STRUCTURAL PROPERTIES OF CHARGED DIBLOCK COPOLYMER SOLUTIONS

P. GUENOUN*, M. DELSANTI, H.T. DAVIS, A. MALDONADO, J.W. MAYS, M. TIRRELL, W. URBACH, L. AUVRAY and D. GAZEAU

We present several experimental evidences of the existence of micelles in charged block copolymer aqueous solutions. A special care has been taken to discriminate the behaviours with respect to those encountered with polyelectrolytes. In particular the effect of counterion condensation will be discussed both from the theoretical and experimental points of view. The above results lead to consider these micelles as charged brushes of spherical symmetry. Correlations between micelles have been also studied by neutron and X-ray scattering and a liquid-like order between micelles is found which is weakly sensitive to the addition of electrolyte.

INTRODUCTION

Diblock copolymers, comprised of a long and nearly fully charged moietie and of a short hydrophobic moietie, may be viewed as polyelectrolytes which are hydrophobically modified. In that respect, they can be considered as very convenient tools enabling to tether charged chains together and form new interfacial structures [1]. This may be achieved by forming micelles in water solution [2]. This paper is devoted to the study of such micellar solutions in order to better characterize them by standard techniques as light, X-ray and neutron scattering. Less common techniques were used in order to get definite proofs of the existence of micellar aggregation such as fluorescence recovery after photobleaching, pulsed NMR spectroscopy and cryo-TEM observation. Once such a proof was established, an estimation of the critical micellar solution was given by means of fluorescence spectroscopy which also confirms that the existence of such micelles is intimately related to the counterion condensation mechanism [3]. Then we show how the existence of such micelles is revealed by light scattering and we explain the actual meaning of the measured polydispersity of the system.

A more accurate view of what a micelle is can be given by neutron scattering. Results precise how close a micelle resembles to a charged brush of spherical symmetry whose interest is to provide a system mimicking colloids protected by charged grafted chains. Such colloids, which could be made either by grafting of chains or adsorption of diblocks such as the ones under study in this paper, are of wide industrial relevance. The protection by charged chains is indeed believed to be very efficient against variations of the ionic strength of the solvent [4]. Interactions between these colloids rule their stability and similar interactions can be studied with the micelles. These micelles are shown to order above some concentration in such a way that they exhibit a correlated liquid-like structure whose order is measured. The quality of this order stays surprisingly constant up to high concentrations (at least 20 wt%) at the difference of homopolyelectrolytes whose correlations are destroyed at even lower concentrations. Similar examples of liquid order are indeed also found in the area of charged stabilized colloids at comparatively lower volume fractions [5]. Addition of electrolyte has little influence on the ordering of the micelles which is a confirmation of the relative insensitivity of such spherical charged brushes to the addition of electrolyte. On the contrary, both polyelectrolytes and colloids are generally disordered upon addition of salt.

1 MATERIALS

Diblock copolymer of poly(ethylene-propylene)-sodium poly(styrene-sulphonate) (PEP-NaPSS) or poly(ter-butyl-styrene)-sodium poly(styrene-sulphonate) (PtBS-NaPSS) were synthesized using methods described elsewhere [6]. The degree of suphonation of the PSS part is about 89% and

* CEA Saclay, SPEC,
  91191 Gif-sur-Yvette Cedex - France

polydispersity indices M_w/M_n are about 1.04. The molecular weight of the PEP-NaPSS is of the order of 5.0×10^4 whereas it is of 8.0×10^4 for the PtBS-NaPSS. These diblock copolymers are highly asymmetric with a small hydrophobic block (weight percentage of 6.8% for PEP-NaPSS and of 4.6% for PtBS-NaPSS) and a large hydrophilic NaPSS block. Solutions were prepared in deionized H_2O water upon passing them through milli Q/millipore system of pore size 0.22 μm (18 Mohm.cm) or in D_2O water. Samples with salt were prepared with NaCl of analytical grade. All the measurements were performed at temperatures close to 25°C.

