



Macromolecular Nanotechnology

Thermoresponsive random and block copolymers based on diethylene glycol methacrylate and a novel thiolated methacrylic monomer for the coating of semiconductor nanoparticles



A. Ferrández-Montero, I. Quijada-Garrido, M. Liras*, O. García*

Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/ Juan de la Cierva, 3, E-28006-Madrid, Spain

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ABSTRACT

The synthesis of smart polymers functionalized with thiol groups offers the possibility to connect the macromolecular structure to the surface of semiconductor nanoparticles, thus combining the amazing properties of the inorganic core and the smart properties of the polymeric coating. With this aim, a new methacrylic monomer containing a protected thiol group 2-(2-acetylthioethoxy)ethyl methacrylate (AcSEOMA) was synthesized. By the atom transfer radical polymerization of AcSEOMA with 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA), thermoresponsive p(MEO₂MA-co-AcSEOMA) random and p[(MEO₂MA-co-AcSEOMA)-*b*-MEO₂MA] block copolymers were prepared. After thiol deprotection, both random and block copolymers, exhibited lower critical solution temperature (LCST) modulated by the pH. These new multi-thiolated copolymers easily replaced the hydrophobic ligand at the Quantum Dot (QD) surface leading to stable amphiphilic photoluminescent nanoparticles. Moreover, QD@polymer photoluminescence was closely related to the thiol content and its distribution along the polymer chains. In addition, functionalization with block copolymers, conducted to a noticeable increase of hybrid water solubility (*ca.* 15 mg mL⁻¹). Finally, the polymer coating triggered a remarkable increase of nanohybrids fluorescence at acidic pH and high temperature (above the LCST). All these hybrids materials are promising for possible applications as biosensors and in the optoelectronics field.

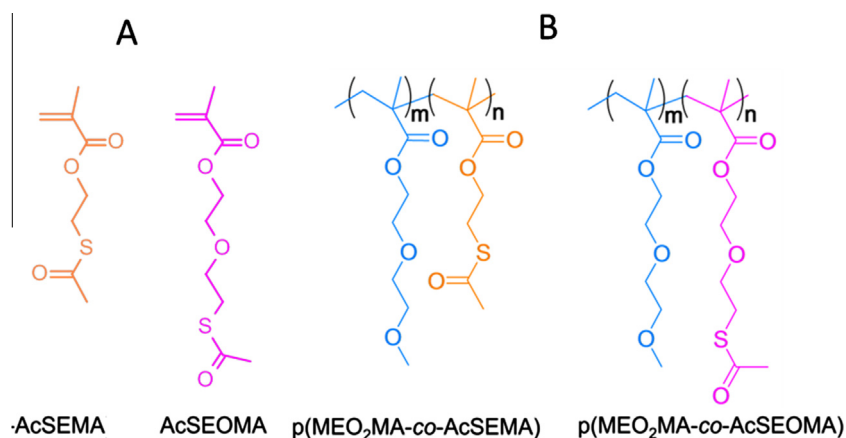
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1. Introduction

The development of new nanostructured multifunctional systems based on the hybridization of polymers with inorganic nanoparticles offers new challenges for Materials Science and presents a significant technological interest considering their direct application in Medicine, Bio/chemistry, Optic and Electronic fields [1–3].

The use of polymers as a tool for the preparation of new hybrid nanomaterials strictly depends on their functionalities. Consequently, any approach that introduces new functional groups, new transformation processes or protection/deprotection protocols is expected to improve the potential of tailoring materials properties [4–8]. Polymers will be designed with controlled structure and functional groups previously introduced into the monomers or derivatives for further

* Corresponding authors at: Instituto IMDEA-Energía, Parque Tecnológico de Móstoles, Avda. Ramón de la Sagra, 3, E-28935 Móstoles-Madrid, Spain (M. Liras).



Scheme 1. Comparative structure of (A) AcSEMA and AcSEOMA monomers and (B) p(MEO₂MA-co-AcSEMA) and p(MEO₂MA-co-AcSEOMA) copolymers.

post-modification, which may be connected either in coatings layers or nanoparticle surfaces [8]. These features also could serve to integrate bio-active molecules (drugs, peptides and aptamers) or molecules with optical properties (dyes, fluorophores) [9]. In this regard, thiols can react via two types of mechanisms: radical and nucleophilic, and the related thiolate anions and thiyl radicals are very reactive and lead to a variety of reactions that are fast and which proceed with high yields under benign conditions, some of them being classified as “click” reactions [10]. The versatility of thiol chemistry allows polythiol copolymers to be efficiently post/functionalized via many different pathways, including thermal, photochemical and redox processes [11]. The diversity of substrates that can be reacted with thiols and the flexibility of reaction conditions make these copolymers perfect building blocks for functional materials in many different areas [4].

Among inorganic nanoparticles, Quantum Dots show remarkable semiconductor and luminescent properties tuneable as function of nature and size, and also environment. However, their low chemical and physical stability, their probable toxicity, low solubility in physiological medium, together with difficulties in their manipulation and are serious inconvenient for their real implementation [12–14]. A strategy to overcome these limitations is hybridization of QDs with polymers in different ways as covalent and non-covalent interactions with mono/multi-dentate polymers, encapsulation with block copolymers or nanogels [15–19]. Moreover, an additional advantage is that the polymeric coating provides the nanostructure with other properties and possibilities of functionalization, transport and delivery of drugs and/or response to stimuli [19,20]. For instance, in our previous works we proved that coating of QDs with methacrylic polymers with protected thiol groups endows with long chemical and photophysical stability and an enhancement of their own luminescent properties [6,21].

In these previous works, a monomer synthesized by our group (AcSEMA), which structure is shown in Scheme 1, was used for the synthesis of random thermoresponsive copolymers. In the AcSEMA monomer, the latent thiol was attached to the main chain by a short spacer, leading to a hydrophobic structure. In this contribution we propose a new monomer with a longer and more hydrophilic spacer, the 2-(2-acetylthioethoxy)ethyl methacrylate (AcSEOMA), which structure is also depicted in Scheme 1. The main motivation was to investigate the effect of the chemical structure of the thiolated monomer on the properties of the synthesized polymers and on the stability and optical properties of coated QDs. The copolymerization of this new monomer with 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA) by atom transfer radical polymerization (ATRP) was used to obtain thermoresponsive random copolymers. Moreover, the effect of the distribution of the thiol groups along the macromolecular structure is other of the contributions of this paper and it has been explored synthesizing block copolymers, with a thiol-enriched block. Furthermore, the new copolymers have allowed the preparation of new multifunctional hybrid materials based on QDs with improvement of their luminescence and smart properties. The relation composition and/or structure with thermo-/pH- response of their emission properties have been established.

2. Materials and methods

For the synthesis of AcSEOMA, methacryloyl chloride (99%, Aldrich), triethylamine ($\geq 99\%$, Aldrich) and 2-(2-chloroethoxy)ethanol (99%, Aldrich), anhydrous sodium sulfate (99%, Qemical), potassium thioacetate (98%, Aldrich) and potassium iodide ($\geq 99\%$, Aldrich) were employed as received. The monomer 2-(2-methoxyethoxy)ethyl methacrylate (MEO₂MA, Aldrich 95%) was purified by passing through a neutral column to remove the antioxidant inhibitor. Unless otherwise noted, reagents were commercially available and used without further purification. 1,1,4,7,10,10-Hexamethyltriethylene netramine (HMTETA, 99%, Aldrich), ethyl 2-bromoisobutyrate (EBRⁱB, 99%, Aldrich), CuCl (99.99%, Aldrich) and the solvent

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