Self-assembly of Porous Nanocarriers from Branched Polymer Templates

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Abstract

The use of branched polymeric materials such as block copolymers micelles as nanotemplating agents has been proven as a versatile tool in the field of nanotechnology, due to the accurate control of the size and polydispersity of the inorganic particles involved. Particularly interesting in this respect is the construction of supra-molecular organic-inorganic nanostructured materials based on microporous and nanoporous materials[1]. We describe the self-assembly of a spherical complex driven by molecular recognition and the incorporation of alluminosilicate in a polymer-based hyperbranched surface made of PDMS-PEO block copolymers[2] and carboxyl-terminated PAMAM dendrimers[3] as polymer templates. By using those hyperbranched polymer species as a macromolecular template for zeolite formation, we detected the formation of stable and (nearly) monodisperse, spherical nano-aggregates with a porous structure. The main features of the self-assembly process has been characterized by means of Small Angle X-ray Scattering (SAXS), Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), X-ray Diffracton (XRD), Energy Dispersive X-ray (EDX) microprobe analysis techniques. In figure 1 we report the main stages of the self-assembly processes during synthesis of block copolymer templated hybrid nano-carriers.

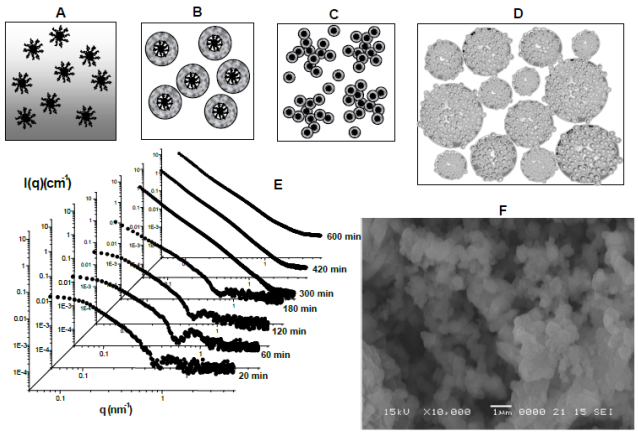

Figure 1. Association of aluminosilicate species into the corona region of the PDMS-PEO copolymer micelles (A) generates primary units with a core-shell morphology (B), followed by the formation of extended secondary fractal structures (C). Further cross-linking, fusion and rearrangement of the secondary particles leads to the formation of final submicron aggregates (D). Time evolution of the SAXS intensity after the mixing of the main components (E) and SEM image of the generated nano-aggregates (F).

The main finding of our results suggest a possible mechanism for nano-aggregates formation based on a secondary aggregation process between primary units. This study puts novel insight in the investigation of alternative protocols for the assembly mechanism of porous materials as well as stimulates the route for the rational design and engineering of novel hybrid (organic-inorganic) nanocarriers with desired functionalities. The structural similarities between the substrate-binding sites of enzymes and the zeolites cavities lead to the development of mesoporous particles capable to mimic the enzyme functions. Mesoporous barriers, in this case, may be employed to promote selective reactions and incorporation of key features of selected enzymes, such as metal complexes.

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[1]L. Bonaccorsi, D. Lombardo, A. Longo, E. Proverbio, A. Triolo, Macromolecules 42, 1239 (2009)
[2]L. Bonaccorsi, P. Calandra, M.A Kiselev, H. Amenitsch, E. Proverbio, D. Lombardo, Langmuir 29, 7079 (2013)
[3]D. Lombardo, Biochem. Res. Int. 2014, ID 837651 (2014)