

PREPARATION OF POLYMERIC NANOPARTICLES IN NANO-EMULSIONS OBTAINED BY LOW-ENERGY METHODS

J. Nolla¹, D. Morales¹, J. Esquena¹, J.E. Puig², J.M. Gutiérrez³, C. Solans¹

¹Institut d'Investigacions Químiques i Ambientals de Barcelona (IIQAB)
Consejo Superior de Investigaciones Científicas (CSIC)
Jordi Girona, 18-26, 08034 Barcelona, Spain

²Departamento de Ingeniería Química
Centro Universitario de Ciencias Exactas e Ingenierías (CUCEI)
Universidad de Guadalajara
M. García Barragán 1451, Guadalajara, Jalisco 44430, México

³Departament d'Enginyeria Química,
Universitat de Barcelona
Martí i Franqués 2, 08028 Barcelona, Spain

Nanoparticles (particles with at least one dimension <100nm) have great scientific interest because they are considered a bridge between bulk materials and atomic or molecular structures. The interesting and sometimes unexpected properties of nanoparticles are mainly due to the fact that their surface properties dominate over the bulk properties. Nanoparticles have found applications in catalysis, chemical synthesis and other reactions, biomedicine, printing processes, surface treatments; as optical, semiconductor, electronic and magnetic materials; to make assembled structures, etc [1]. Accordingly, nanoparticles with different chemical nature (metals, polymers, hybrid compositions, etc) and morphologies (nanospheres, nanorods, nanocapsules, etc.) have been described. Among the various methods of nanoparticle preparation, the use of colloidal systems as reaction media is of particular interest [2,3]. These systems have advantages compared to other methods: they allow a good control of size and morphology, soft conditions of reaction and they are technologically feasible processes [2]. Microemulsions [3,4] and nano-emulsions [5-8] are interesting examples of colloidal systems that have been used efficiently for the preparation of nanoparticles.

Nano-emulsions are a class of emulsions with droplet size typically in the range 20-500 nm [8]. Because of their characteristic size, some nano-emulsions appear transparent or translucent to the naked eye (resembling microemulsions) and possess stability against sedimentation or creaming. Nano-emulsions (which are kinetically stable) cannot be formed spontaneously, contrary to microemulsions (which are thermodynamically stable). Consequently, energy input is required to prepare nano-emulsions, generally from mechanical devices (dispersion or high-energy emulsification methods) or from the chemical potential of the components (condensation or low-energy emulsification methods). The low-energy methods make use of the phase transitions taking place during the emulsification process, by change of temperature at constant composition (phase inversion temperature, PIT, method [9]), or by change of composition at constant temperature. Generally, low-energy methods provide nano-emulsions with smaller and more homogeneous droplet size [8].

The use of nano-emulsions for the preparation of polymeric nanoparticles (the so-called miniemulsion polymerization method) is well known [5-8]. However, in the published work related to this subject, the nano-emulsions used are obtained by high-energy methods (ultrasonication, high-energy homogenization, etc.). To our knowledge, preparation of nano-emulsions by low-energy methods, using polymerizable oils (monomers), as dispersed phase, has not been reported yet.

The aim of this work is the use of nano-emulsions prepared by low-energy emulsification methods as templates for the preparation of polymeric nanoparticles. In this communication the preparation of polymeric nanoparticles from nano-emulsions of the O/W type, prepared by the PIT method, at 25 °C, is described. The oil component of the nano-emulsions consisted of a monomer (e.g. butyl acrylate), the surfactants were of the polyoxyethylene type and the reactions were initiated by a redox pair (e.g. $K_2S_2O_8 / FeSO_4$). Characterization of the nano-emulsions as well as the nano-particles by dynamic light scattering (DLS) and transmission electron microscopy (TEM) have showed that nanoparticle size is of the same order as nano-emulsion droplet size (e.g. 50 nm). Therefore, controlled size and low polydispersity polymeric nanoparticles can be obtained from nano-emulsions prepared by low-energy methods.

- [1] Günter Schmid (Editor): *Nanoparticles: From Theory to Application*. John Wiley & Sons, Ltd., 2004.
- [2] H-P. Hentze, E.W. Kaler: Polymerization of and within self-organized media Hentze. *Current Opinion Colloid & Interface Sci.* 8 (2003), 164-178.
- [3] López-Quintela, MA.: Synthesis of nanomaterials in microemulsions: formation mechanisms and growth control. *Current Opinion Colloid & Interface Sci.* 8 (2003), 137-144.
- [4] I. Katime, J. Arellano, E. Mendizábal, J.E. Puig: Síntesis and characterization of poly(n-hexyl methacrylate) in three component microemulsions. *European Polymer Journal* 37 (2001), 2273-2279.
- [5] E.D. Sudol, M.S. El-Aasser: Miniemulsion Polymerization. In: *Emulsion Polymerization and Emulsion Polymers*, edited by P.A. Lovell and M.S. El-Aasser. John Willey and Sons, 1997, 699-722.
- [6] M. Antonietti, Landfester K: Polyreactions in miniemulsions. *Prog Polym Sci* 27 (2002), 689-757.
- [7] Asua J.M.: Miniemulsion Polymerization. *Prog Polym Sci* 27 (2002), 1283-1346.
- [8] C. Solans, P. Izquierdo, J. Nolla, N. Azemar, M.J. García-Celma: Nano-emulsions. *Current Opinion Colloid & Interface Sci.* 10 (2005), 102-110.
- [9] K. Shinoda, H. Saito: The effect of temperature on the phase equilibria and the types of dispersion of the ternary system composed of water, cyclohexane, and nonionic surfactant *Colloid Interface Sci.* 26 (1968), 70-74.