Short Communication

Temperature-driven self-assembly of self-limiting uniform supraparticles from non-uniform unimolecular micelles ☆

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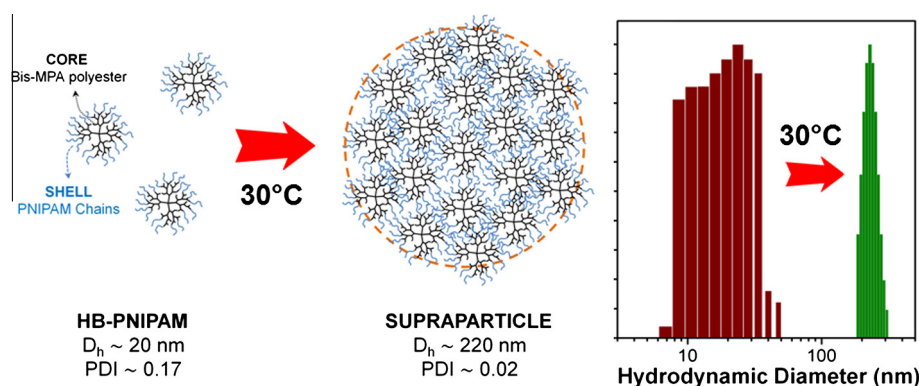
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GRAPHICAL ABSTRACT

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ABSTRACT

In this work, the self-assembly of non-uniform unimolecular micelles constituted of a hyperbranched polyester core decorated with a corona of thermoresponsive poly(N-isopropylacrylamide) (PNIPAm) chains has been studied. As revealed by dynamic light scattering (DLS), transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS), these unimicelles form uniform supraparticles through a thermally-induced self-limited process, as well as exhibit molecular features commonly observed in PNIPAm-based gels. We believe that these results provide new insights into the application of stimuli-responsive polymeric materials as versatile building blocks to build up soft supraparticles displaying well-defined dimensional characteristics.

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1. Introduction

Self-assembly plays a central role in supramolecular chemistry [1] as well as in soft-matter based systems [2]. Several examples of versatile assemblies with tunable properties have shown the importance of this phenomenon [3], and owing to this, over the

past decades, self-organization processes have been explored among many different systems such as lipids [4], block copolymers [5], dendrimers [6], polyelectrolytes [7] or nanoparticles [8] providing new insights and fresh perspectives in different fields such as drug delivery and functional materials.

In parallel, unimolecular micelles [9] have gained increasing interest because of their impact on supramolecular host-guest chemistry [10]. Unimicelles are constituted of a dendritic polymeric core surrounded by a covalently attached shell consisting of moieties having a contrasting solvent affinity compared to the core. These structures exhibit micellar properties as a single amphiphilic macromolecule, and unlike traditional multimeric micelles, they can act in wide range of scenarios since all the entity is held together by covalent bonds [11]. Although the very first examples of such structures were illustrated by the use of perfect dendrimers [12], their imperfect analogues, hyperbranched polymers [13], are also attractive building blocks owing to their large scale availability at reasonable costs. Dendritic amphiphilic macromolecules and unimicelles can self-assemble in the presence of different environmental stimuli such as concentration [14], temperature [15], pH [16], solvent composition [17], redox activity [18] or dye uptake [19], among others [20].

Self-assembly is a powerful and versatile strategy to create supramolecular materials and nanostructures with tailored physical/chemical properties from molecular, macromolecular and nanoscopic assembly units [21]. For instance, Kotov and his collaborators [22] recently reported that nanoparticles in solution can spontaneously assemble into well-defined uniform supraparticles as a result of the balance between van der Waals (attractive) and electrostatic (repulsive) forces among interacting nanoparticles. Once equilibrium was reached, the self-assembly process stops giving origin to the *self-limited* growth of the supraparticle. Today, there is a general consensus that such self-limiting assembly has the potential to be a general approach to create hierarchically organized supramolecular materials [23].

