Polymer 55 (2014) 788–797

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Mechanism of particle formation in radical emulsion copolymerization of styrene with α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol macromonomer

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ARTICLE INFO

Article history:
Received 3 August 2013
Received in revised form
27 November 2013
Accepted 4 December 2013
Available online 12 December 2013

Keywords:
Macromonomer
Emulsion copolymerization
Mechanism of particles formation

ABSTRACT

In the batch emulsion copolymerization of styrene and α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol macromonomer, carried out at macromonomer concentrations exceeding the critical micelle concentration (c_{mc}), particles are formed by a two-step coagulative nucleation mechanism. This mechanism leaves its mark on morphology of particle interface, rate of polymerization and on molecular weight distribution of the obtained polymer. AFM studies revealed that the interface of particles is composed of objects with dimensions close to dimensions of the primary particles. Compartmentalization of styrene in the macromonomer micelles leads to the higher initial rate of styrene conversion than in the similar macromonomer free homopolymerization of styrene. The initial polymerization in the monomer-swollen macromonomer micelles, similar to the microemulsion polymerization, is responsible for the formation of the highest molecular weight component. In the mature particles there are two different polymerization loci: the interfacial layer and the core. This leads to bimodal molecular weight distribution of the formed polymer.

1. Introduction

Uniform nano- and microparticles with tailored interfacial properties found many applications in such diverse areas of technology as formation of optical colloidal crystals [1–3], production of composite materials [4–8], as well as in more traditional paints and coatings industry [9–11]. Applications of functional particles in medicine and biotechnology, in particular as carriers of drugs and other bioactive compounds [12–16], elements of biosensors [17–19], components of diagnostic kits [20,21], fillings of hemoperfusion columns [22–24], and many other areas are of high importance.

Particles with functional groups or segments providing desired properties (e.g. hydrophilicity) in their interfaces were obtained by emulsion or related homopolymerization of monomers with needed functions [25–29], homopolymerization of monomers without functional groups carried out in the presence of functional low or high molecular weight surfactants [30–32], post-polymerization modification [33–35], seeded polymerization in which second monomer contains required groups [34,36–39], copolymerization involving surface-active comonomers (surfmers) and macromonomers with chains containing functional groups [40–47]. The latter process in many instances may be superior to the others listed above because it often provides a quite unique possibility to introduce polymer chains with tailored chemical structure and well controlled molecular weight into the particle interfacial layer.

Emulsion homopolymerization of monomers with special functional groups (e.g. hydroxyl, carboxyl or amine) limits the number of possible types of particles and thus imposes restrictions on their properties. Application of surfactants with functional groups yields particles with properties changed during storage due to the gradual leaking of surfactant molecules from the particle surface. Post-polymerization modifications, regardless whether by reactions with polymer chains in the particle surface or by covering the seed particles with shells composed of functional polymers in seeded polymerization, are usually less convenient than one-step processes.

In spite that emulsion copolymerization of typical vinyl monomers, e.g. styrene, with hydrophilic macromonomers is known for

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http://dx.doi.org/10.1016/j.polymer.2013.12.008

more than a quarter of century, the knowledge of fundamental aspects of this process is still very limited. Studies were carried out mainly for emulsion or dispersion copolymerization of styrene with macromonomers of poly(ethylene oxide) (PEO) [48–51], poly(N-vinyl pyrrolidone) [52], polyoxazoline blocks [53], poly(-methacrylic acid) [46], and of polyaspartate [54], copolymerization of *n*-butyl acrylate with macromonomer of poly(ethylene oxide) (PEO) [55], and dispersion copolymerization of methyl methacrylate with macromonomers of poly(N-vinyl pyrrolidone) [52]. However, studies of kinetics of polymerization and mechanism of particle formation were performed only for emulsion copolymerization of styrene with poly(ethylene oxide) macromonomer [48]. Investigations of emulsion copolymerization of styrene with poly(ethylene oxide) macromonomers led to hypothesis that particles are formed by micellar nucleation and then grow by fast polymerization within these primary particles during polymerization supported by the continuous and rapid monomer supply from the monomer droplets [48]. However, the aforementioned hypothesis was also based on some speculations and therefore, formulation of the mechanism of emulsion copolymerization of styrene with hydrophilic macromonomers needed further studies.

We would like to mention that hydrophilic macromonomers may be also surface active. However, because their primary function is to participate in polymerizations as monomers the processes without addition of any other surfactants are called emulsifier-free polymerizations (for example emulsion copolymerization of styrene with poly(ethylene oxide) macromonomer) [49]. Using the mentioned above term is even more justified when poly(styrene-*co*-macromonomer) is a better stabilizer of colloid particles than the macromonomer alone.