2 CRYO-TEM OBSERVATION AND SELF-DIFFUSION

Photographs of 1 wt% solutions of PtBS-NaPSS solutions in water were taken by Cryo-Transmission Electron Microscopy (Fig. 1). The structures observed are compatible with cores of micelles of order 6 nm of diameter whereas NaPSS solutions do not show any contrast. Neutron scattering on D_2O solutions at the same concentration provides consistent results since one gets a diameter of 6.8 ± 0.3 nm. This is a first indication of an association
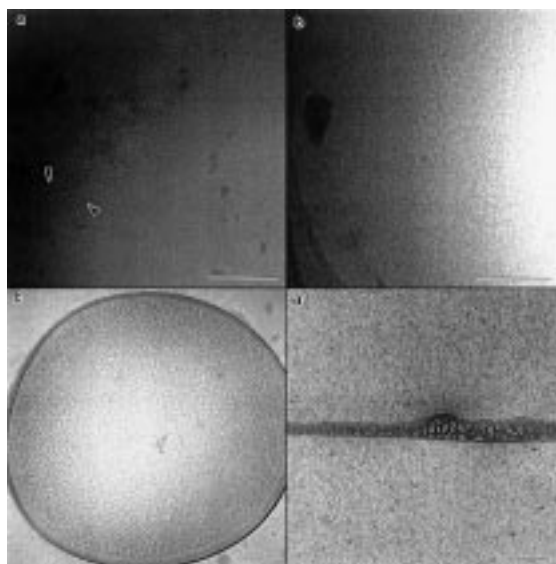

Figure 1

Cryo-TEM pictures of a PtBS-NaPSS solution (1 wt%) at different salinities:
a) No added salt (10^{-4} M NaCl). Arrows point to possible start and end of a long thread-like micelle;
b) 10^{-2} M NaCl;
c) 10^{-1} M NaCl;
d) 0.85 M NaCl. The bar is 200 nm length.

phenomenon which implies an association of the hydrophobic hydrophobic segments at the center of a charged corona. Since collective diffusion measurements, such as the ones provided by quasi-elastic light scattering (QELS), can result in spurious results due to the large interactions of charged species, we turned to self-diffusion measurements by fluorescence recovery after photobleaching and pulsed NMR spectroscopy. Sizes provided by the latter techniques are in good agreement with collective measurements by QELS and revealed the existence of micellar objects whose corona is made of extended chains, close to rods, surrounding a comparatively small core. Critical micellar concentrations can be estimated by monitoring the fluorescence of the PSS groups and noticing that, around a concentration on order 2×10^{-4} wt%, an enhancement of the excimer emission is observed [3]. This enhancement was interpreted as due to the trapping of the counterions within the corona of the micelle, a fact both confirmed by recent theoretical work [7] and by the weakness of interactions between the nearly neutral micelles as shown by light scattering.

3 LIGHT-SCATTERING AND POLYDISPERSITY

Characterization of the solution by light-scattering experiments show the existence of a bimodal population of scatterers. For instance, the total intensity scattered by a dilute sample (c = 2×10^{-2} wt%) of PEP-NaPSS for which interactions are negligible is slightly q^2-dependent at large q values (where q is the transfer wavevector) whereas at small q values the intensity dramatically increases. The strong curvature observed can be only explained by the presence of a small amount of very large scatterers and a large amount of small scatterers. This point is confirmed by QELS measurements on the same sample since typical correlation function g(t) obtained at small q clearly exhibit a non exponential decay. In order to determine the distribution, $A(\Gamma)$, of the decay rates Γ defined by g(t) = $\int A(\Gamma)$ exp $(-\Gamma t)d\Gamma$, a maximum entropy method was used [8] and the results confirm that the distribution, $A(\Gamma)$, of the decay rates Γ is bimodal at low q values (Fig. 2). The nature of the large aggregates is still conjectural but one can think of supra-micellar objects hold together by residual non-sulfonated segments of the corona chains.

