

Cite this: *Chem. Commun.*, 2011, **47**, 3802–3804

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COMMUNICATION

Thermoreversible formation and negative thermal expansion of supramacromolecular assemblies of unimolecular micelles in solution†

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Received 9th December 2010, Accepted 19th January 2011

DOI: 10.1039/c0cc05472k

We report the thermoreversible formation of superstructural assemblies of unimolecular micelles in solution displaying negative thermal expansion behaviour.

In the recent years, supramacromolecular assembly has demonstrated unparalleled versatility to build up functional materials entirely from scratch.^{1,2} For instance, it is now well accepted that the manipulation of the aggregation structure of macromolecular assemblies can be a powerful method to tune the physicochemical properties of supramolecular materials.³ Among the traditional building blocks for preparing self-assembled supramacromolecular architectures, amphiphilic polymers have many advantages in the assembly of nano- and mesostructures owing to the contrasting properties of their hydrophilic and hydrophobic groups.⁴ Along these lines, dendrimers with amphiphilic core-shell structures displaying micelle-like properties emerged as very attractive building blocks to form supramolecular materials with tailored properties.⁵ In particular, the modification of peripheral groups of dendrimers with hydrophobic tails led to the creation of molecularly defined systems with inverse micelle properties.⁶ Seminal works of Percec and co-workers provided the framework for designing an unprecedented number of superstructural assemblies from precisely engineered dendrons and dendrimers.^{7,8} However, dendrimer multistep synthesis limits the practical use almost exclusively to a laboratory scale. For this reason, hyperbranched polymers, dendritic polymers with less structural regularity, prepared in a one-step process have gained increasing interest within the materials science community.⁹ Furthermore, they also display unique properties as manifested by their globular structure and large number of terminal groups.¹⁰ In a similar vein, amphiphilic core-shell hyperbranched polymers exhibit unimolecular reverse properties in analogy with amphiphilic dendrimers.¹¹ Most of the structural studies of unimolecular micelles based on hyperbranched polymers indicate that these systems exist as

unimolecular entities or large *amorphous* aggregates depending on the solvent or the temperature conditions.¹² To date, in contrast to amphiphilic dendrimers, there are no studies suggesting the formation of superstructural assemblies in solutions of hyperbranched unimicelles. As such, finding experimental evidence demonstrating the presence of long-range supramacromolecular order in solutions of unimolecular unimicelles is a major stepping stone toward the realization of ordered mesoscale superstructural assemblies by using robust building blocks easily provided in large quantities.¹³ Herein, we present unprecedented experimental evidence revealing outstanding superstructural features of unimolecular micelles that include: (i) long-range order in solution, (ii) fully reversible “crystal-to-colloid” transition, and (iii) negative thermal expansion of the supramacromolecular assembly.

The unimolecular micelles were constituted of hyperbranched polyethyleneimine (hydrophilic core) covalently modified with a hydrophobic shell of palmitoyl chains (HPEI-C16) (Mn: 39.3 kDa) (Fig. 1). These building blocks were synthesized according to the protocol described by Stiriba and co-workers.¹⁴ Small-Angle X-ray Scattering (SAXS) experiments were performed using a SAXSess-mc² system from Anton Paar (Graz—Austria)

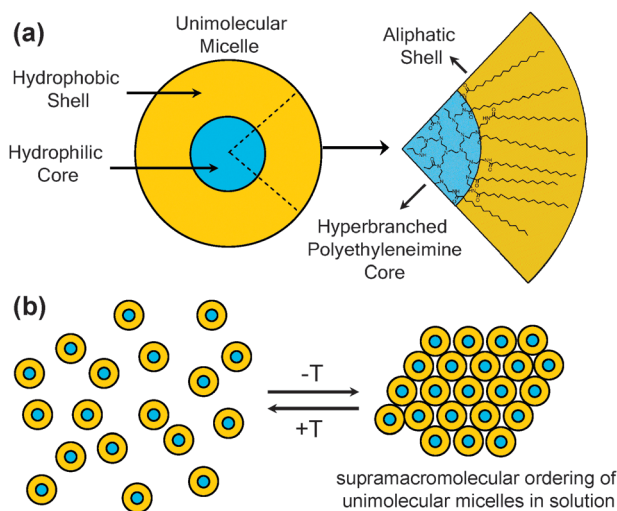


Fig. 1 (a) Simplified cartoon depicting the core-shell architecture of the unimolecular micelle. (b) Scheme describing the supramacromolecular ordering process taking place in the micellar solution.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0cc05472k

