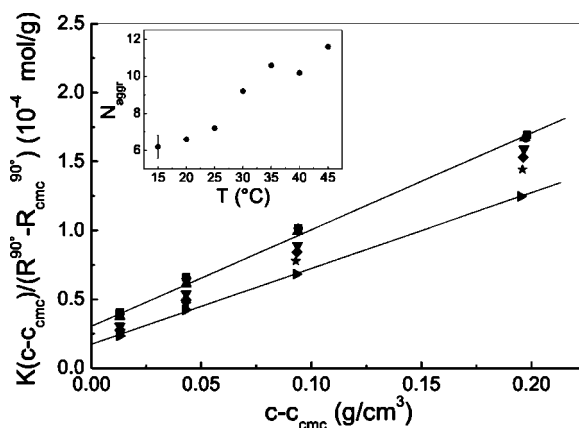

FIG. 7. Normalized inverse absolute intensity of micelles as a function of micelles concentration for different temperature values; solid lines are the linear fit according to the virial expansion [Eq. (8)]. In the inset the mean aggregation number of micelles is reported as a function of temperature.
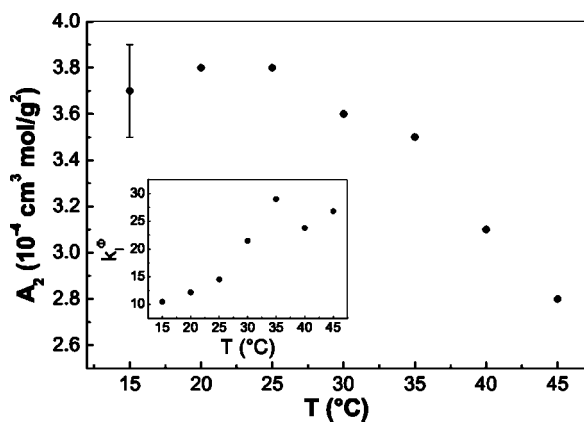
FIG. 8. Temperature dependence of the static virial coefficient, A_2. In the inset the corresponding static virial coefficient, k_I^ϕ, is reported when concentration is expressed as volume fraction.

changed micelles' hydrodynamic radius in the explored temperature range.

An estimate of the hydration of micelles can be done considering the difference between the hydrodynamic micellar volume and the copolymer volume in a micelle. The latter quantity, obtained from density measurements, was calculated assuming additivity of the specific volumes of the components at the appropriate temperature, through the following relation [34,35]:

$$v_{\text{pol}} = \frac{M_{wF}}{N_A}\left[\frac{1}{\rho_0} + \frac{1}{c}\left(1 - \frac{\rho}{\rho_0}\right)\right]. \tag{9}$$

The hydration number per polymer turns out to vary from about 370 (corresponding to about 4 water molecules per ethylene oxide (EO) monomer, in analogy with that found in literature for EO [22,36,37]) at $20°C$ to about 100 at $45°C$. Therefore, the average ratio between the volume of hydration solvent to the polymer volume goes from 1.5 to about 1, which corresponds to polymer volume fraction in a micelle ranging from 40% to about 70%.

As far as A_2 is concerned, Fig. 8 shows that it slightly decreases on increasing temperature, in qualitative agreement with the temperature dependence of k_D^c. It is known that, if concentration is expressed in volume fraction ϕ, the following relation between the virial coefficients of thermodynamic and hydrodynamic interactions there exists:

$$k_D^\phi \approx k_I^\phi + k_f^\phi, \tag{10}$$

where k_f^ϕ is the virial coefficient of the friction interactions [15,24].

In order to obtain previous quantities, the $\phi/(c-c_{\text{cmc}})$ ratio is calculated to be 2.3 [38]. It follows that $k_I^\phi = 2A_2 M_{wF}(c-c_{\text{cmc}})/\phi$ is very close to that for hard spheres at lower temperatures and increases on increasing temperature (see inset of Fig. 8). Negative values of k_D^ϕ, and hence, attractive interactions, are not compatible with a k_I^ϕ value higher than 8 (the value for hard spheres). This occurrence can be explained by considering that virial coefficients furnish exact information about interparticle interactions provided that the aggregation number does not change with con-
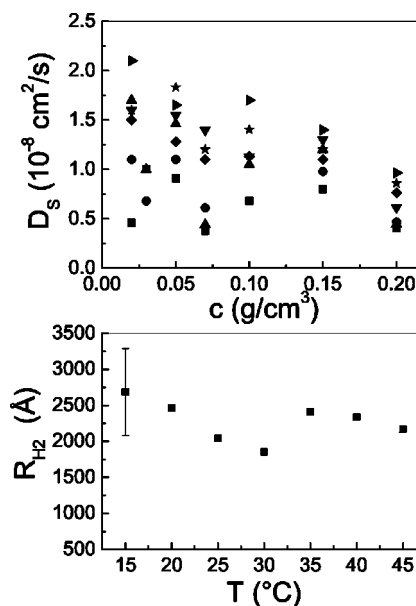

FIG. 9. Plots of clusters' diffusion coefficient and of the temperature dependence of clusters' hydrodynamic radius.

centration [39,40]. If this is not the case, whereas the extrapolated value to zero concentration is not significantly affected, the virial coefficients can change.