During the last few years we developed methods for synthesis of particles with polystyrene cores and shells enriched with polyglycidol (P(S/PGL) microspheres) by emulsion copolymerization of styrene and α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol [6,56–58]. The obtained particles were suitable for various diagnostic applications [20,59]. Their properties were strongly related to the polymerization conditions, however, the mechanism of their formation was never investigated. In the case of emulsion copolymerizations of hydrophobic copolymers with macromonomers containing hydrophilic chains and hydrophobic polymerizable end-groups initiated with water soluble initiators (like $K_2S_2O_8$) one should take into account the following possibilities: (i) formation of primary particles by polymerization of hydrophobic monomer in monomer-swollen macromonomer micelles and subsequent growth of these primary particles resulting from fast diffusion of monomer and propagating oligomers into them, (ii) homogeneous nucleation of particles stabilized by adsorption of copolymers of monomer and macromonomer, (iii) parallel micellar and homogeneous nucleation with subsequent aggregation of particle nuclei into the colloidally stable particles in which the main part of polymerization does occur. The first possibility was advocated by L.H. Chew and co-workers for emulsion copolymerization of styrene with poly(ethylene oxide) macromonomer [48]. In our work, described in this paper, we wanted to clarify whether copolymerization of styrene and α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol macromonomer (VB-polyGL) proceeds according to the same very simple mechanism or the polymerization process is more complex.

2. Materials and methods

2.1. Materials

Styrene (Aldrich) was purified from the stabilizer (4-tert-butylcatechol) by distillation at 30 °C under reduced pressure. *p*-Chloromethylstyrene (Aldrich) was distilled at 80 °C under reduced pressure; ethyl vinyl ether (Fluka), potassium persulfate ($K_2S_2O_8$, from Fluka), hydrochinone (Aldrich), $AlCl_3x6H_2O$ (Sigma–Aldrich) were used without further purification. Triple distilled water with pH adjusted to 6.8 by addition of needed amount of $KHCO_3$ was used for the synthesis of microspheres.

2.2. Methods

^{1}H NMR spectra were recorded using a Bruker AV200 NMR spectrophotometer operating at 200 MHz.

GPC traces were recorded using a system composed of an 1100 Agilent isocratic pump, a MALLS DAWN EOS photometer (Wyatt Technology Corporation, Santa Barbara, CA), and a K-2300 differential refractometer (Knauer). ASTRA 4.90.07 software (Wyatt Technology Corporation) was used for data collecting and processing. Two TSK Gel columns (G 2000 H and G 6400 H) were used for separation. Samples were injected dissolved in methylene chloride. Volume of the injection loop was 0.1 ml. Methylene chloride was used as a mobile phase at the flow rate of 0.8 ml/min.

Scanning electron microscopy (SEM) microphotographs were registered using a JEOL 5500LV apparatus. Prior to SEM analysis samples of dry microspheres were coated with gold. Number average diameters of microspheres (D_n) and diameter dispersity parameters (D_w/D_n) were calculated on the basis of measurements of diameters of at least 700 microspheres (randomly chosen from different microphotographs).

AFM studies were carried out using a Nanoscope IIIa atomic force microscope (Digital Instruments/Veeco) operated in the tapping mode. High accuracy composite probes HA_NC Etalon (NT-MDT) of nominal tip radius of 10 nm and tip cone angle of ca 22° were used in all experiments. Thin films of microspheres used for AFM studies were obtained from suspension by drop casting on a glass plate at the temperature of 80 °C.

Hydrodynamic diameters of microspheres were measured by photon correlation spectroscopy (PCS) using a ZetaSizer Nano ZS instrument (Malvern). The apparatus was equipped with a laser emitting light at 633 nm and detector recording intensity of light scattered at 173°. Measurements were performed at 25 °C. Data were analyzed using the cumulants method on the basis of 30 measurements for each sample.

Chemical composition of interfacial layer of P(S/PGL) microspheres was determined by X-ray photoelectron spectroscopy (XPS) of lyophilized particles. A sample of particles was placed on a holder in the instrument. Spectra were recorded using a Thermo VG Scientific ESCALAB 250 system equipped with a monochromatic Al Kα X-ray source (1486.6 eV) and a magnetic lens which increases the sensitivity. An X-ray beam of 650 μm diameter was used at 20 mA and 15 kV. The spectra were acquired in the constant analyzer energy mode with pass energy of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun operated in the presence of argon at the partial pressure of 2×10^{-8} mbar. Atomic ratio of carbon and oxygen atoms was calculated from the intensity ratio of corresponding XPS signals (for carbon atoms in the range from 285.0 to 291.6 eV, including a shake-up signal due to the polystyrene aromatic ring, for oxygen atoms at 532.0 eV) corrected for the relevant sensitivity factors. Taking into account that each polystyrene monomeric unit contains 8 carbon atoms and in the polyglycidol unit there are three carbon and two oxygen atoms, the mole fraction of polyglycidol and polystyrene could be elucidated from the relative carbon and oxygen atom content [56].

Concentration of acidic groups on the surface of microspheres was determined by conductometric titration with KOH. Prior to titration, a sample of suspension of microspheres was passed through Dowex 50WX4 ion-exchange resin.