Development of polymer-based self-assembly systems for advanced applications

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Abstract

In recent years, the application of living polymerization concept to radical polymerization has allowed developing the so-called controlled/"living" radical polymerization methods.[1] The high chemical tolerance of radical polymerization allowed, for the first time, to prepare polymeric materials of pre-determined narrow molecular weight distributions and telechelic structure from a broad range of monomers. Additionally, the living nature of the prepared polymers by CLRP made possible the design and preparation of block copolymers of well defined composition, molecular weight and architecture, which were not possible to be afforded using the available polymerization technology.

In block copolymers, the thermodynamic incompatibility of their polymeric segments, while bonded covalently, leads to phase separation at a nanometer size range that is crucial for the preparation of well defined nanostructured materials.[2] For this reason, block copolymers have been for long known as a solution to tailor property profiles of synthetic materials and as effective compatibilizers or dispersion promoters, for a wide variety of applications based in polymeric formulations, such as in plastics, coatings, micro-optoelectronics or even in biomedicine.

For the last few years, our research group has been involved in the development of CLRP methods to prepare block copolymers for advanced applications. Development of this methodology using methods applicable to a semi-industrial scale allowed obtaining poly(vinyl chloride) (PVC) block copolymers including flexible poly(n-butyl acrylate) (PnBA)[3] and hydrophilic poly(hydroxypropyl acrylate) (PHPA) segments with reasonable control over their molecular weight distribution and composition[4]. These materials were shown to be able to provide PVC-based materials with, respectively, enhanced flexibility, without the need of using external plasticizers,[5] and improved thermal stability and interaction properties to other hydrophilic materials, such as to wood flour.[6] PVC and PHPA were further shown to be effective coupling agents in PVC and wood flour composites, providing composites with superior mechanical performance.[7]

Additionally, the self-assembly of block copolymers in solution media has been explored to afford complex and well defined structures as nature has always done in biological systems [8]. Depending on the nature of the polymeric segments used, these systems may even respond to environmental stimuli and by this way, change their self-assembly structure, providing a change in their performance properties or providing a triggerable release of specific components. This methodology has received significant interest for the development of new polymer-inorganic hybrid nanoparticles or for advanced drug delivery applications [9].

On the hybrid nanoparticles development, recently, we have developed superparamagnetic iron oxide nanoparticles based on aqueous self-assembly of Fe_3O_4 nanoparticles in the presence of an amphiphilic block copolymer that contained a good steric stabilizer and polymeric segment that can coordinate metallic species. The effect of changing the block copolymers composition and molecular weight on the hybrid nanoparticle formation was studied. Additionally, the introduction of other polymeric segments, such as a responsive and a mechanical stability enhancer, to afford responsive magnetic nanoparticles was evaluated.[10, 11]

Furthermore, some of our recent research work has been involved in the development of polymeric structures via CLRP methodologies for biomedical applications, including the development of advanced polymer-liposomes systems, highly branched stimuli-responsive polymeric-structures or controlled drug delivery. An overview of the synthesis strategies that are accessible from CLRP methodologies to afford these advanced self-assembly structures will be provided and their potentialities for advanced biomedical applications will be discussed.

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