In most light scattering studies of micellar solutions, the aggregation number of micelles is high enough that the virial coefficient is not affected by its small change on increasing concentration. In the present case, instead, as it has been shown, the aggregation number is small; therefore, even a small increase, due to an increase of concentration, gives rise to a significant increase in the normalized absolute scattered intensity, which, therefore, is not related anymore only to interactions. As a consequence, the values of k_I^ϕ are overestimated, leading to not conciliable values of the static and dynamic virial coefficients.

The existence of clusters of micelles, together with the negative values of k_D, however, reasonably indicates that intermicellar attractive interactions take place.

As far as the slow mode is concerned, in Fig. 9 the slow diffusion coefficient is plotted against the total concentration. In this concentration range (where the micelle volume fraction increases up to about 0.4) the viscosity of solution strongly increases [41–43], whereas the diffusion coefficient is constant. If this mode represented a heterogeneity or tracer motion [24,25] (due to the polydispersity in composition of the block copolymer) it would be related to the micellar self-diffusion. Unlike the collective diffusion, representing the micelle Brownian motion in the solvent, the self-diffusion implies the motion through the nearest neighbors. So, the self-diffusion coefficient roughly depends on the inverse viscosity of the solution [24]. Therefore, the fact that D_S is nearly constant as a function of micelle volume fraction confirms the presence of clusters undergoing Brownian diffusion; self-diffusion, instead, is not detectable likely because of the low polydispersity in composition of the block copolymer. Moreover, the independence of D_S from the mass concentration suggests that the number density of clusters re-
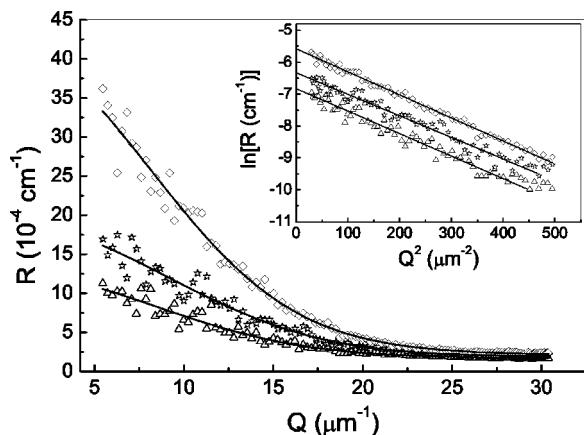
FIG. 10. Excess absolute intensity profile at $T=25\,°C$ (as an example) for different concentration: $c=0.05$ g/cm^3 (up triangles), $c=0.1$ g/cm^3 (stars), and $c=0.2$ g/cm^3 (diamonds). The continuous lines are the fit according to the polydisperse sphere form factor. In the inset the same data are reported in a Guinier-type plot, together with the Guinier fit.

mains small enough that they do not interact appreciably. The value of the hydrodynamic radius of clusters, R_{H_2}, is about 2000 Å independently from temperature as it is shown in Fig. 9.

Figure 10 reports on the scattered intensity profiles for higher concentrations at $T=25\,°C$.

In these spectra micelles contribute with Q-independent background, which is the only one surviving at higher Q. After taking into account this flat background the diffraction spectra can be fitted. From the fit of the scattered intensity profile by using the Guinier's law (as it can be seen in the inset of Fig. 10) a radius of gyration $R_{g2}=1400\pm100$ Å is obtained. Over this range, we get $0.7\leqslant QR_{g2}\leqslant3$; this occurrence implies that the value of the radius of gyration can be underestimated [44–46].

Considering that the micelles form factor $P_F(Q)$ is equal to 1, that their structure factor $S_F(Q)\approx S_F(0)$ and that the clusters structure factor $S_S(Q)=1$ (low clusters concentration), from Eq. (7) the cluster form factor can be expressed in terms of the ratio between the amplitude of the slow and fast modes of the autocorrelation function

$$P_S(Q) = \frac{c_F M_{wF} S_F(0)}{c_S M_{wS}} \frac{A_S(Q)}{A_F(Q)}. \qquad (11)$$

In Fig. 11 the ratio A_S/A_F, reported together with the Guinier law for $R_g=1400$ Å, confirms the good agreement between the static and dynamic results. It can be seen that the contribution of clusters to the total intensity at 90° is about 5%.

It has been also found that the relative amplitude of the slow mode only slightly depends on temperature.

