SYNTHESIS OF SINGLE-CHAIN POLYMERIC NANOPARTICLES BY A COMBINATION OF RAFT POLYMERIZATION AND "CLICK" CHEMISTRY TECHNIQUES

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The synthesis and characterization of polymeric nanoparticles has attracted significant attention in recent years due to new and promising properties of nano-objects compared to bulk materials [1]. A good example is the viscosity drop observed in polystyrene melts upon nanoparticle addition, against classical Einstein´s predictions [2]. In spite of this general interest, synthetic routes to single-chain cross-linked polymeric NPs in the 5 - 20 nm size range are certainly scarce and have severe limitations.

The aim of this work was to design, synthesize and characterize new functional polymeric nanoparticles with improved properties. Hence, RAFT polymerization has been employed for the synthesis of well-defined functional terpolymers and "click" chemistry has been used to promote efficient single-chain intramolecular cycloaddition leading to individual single-chain nanoparticles in high yield [3].

In a first step, a terpolymer of methyl methacrylate, 3-azidopropyl methacrylate and 3-(trimethylsilyl)propyn-1-yl methacrylate has been prepared under reversible addition fragmentation chain transfer (RAFT) conditions.

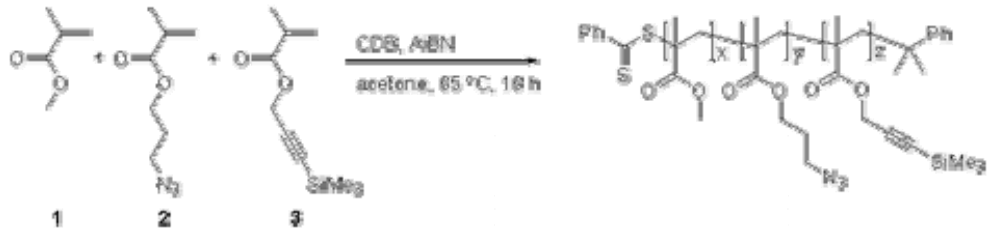

Figure1. Synthesis of poly(methyl methacrylate$_x$–co-3-azidopropyl methacrylate$_y$-co-3-(trimethylsilyl)propyn-1-yl methacrylate$_z$) terpolymers by RAFT polymerization.

In a second step, one-pot deprotection of the propargyl monomer units in the terpolymer has been performed followed by single-chain intramolecular Cu^I-catalyzed azide alkyne 1,3-dipolar ("click") cycloaddition at room temperature using a continuous addition technique.

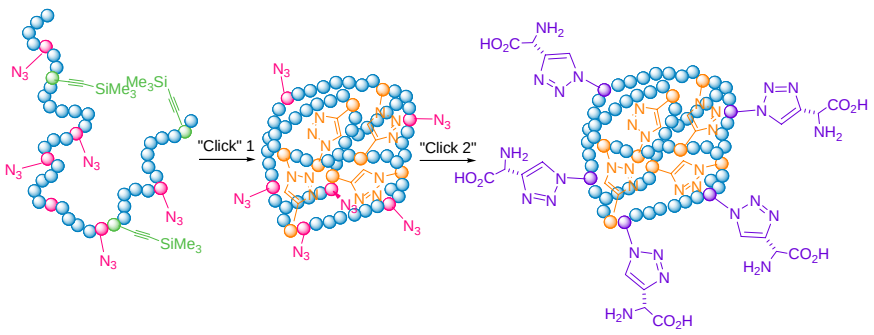

Figure 2. Preparation single-chain cross-linked PMMA NPs and bioconjugated nanoparticles thereof.

As illustrated in Fig. 2, this general method can be easily extended leading to obtain functionalized nanoparticles such as aminoacid-PMMA bioconjugated nanoparticles.

AFM and TEM images of the resulting single-chain polymeric nanoparticles are shown in Figure 3. The average nanoparticle size was determined to be 5 ± 1.5 nm by AFM and 6.5 ± 1.4 nm by TEM.

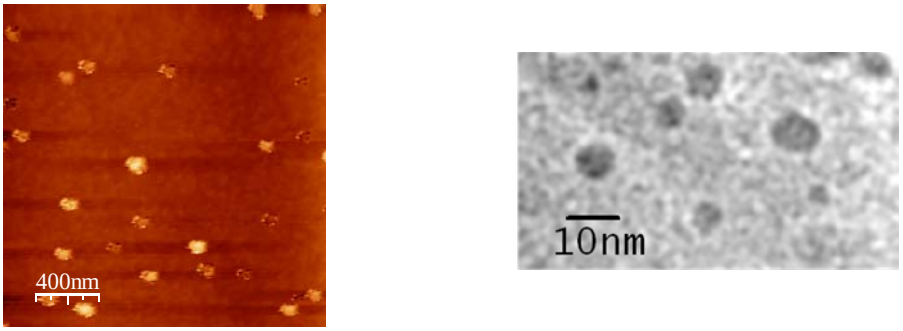

Figure 3. AFM (left) and TEM (right) images of single-chain polymeric nanoparticles synthesized by a combination of RAFT polymerization and "click" chemistry techniques.

References:

[1] A. C. Balazs, T. Emrick and T. P. Russell, "Nanoparticle polymer composites: where two small worlds meet", Science, vol. 314, pp. 1107-1110, 2006.
[2] M. E. Mackay, T. T. Dao, A. Tuteja, D. L. Jo, B. v. Horn, H-C. Kim and C. J. Hawker, "Nanoscale effects leading to non-Einstein-like decrease in viscosity", Nature Materials, vol. 2, 762-766, 2003.
[3] Alaitz Ruiz de Luzuriaga, Nerea Ormategui, Hans J. Grande, Ibon Odriozola, José A. Pomposo and Iraida Loinaz, "Intramolecular click cycloaddition: an efficient route towards bioconjugable polymeric nanoparticles at room temperature", Macromol. Rapid Commun. In press.