4 NEUTRON SCATTERING

Neutron scattering at small angles was used to directly characterize the hydrophobic association by use of the contast matching technique. We made use of a mixture of H_2O and D_2O (44% in volume of D_2O) which exactly matches the PSS part, making it invisible to neutrons. For dilute solutions the scattering curves are nicely fitted by a
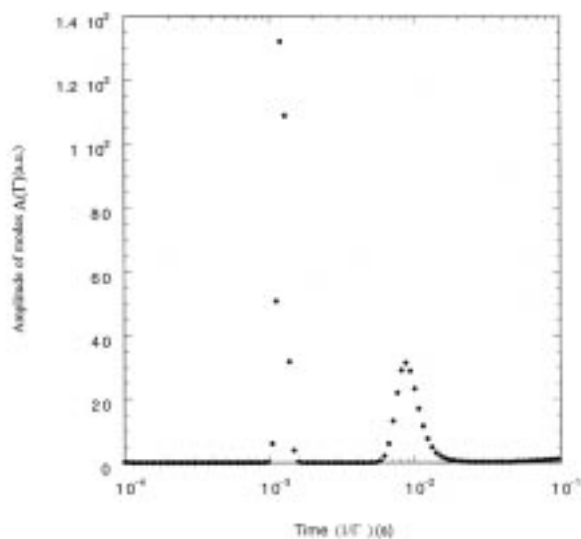
Figure 2

Distribution of relaxation times deduced by the maximum entropy method for a QELS experiment at a wavevector of 1.1×10^5 cm^{-1} for the PEP-NaPSS diblock at 0.02 wt%. Using this method we found no change on the results by varying the input window of relaxation times contrary to the case where we used the CONTIN method.

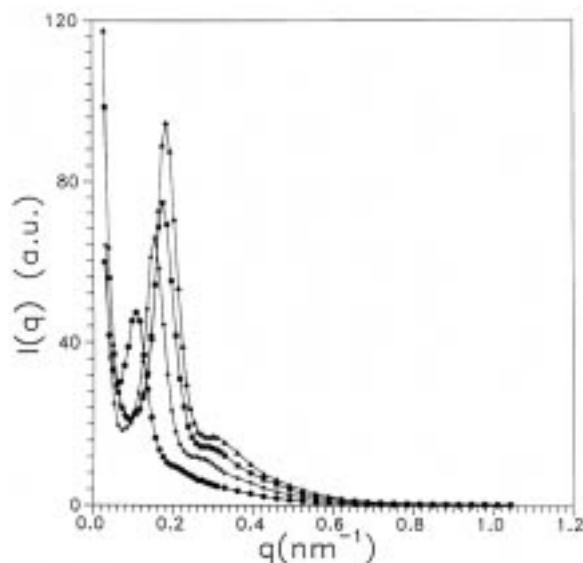[Provencher S.W.(1982) *Comput. Phys. Comm.*, **27**, 213].

Figure 3

Scattered intensity I(q) versus wavevector q by salt-free solution of PEP-NaPSS diblock at various concentrations:
(●) 5 wt%,
(∗) 10 wt%,
(■) 15 wt%
(▲) 20 wt%.

form factor of spheres of radius $R_c = 5.2 \pm 0.2$ nm for the PEP-NaPSS polymer. A good agreement is obtained with a determination by light scattering which provides $R_c = 5.3 \pm 0.5$ nm when carefully removing the influence of the large aggregates.