Until now, however, the self-limiting assembly has only been demonstrated for inorganic nanoparticles and nanomaterials. Also, despite their promising prospects, few is known about the application of environmental stimuli to trigger the self-limited assembly process [24].

In this work we present unprecedented experimental evidence revealing the thermally driven formation of highly uniform supraparticles resulting from the self-limited assembly of non-uniform unimicelles. The unimolecular micelles (HBPE-g-PNIPAm, Mn = 41,000 Da) were constituted of hyperbranched polyester core (bis-MPA polyester-64-hydroxyl, Mn = 7300) and a shell constituted of poly(N-isopropylacrylamide) (PNIPAm) [25] using ATRP (atomic transfer radical polymerization) technique. The synthetic protocol is depicted in Fig. 1 and explained in detail in the Electronic Supporting Information (ESI) file.

2. Results and discussion

PNIPAm is one of the best known thermoresponsive polymers [26]. In aqueous solution, it presents a lower critical solution temperature (LCST) around 32 °C, which involves a hydrophobic collapse with disruption of the hydration of both hydrophobic and hydrophilic groups, inducing a coil-to-globule transition in the polymer [26,27]. Dynamic light scattering experiments (Fig. 2) revealed that HBPE-g-PNIPAm behaves as a unimolecular entity with a hydrodynamic diameter (D_h) $\sim$ 20 nm until reaching a transition temperature (T_t) around 28–29 °C. Surprisingly, above T_t, unimicelles aggregate forming nearly uniform supraparticles with $D_h \sim$ 220 nm. This is a non-trivial observation provided that in most of cases thermo-induced aggregation of PNIPAm-modified polymers lead to the uncontrolled formation of non-uniform aggregates. In this case, it seems to be that the decoration of the periphery of the hyperbranched core with PNIPAm chains together with the modification on the hydration of PNIPAm chains above the transition temperature facilitates the controlled assembly of the macromolecular building blocks ending with the formation of uniform supraparticles. The presence of such supraparticles assembled above the transition temperature was confirmed by transmission electron microscopy (TEM) imaging (Fig. 3). A schematic representation of HBPE-g-PNIPAm self-assembly can be found in Fig. 4.

The most remarkable feature of the assembly process of HBPE-g-PNIPAm is the sharp decrease in the polydispersity of the supraparticle as compared with the constituting building blocks, *i.e.*: unimicelles. Note that in DLS experiments polydispersity is usually expressed as $PDI = \delta^2/D_h^2$, where δ is the standard deviation and D_h is the hydrodynamic diameter. Below T_t, for isolated particles the *PDI* value is $\sim$0.18 ($\delta \sim$ 8.5 nm) while above T_t the supraparticles present a $PDI \sim 0.02$ ($\delta \sim$ 31 nm) (see Fig. 2). The noticeable increase in PDI (while D_h remains almost unchanged) just below the LCST, may be reflecting the onset of the critical fluctuations occurring at Tc. We hypothesize that shape changes during the first stages of HBPE-g-PNIPAm aggregation, induced by the fluctuations near Tc, may influence PDI while the size of the supramolecular aggregates remains almost unchanged.

Finally, the reduction on critical temperature (from 32 °C expected for free PNIPAm to 28.8 °C observed here) can be rationalized following the arguments outlined by DeGennes et al. [28] about the formation of dense clusters due to n-body attractive interactions that ultimately leads to a decrease in LCST.