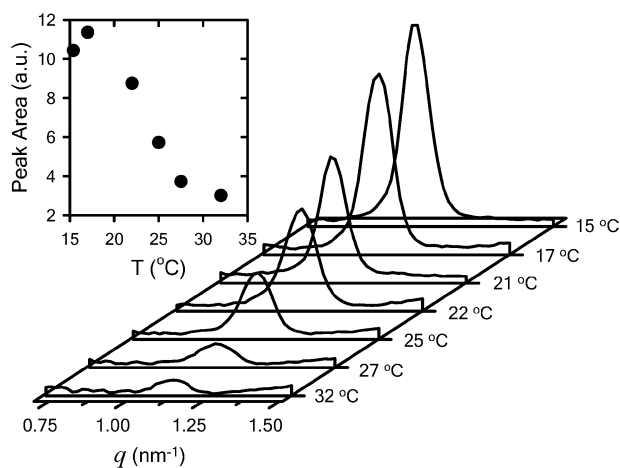


Fig. 2 (a) SAXS intensity profiles of a toluenic HPEI-C16 solution (10 g L^{-1}) obtained under different temperature conditions. The inset shows the evolution of the SAXS peak areas as a function of temperature.

and at the D01B-SAXS1 beam line of the Laboratório Nacional de Luz Síncrotron (LNLS—Brazil).

Fig. 2 displays the SAXS patterns obtained upon varying the temperature of HPEI-C16 solutions (10 g L^{-1} in toluene) from $15 \text{ }^\circ\text{C}$ to $32 \text{ }^\circ\text{C}$. The SAXS intensity profiles at lower temperatures show the presence of a pronounced peak indicating the existence of long-range structural order in the system due to intermicellar interactions in solution. These SAXS patterns resemble those recently reported for superstructural assemblies of negatively charged PAMAM dendrimers in aqueous solution,¹⁵ thus reinforcing the asseveration that long range order is present in the solution of unimolecular micelles. The thermal evolution of the Bragg peak indicates that the ordered phase vanishes around $33 \text{ }^\circ\text{C}$ giving rise to a typical SAXS pattern for a dilute system, *i.e.*: isolated particles (Fig. 3a). The Kratky, volume and pair distance distribution function (PDF) plots of HPEI-C16 in the high temperature phase clearly indicate that the molecule behaves as a globular particle with a radius of gyration (R_g) equal to $1.87 \pm 0.02 \text{ nm}$ (Fig. 3). In addition, the SAXS-derived excess electron density profile corroborates the expected core-shell structure of the unimicelle (see ESI† for further information) (Fig. 3d). Moreover, a simple mathematical model was derived to explain the monotonic decrease of the excess electron density (see ESI† for further information). Referring back to Fig. 2, the temperature-dependent changes in the SAXS pattern eloquently illustrate the existence of an ordered supramolecular “aggregate” that is disassembled into its constituting building blocks, *i.e.*: unimicelles, upon increasing the solution temperature.

The “crystal-to-colloid” transition occurring around $33 \text{ }^\circ\text{C}$ was determined to be fully reversible. We performed several thermal cycles with full recovery of the SAXS pattern of the low temperature phase within few minutes (Fig. 4).

A closer look to the evolution of the SAXS patterns revealed an intriguing finding. The “crystallite size” (134 nm in toluene at $22 \text{ }^\circ\text{C}$), as obtained from the Bragg peak using the Scherrer formula, displays a systematic tendency to decrease during gradual heating (Fig. 5). This kind of observation was

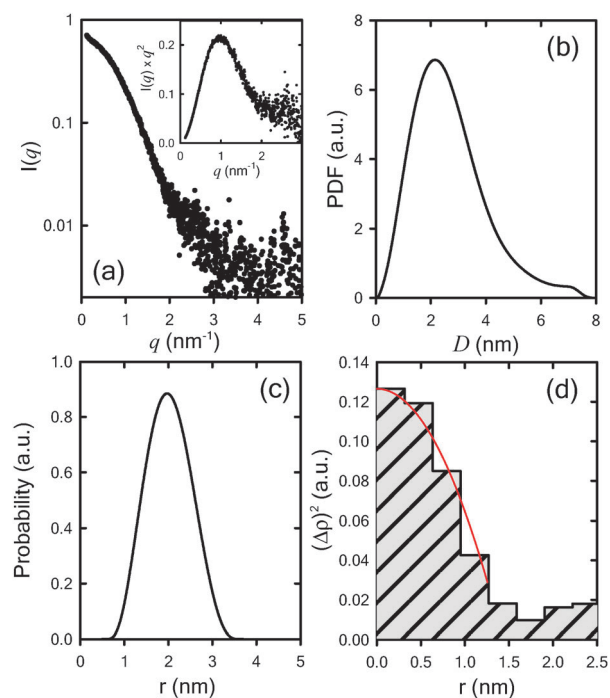


Fig. 3 (a) Raw SAXS data corresponding to HPEI-C16 micelles measured at $40 \text{ }^\circ\text{C}$ in toluene (inset: Kratky plot). The figure also displays the SAXS-derived pair distance distribution function (PDF) (b) and volume plots (c) and the electron density spatial profile (d). The full red line corresponds to the fit of model for the excess electron density to the experimental data.