The obtained radius of gyration remains constant over the whole concentration and temperature range explored and it is compatible with the previously determined hydrodynamic radius. The value of the ratio $R_{g2}/R_{H2}\approx0.7$ suggests that the internal structure of clusters presents a homogeneous distri-
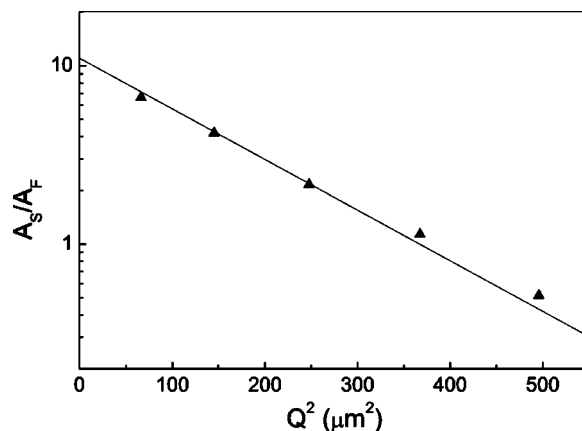

FIG. 11. Wave vector dependence of the ratio between the amplitude of the slow and fast modes of the autocorrelation function at $c=0.1$ g/cm^3 and $T=25\,°C$. The solid line is the Guinier fit with $R_g=1400$ Å.

bution which does not depend either on concentration or on temperature.

In view of these results a refinement of the fitting procedure can be made considering clusters as polydisperse sphere, with a polydispersity factor Δ:

$$R(Q) = R(0) \int [F(\Delta)]^2 d(\Delta) + X_B,$$

$$F(\Delta) = \frac{3\{\sin\left[Q(R_c+\Delta)\right] - Q(R_c+\Delta)\cos[Q(R_c+\Delta)]\}}{[Q(R_c+\Delta)]^3}.$$

$$\qquad (12)$$

The term X_B represents the contribution of micelles to the total scattered intensity and it is equal, within some percent, to the value of $R^{90°}$ reported in Fig. 1. This fit procedure gives for the radius of clusters a value of $R_c=1800\pm300$ Å, which does not depend on concentration and temperature.

The presence of these clusters can be attributed to the surface adhesion between different micelles caused by the displacement, or depletion, of the solvent molecules in the outer layer of micelles in which PEO chains interpenetrate [5]. In fact, a thin layer exists at the micelle surface where the chain conformations can be significantly perturbed. When two micelles come into contact, there is an overlapping region where polymer chains can interpenetrate and squeeze out some solvent molecules. The interpenetration gives rise to an effective attraction at the micellar surface.

Considering that both clusters and micelles are homogeneous spheres, from the extrapolation of $R(Q)$ at $Q=0$ it is possible to evaluate the mass concentration ratio between micelles and clusters through the relation

$$\frac{R(0)}{X_B} = \frac{c_S}{c_F}\left(\frac{R_{H_2}}{R_H}\right)^3. \qquad (13)$$

For the most concentrated solution ($c=0.2$ g/cm^3) an estimate of the mass ratio gives the value of $c_S/c_F\approx1:10^5$, independently from temperature, thus confirming that clus-

ters concentration is negligible with respect to that of micelles. This occurrence, as well as clusters' size invariance with concentration and temperature, suggests the weakness of the attractive potential.

The simultaneous presence of micelles and clusters depends crucially from both the proper choice of the selective solvent and the PEO length.

In other studies [47–49] spontaneous formation of large spherical and cylindrical micelles has been recently observed in water solution of PDMS-b-PEO diblock copolymers. The change in the balance between the hydrophobic and hydrophilic components allows for the modulation of the thermodynamic equilibrium. This results in a modification of the micelle morphologies [1,50]. It has been shown [48] that formation of vesicles and lamellar structures can be obtained for a short chain PDMS-b-PEO diblock copolymers with different ratios between the hydrophobic and the hydrophilic segments. In that case a critical aggregation concentration, which increases with increasing the length of the hydrophobic chain, has been observed [49].

On this basis we performed light scattering analysis on the same diblock copolymer in Tetrahydrofuran, a selective solvent for PDMS segments. Evidence of the predominant formation of large micelles (or vesicles), of the order of some thousands of angstroms, is found. Correlation functions are constituted by a single relaxation decay. This confirms the circumstance that size (as well as aggregation number) of micelles of block copolymers in a selective solvent critically depends on the relative lengths of the hydrophobic and hydrophilic components [51–53].

IV. CONCLUSION

Combination of static and dynamic light scattering experiments allows for a detailed investigation of the association and interaction properties of a diblock copolymer micellar solution in water. The proper choice of a weak amphiphile, characterized by a long hydrophilic PEO chain, allows for the study, in a convenient way, of most of the relevant properties of the system.

On increasing temperature dehydration of micelles has been observed together with a contemporaneous increase in the aggregation number, whereas the hydrodynamic radius remains constant in the whole temperature range investigated.

Micelles are in equilibrium with monodisperse clusters of entangled micelles (from just above cmc) whose origin can be attributed to a weak attractive interaction. This can be due to the partial interpenetration of PEO chains between different micelles which causes the displacement of water molecules from the outer micelles layer. Clusters maintain their structural properties unchanged in a wide range of concentrations and temperatures, and provide indirect evidence of a weak attractive component to the intermicellar interaction potential.

The present study can get insight into the stability problem of colloidal aggregates and associating properties of block copolymer systems in view of the fact that the biocompatibility of the PDMS-b-PEO makes it a good candidate for drug delivery applications and biotechnology.

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