Although some polydispersity reduction can be expected from statistical considerations, the dramatic difference between PDIs of unimers and supraparticles cannot be accounted just by statistical arguments. For instance, considering both the unimers and the supraparticles as spheres, the number of HBPE-g-PNIPAm units (N_{uni}) constituting the aggregate can be estimated, using the
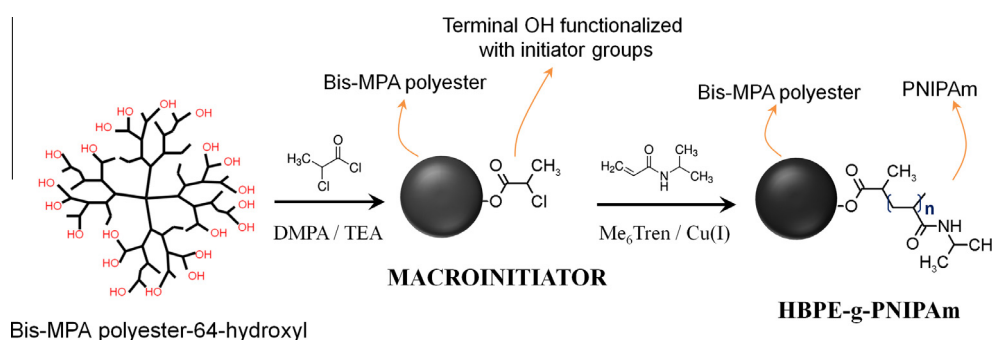

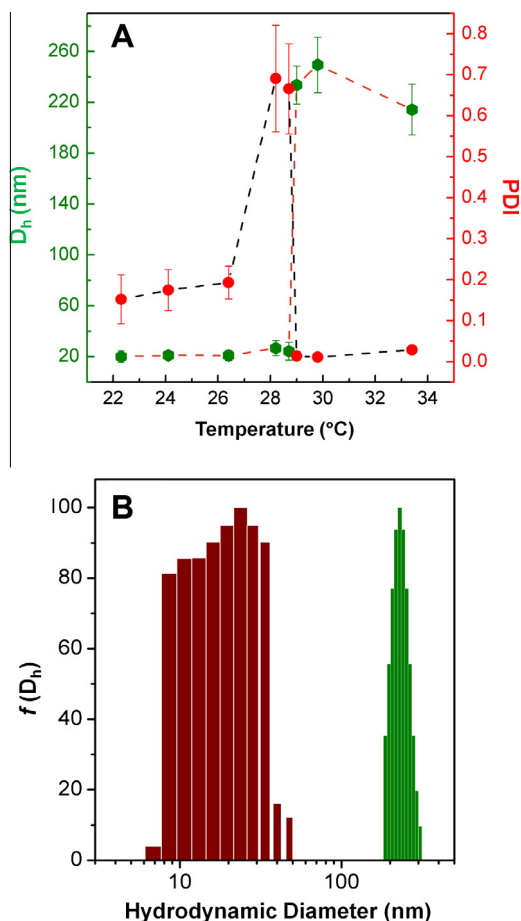**Fig. 1.** Schematic representation of the synthesis of HBPE-g-PNIPAm.

Fig. 2. (A) Evolution of D_h (by intensity) and PDI of HBPE-g-PNIPAm in aqueous solution (1.5 g/l) as a function of temperature. (B) Size distribution (by intensity) of unimers (HBPE-g-PNIPAm at 24 °C, in red) and supraparticles (HBPE-g-PNIPAm at 30 °C, in green) obtained by DLS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
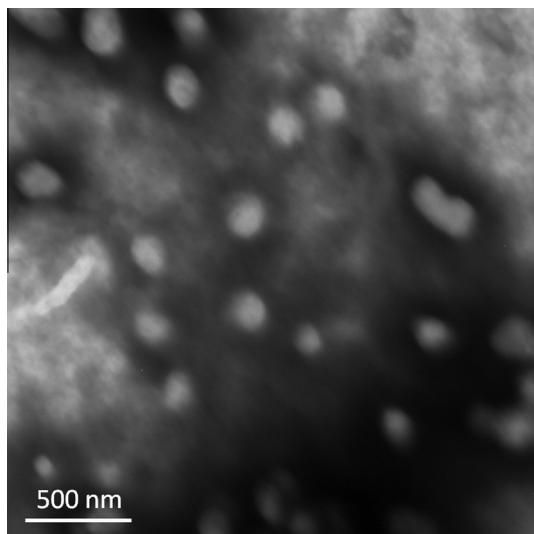