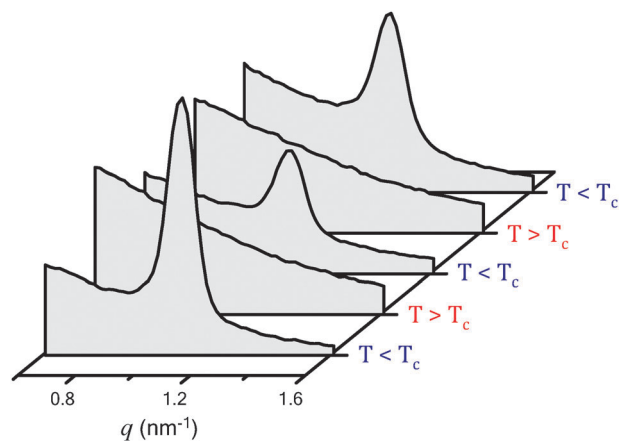


Fig. 4 (a) SAXS intensity profiles of a toluenic HPEI-C16 solution (10 g L^{-1}) obtained upon cycling the temperature above and below the “crystal-to-colloid” transition temperature (T_c).

expected provided that the increasing thermal energy enables the unimicelles to denucleate from the ordered aggregate.

However, the interplanar spacing obtained from the peak position in the SAXS patterns revealed a noticeable decrease upon increasing the temperature close to the “crystal-to-colloid” transition (Fig. 5). This experimental observation reveals that the supramacromolecular assembly of unimicelles displays a negative thermal expansion of the interplanar spacing.

The negative thermal expansion (NTE) is a very unusual phenomenon that has been studied in several inorganic systems.¹⁶ However, organic and supramolecular systems

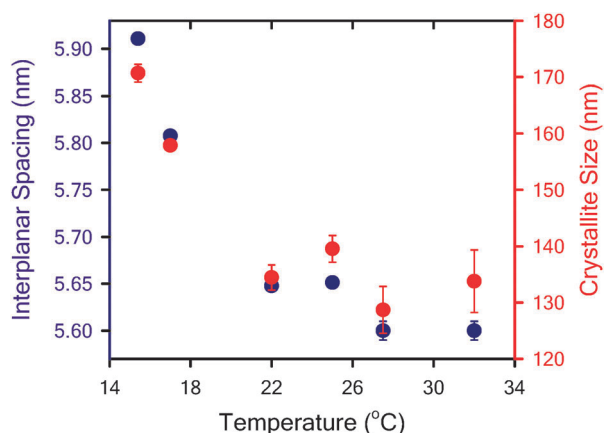


Fig. 5 (a) Representation of the interplanar spacing (left, ●) and crystallite size (right, ●) as a function of temperature.

displaying NTE have very rarely been reported.¹⁷ In conventional materials, as volume expands, disorder (or entropy) also increases giving rise to positive thermal expansion coefficient. But in some systems, the delicate interplay between constrained conformations, molecular ordering, steric hindrance and supramolecular organization in the presence of van der Waals interactions may lead the macromolecular system to a more ordered state (negative dS) as the volume expands giving rise to NTE.¹⁸ To the best of our knowledge, this is the first experimental observation of NTE in assemblies constituted of unimolecular micelles. In our case the intermicellar spacing decreases from 5.91 to 5.64 nm upon increasing the solution temperature from 15 to 32 °C. This thermally induced structural transformation, *i.e.*: shrinkage, is associated to a negative coefficient of thermal expansion equal to $-6.5 \times 10^{-3} \text{ K}^{-1}$. It is worthwhile mentioning that this value represents a large negative thermal expansivity that is comparable to that recently reported for discotic liquid crystals of hexa-*per*-hexabenzocoronenes.¹⁹ We consider that these findings may lead to new strategies for designing supramacromolecular materials displaying exotic thermoactive properties. More importantly, these thermoresponsive features emerge from long-range supramacromolecular organization of robust building blocks that can be easily provided in large quantities *via* simple synthetic protocols.

In summary, we have demonstrated that the aggregation of hyperbranched unimolecular micelles can lead to the formation of thermoreversible superstructural assemblies in solution. This work also provides the first experimental observation of negative thermal expansion in supramolecular assemblies formed by unimolecular micelles. We believe that these results will further broaden the exploration of hyperbranched unimolecular micelles as robust assemblable building blocks leading to the formation of self-organized organic nanostructures with unprecedented functional features.

A.S.P. gratefully acknowledges CONICET for a scholarship. This work was supported by CONICET (PIP112-200801-00362),

ANPCyT (CINN – PRH 2007 No. 74-PIDRI No.74-PICT-PRH 163/08) and Laboratorio Nacional de Luz Síncrotron (LNLS) (D11A-SAXS1-8575/9108/9868). We are grateful to Peter Worsch for granting us access to Anton Paar facilities in Graz – Austria. O.A. and M.C. are staff members of CONICET. M.C. is a Full Professor at UNNOBA, Argentina.

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