Concentrated solutions of PEP-NaPSS in pure D$_2$O exhibit a correlation peak in the scattered intensity I(q) within a range of concentration 5-20 wt% as can be seen on Figure 3. We interpret this correlation peak as the signature of liquid-like correlations between packed micelles since the first occurrence of this peak, at a concentration about 5 wt%, is related to the crossing of the concentration c* where the arms of the micelles begin to contact. The hypothesis of packing is consistent since it enables another determination of the micellar core radius to be made, which again recovers the value of 5.2 nm. For higher concentrations the increase in q* denotes either a contraction of the arms or an interpenetration of them. We favor the first interpretation since the degree of order, as measured by the height of the peak at q* in a representation of I(q)/c, stays constant from 7 wt% up to 20 wt%. It is worth comparing these results with the evolution of the so-called polyelectrolyte peak which is currently observed by neutron or X-ray scattering on solutions of NaPSS [9]. This peak evolves as $q^* \propto c^{1/2}$ and has an absolute value which, for the same concentration of NaPSS and diblock and nearly the same molecular weight (a parameter which does not shift the peak much for polyelectrolyte), lies an order of magnitude above the one we observed. Moreover it can be checked that for concentrations above 10 wt%, the polyelectrolyte peak nearly vanishes while the diblock peak is still well defined. The variation of the peak position q* with c in the range 2 to 20 wt% for diblock solutions is well fitted by the law $q^* \propto c^a$ with a close to 1/3 confirming the idea of ordering of spheres.

Addition of monovalent electrolyte (NaCl) has little effect on the existence and position of the peak which is slightly shifted to lower values as the salt concentration reaches 0.5 M. This is reminiscent of similar behaviors obtained about solutions of charged latex or silica particles where the ordering peak is nearly unchanged in position by addition of salt [5] although the height of the peak is drastically affected by the salt addition. On the contrary, the ordering peak of the diblock copolymer slightly decreases when the added salt concentration corresponds to a ionic strength comparable to the one inside the micelles. For each polymer concentration, the low angle scattered intensity is also affected when some threshold in electrolyte is passed over, indicating when the additional screening of the micellar interactions by the electrolyte overcomes the already large screening due to the counterions brought by the diblock itself.

More specifically, using X-ray scattering, we also investigated the differences between the signals scattered by the PEP-NaPSS diblock and by an homopolymer NaPSS of comparable molecular weight. At a concentration of 10 wt% and a salinity of 0.1 M, the ordering peak of NaPSS is no longer observed while the ordering peak of the PEP-NaPSS still subsists. However the peak for the diblock is now shifted towards higher q values, this shift being larger than the one observed by neutrons. This small shift results from the changes in the electronic densities due to the addition of salt which affect both the form factor and the structure factor and, consequently, the total scattered intensity.

REFERENCES

1 Halperin A., M. Tirrell and T.P. Lodge (1991), *Adv. Pol. Sci.*, **100**, 31.

2 Guenoun P., H.T. Davis, M. Tirrell. and J.W. Mays (1996), *Macromolecules*, **29**, 3965.

3 Guenoun P., S. Lipsky, J.M. Mays and M. Tirrell (1996), *Langmuir*, **12**, 1425.

4 Pincus P. (1991), *Macromolecules*, **24** , 2912.

5 Härtl W., H. Versmold, U. Wittig and V. Marohn (1983), *Molecular Physics*, **50**, 815.
Goodwin J.W. and R.H. Ottewill (1991), *J. Chem. Soc. Faraday Trans*, **87**, 357.
Chang J., P. Lesieur, M. Delsanti, L. Belloni, C. Bonnet-Gonnet and B. Cabane (1995), *J. Phys. Chem.*, **99**.

6 Valint P.L. and J. Bock (1988), *Macromolecules*, **21**, 175.

7 Huang C., M. Olvera de la Cruz, M. Delsanti and P. Guenoun, submitted to *Macromolecules*.

8 A program kindly provided to us by J. Langowski who conceived it: J. Langowski and R. Bryan (1991), *Macromolecules*, **24** , 6346.

9 Nierlich M., C. Williams, F. Boué, J.P. Cotton, M. Daoud, B. Farnoux, G. Jannink, C. Picot, M. Moan, C. Wolff, M. Rinaudo and P.G. de Gennes (1979), *J. de Phys.*, **40**, 701.

Final manuscript received in January 1997