Fig. 3. Transmission electron micrograph of HBPE-g-PNIPAm supraparticles assembled at 34 °C in aqueous solution (1.5 g/l).

spherical cluster approximation [29], as $N_{uni} \sim (D_{sup}/D_{uni})^3 \times f$ where D_{sup} and D_{uni} are the diameters of the supraparticle and unimer, respectively, and f is the packing fraction. Taking this into
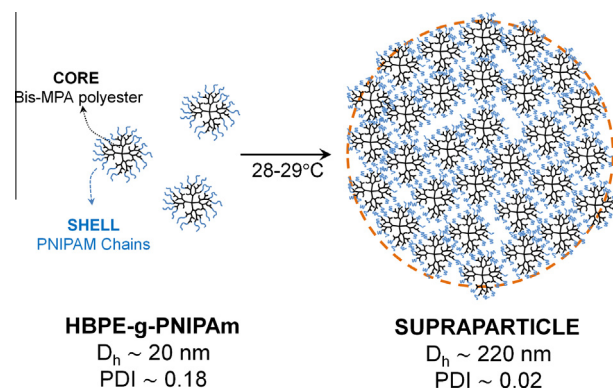

Fig. 4. Schematic representation depicting the self assembly of HBPE-g-PNIPAm unimers into supraparticles.

account, it is possible to derive a simple equation relating the standard deviation of the unimer (δ_{uni}) and supraparticle (δ_{sup}) as $\delta_{sup} \sim (N_{uni}/f)^{1/3} \times \delta_{uni}$. Since the observed D_{uni} and D_{sup} are $\sim$20 nm and $\sim$220 nm, respectively, and $\delta_{uni} \sim 8.5$ nm, considering the limiting (yet unrealistic) case $f = 1$, the computed expected value of the supraparticle polydispersity is $PDI_{sup} \sim 0.15$, being this value well above the actual value of PDI_{sup} (0.02) derived from DLS experiments.

Therefore, the convergence of HBPE-g-PNIPAm assemblies in supraparticles with well-defined diameters and narrow size distribution must imply concerted interactions among the building blocks as well as within the supraparticles, that cannot be explained just by considering statistical arguments. *It is now widely accepted that* self assembly of uniformly sized supraparticles is a process governed by competition between repulsive and attractive forces [30]. In our case we hypothesize that self-limitation leading to the formation of narrowly uniform supraparticles is likely to arise from competition between long-range steric repulsive interactions (arising from excluded volume effects of the PNIPAm chains) and attractive short-range hydrophobic interactions (arising from hydrophobic PNIPAm chains above LCST).

On the other hand, different models describing the formation of uniformly sized spherical aggregates are well known in the field of inorganic colloids [31]. In particular, the formation of secondary particles with low polydispersity is assumed to be a diffusion-controlled process [32]. This type of process can be responsible of the narrow size distribution observed in the HBPE-g-PNIPAm supraparticles. Nevertheless, more experiments will be necessary to corroborate this mechanism.

To gain insights into the structure of both the unimicelle and the supraparticle we performed *in-situ* SAXS experiments. Since HBPE-g-PNIPAm shows low contrast in aqueous solution, we used a higher concentration than the used for DLS experiments to improve the signal to noise ratio.

Even though the concentration was high, the transition occurred at the same temperature as observed by DLS and SAXS. Below T_t, the scattering pattern presents two main features, in the low angle part of the diagram ($q < 2$ nm^{-1}), the scattering is originated in isolated unimicelles (see below). At high q, a broad correlation peak $q_{peak} = 5.35$ nm^{-1} originates in a correlation distance ($D_{cor} = 2\pi/q_{peak}$) of 1.17 nm (see Fig. 5). This last feature is commonly found in different PNIPAm-based gels and assigned to correlations between PNIPAm chains [33–37]. As explained by Perez et al., this peak may arise from a local packing having its origin in the interaction between two neighbor chains [33], via hydrogen bonds between amide functions and/or hydrophobic association of isopropyl groups [38]. Below T_t the system is constituted of isolated particles and the peak arises from intra-unimer and inter-PNIPAm chain correlations.
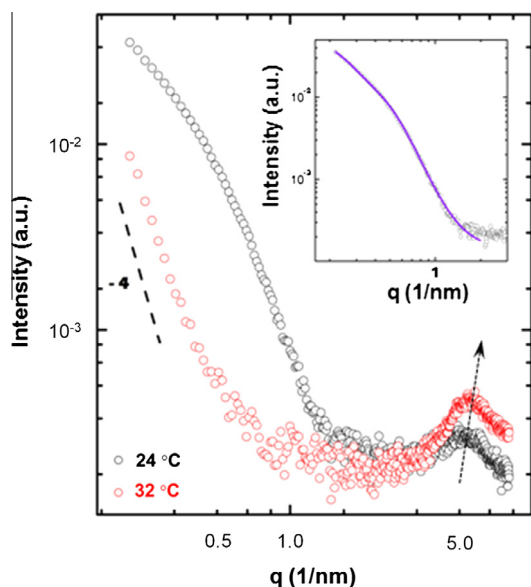
Fig. 5. SAXS patterns of HBPE-g-PNIPAm in aqueous solution (15 g/l) below and above the transition temperature. The upper inset shows the fit of the experimental scattering pattern (at low angles, q < 2 nm^{-1}) of HBPE-g-PNIPAm at 24 °C using the Unified Fit model (see text).

The scattering at low angle ($q < 2$ nm^{-1}) can be modeled using the Unified Fit Model proposed by Beaucage [39], which has been successfully applied to hyperbranched systems [40]. Considering one hierarchical level, the isolated particles of HBPE-g-PNIPAm possess a radius of gyration $R_g = 6.9$ nm corresponding to an apparent sphere radius ($R_s \sim 1.29 \times R_g$) of 8.9 nm, in fairly well accordance with DLS results. The fitted curve is shown in the inset of Fig. 5 (see ESI file for a detailed explanation of the model and fitting results).

Above T_t, at low angles the SAXS pattern shows a well defined power law behavior with an exponent equal to -4 (see dashed line in Fig. 5 for comparison). This can be attributed to the surface scattering (Porod regime) of large particles, *i.e.*: supraparticles). On the other hand, upon increasing the temperature the correlation peak increases its intensity and is shifted toward wider angles (see dotted arrow in Fig. 5) from 5.35 nm^{-1} ($D_{cor} = 1.17$ nm) to 5.55 nm^{-1} ($D_{cor} = 1.13$ nm). This behavior has also been observed in PNIPAm-based gels during the thermal transition. Chalal et al. in a work dealing with PNIPAm-based gels using MBAA as crosslinker, have attributed this weak variation in peak position to changes in the hydrogen bonding of water at C=O or N—H sites, which finally may lead to small modifications in the conformation of the PNIPAm chains [37]. This asseveration is in agreement with the observations reported by Ahmed and coworkers for PNIPAm nanoparticles studied by UV resonance Raman experiments [41]. It is important to note that in the present case, above T_t, unimicelles are self-assembled forming supraparticles, and owing to this, the interactions between PNIPAm chains may arise not only from intra-unimer interactions, but also from inter-unimer correlations.

3. Conclusions

In summary, we have demonstrated that the self-assembly of thermoresponsive non-uniform unimolecular micelles can lead to the formation of uniform supraparticles. SAXS experiments have shown that HBPE-g-PNIPAm unimicelles exhibit many molecular features that resemble those observed in PNIPAm-based gels. We believe that these results provide new insights into the application of environmental stimuli to trigger the self-limited growth of supramolecular soft nanoparticles with narrow size distribution.

Appendix A. Supplementary material

Synthesis and characterization (NMR, FT-IR and GPC) of HBPE-g-PNIPAm, details on DLS and SAXS experiments and SAXS data modeling. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.03.005.

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