European Polymer Journal 49 (2013) 601–612

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

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

Macromolecular Nanotechnology

Controlling the size and swellability of stimuli-responsive polyvinylpyrrolidone–poly(acrylic acid) nanogels synthesized by gamma radiation-induced template polymerization

Hassan A. Abd El-Rehim [a,*], El-Sayed A. Hegazy [a], Ashraf A. Hamed [b], Ahmed E. Swilem [b]

[a] Department of Polymers, National Center for Radiation Research and Technology, Nasr City, Cairo 11371, Egypt
[b] Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo 11566, Egypt

ARTICLE INFO

Article history:
Received 28 May 2012
Received in revised form 7 December 2012
Accepted 9 December 2012
Available online 20 December 2012

Keywords:
Nanogel
Gamma radiation
Polyvinylpyrrolidone
Template
pH-sensitive
Interpolymer complex

ABSTRACT

Polymeric pH-sensitive hydrogel nanoparticles (nanogels) of narrow size distributions were directly prepared by gamma radiation-induced polymerization of acrylic acid (AAc) in an aqueous solution of polyvinylpyrrolidone (PVP) as a template polymer. The driving force of PVP/PAAc nanoparticles formation was attributed to the complexation between PAAc (proton-donor) and PVP (proton-acceptor) through the hydrogen bonding interaction. In addition to the hydrogen bonding interaction between the components, the nanoparticles are further stabilized by covalent bonds as a result of the radiation-induced crosslinking process. Particle size and swellability of the prepared nanogels can be controlled by feed composition and concentration, PVP molecular weight as well as irradiation dose, temperature, and atmosphere. The prepared PVP/PAAc nanogel particles were characterized by dynamic light scattering (DLS), viscometry, transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques.

1. Introduction

Recently, there is a growing interest in synthesis and design of soft nanomaterials to be applied in the biomedical field. Among these materials, hydrogel nanoparticles have gained considerable attention due to their tunable dimensions, large surface area, stable interior network structure, and fast response to environmental factors, such as ionic strength, pH, and temperature. These properties demonstrate the great potential of nanogels for bio-related applications such as drug delivery systems (DDS) and bioimaging [1–6].

Majority of methods utilized for nanogel synthesis are often performed in microemulsion in order to prevent formation of bulk material [7,8]. However, the formation of hydrogel nanoparticles without using organic solvents and surfactants is considered a challenge. Recently, the concept of interpolymer complexation via hydrogen bonding has been exploited for this purpose [9]. Hydrogen-bonded interpolymer complexes (IPCs) are formed between proton-donating poly(carboxylic acids) and proton-accepting non-ionic polymers. An interesting example which has attracted a continuing interest as a model of biological systems is the formation of polymer complexes between poly(ethylene oxide) and poly(acrylic acid) via H-bonding in aqueous media. These complexes are novel individual compounds and their properties are entirely different from the properties of their component polymers. Moreover, they are pH-sensitive since their formation depends on the degree of ionization of the poly(carboxylic acid) and thus on the environmental pH.

In the literature, different strategies to obtain nanogels based on hydrogen-bonded IPCs have been studied. For example, Liao et al. have reported a surfactant-free synthesis of poly(acrylic acid) nanogels based on its complexation with Hydroxypropylcellulose (HPC) [10]. The method involved polymerization of acrylic acid in the presence of

* Corresponding author. Tel.: +20 2 22872451; fax: +20 2 2749298.
E-mail address: ha_rehim@hotmail.com (H.A. Abd El-Rehim).

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2012.12.002

HPC as a template and *N*,*N*′-methylenebisacrylamide as a crosslinking agent. Dou et al. have demonstrated the possibility of preparation of hollow spheres and microgels based on graft-copolymer of hydroxyethylcellulose-*g*-polyacrylic acid [11]. Under acidic conditions, this graft-copolymer formed intramolecular complex stabilized by hydrogen bonding. This complex was then chemically crosslinked. By controlling the reaction time and the amount of crosslinking agent, particles of typical microgel structure were obtained. Peppas group applied microemulsion and surfactant-free emulsion method to the UV-induced synthesis of micro- and nanoparticles based on poly(methacrylic acid)–graft-poly(ethylene glycol) (PMAA–g-PEG) [12–14]. Pulse radiolysis for IPC nanogel formation was also investigated. Henke et al. reported an approach that involved irradiation of PVP–PAAc complexes by pulses of fast electrons in dilute, deoxygenated solutions [15]. The radiation treatment of IPC induces intramolecular (intracomplex) crosslinking leading to the formation of permanent PVP–PAAc nanogels. Practically, nanogels produced by this method are especially well suited for biomedical applications because they are free of residual toxic chemicals, e.g. monomers, initiators or crosslinkers, and there is no need for additional purification steps.

In fact, the use of gamma rays to form nanogels is very limited. Thus, this study aims to develop a simple and efficient method of producing nano-sized gel particles based on hydrogen-bonded IPCs using gamma radiation. In this regard, acrylic acid in an aqueous solution of polyvinylpyrrolidone (PVP) as a template polymer was exposed to gamma rays to produce chemically crosslinked PVP/PAAc nanogels. The method does not involve any organic solvent, surfactant, crosslinker or chemical initiator. Many parameters affecting the nanogel products were investigated in order to have a successful production of pH sensitive nanogel particles with controlled size and crosslinking density. Characterization of the PVP/PAAc nanogels is carried out, including morphological structure and equilibrium swelling studies.

2. Experimental section

2.1. Materials

Polyvinylpyrrolidone (PVP; K16–18, M_w = 8000; K29–32, M_w = 58,000; K85–95, M_w = 1,300,000) and acrylic acid (AAc) were obtained from Acros Organics (Belgium), and were used as received. All reagents were of analytical grade and were used without any purification. Deionized water was used in all experiments.

2.2. Preparation of PVP/PAAc hydrogel nanoparticles

PVP/PAAc hydrogel nanoparticles were prepared via gamma radiation-induced polymerization of AAc in an aqueous solution of PVP. Aqueous solutions containing different feed compositions of PVP/AAc mixtures were introduced into glass bottles and subjected to γ-rays generated from a ^{60}Co source provided with a temperature control unit at a dose rate of 3.85 kGy/h. The irradiation process was carried out at ≈35 °C under air atmosphere; otherwise conditions will be mentioned. In some cases, the feed solutions were purged with nitrogen or nitrous oxide for 20 min to remove the dissolved oxygen, and then the bottles were sealed and irradiated. To calculate the yield of nanoparticles, the colloidal nanogel suspensions were centrifuged (SORVALL® ULTRA 80, USA) at 20,000 rpm for 30 min. at 4 °C. Supernatants as well as aggregated nanogels were collected and freeze-dried in order to determine the weight of the polymers which formed nanogels. The production yields were calculated from the mass ratio of polymers forming nanogel and the polymer and monomer initially introduced in the preparation procedure.

2.3. Particle size measurements

Particle sizes of PVP/PAAc nanogels were measured by the dynamic light scattering (DLS) technique using a PSS-NICOMP Zeta Potential/Particle Sizer 380ZLS (PSS-NICOMP, Santa Barbara, CA, USA). Samples were properly diluted with freshly prepared deionized water (filtered with a 0.2 μm syringe filter) until an intensity of 250–350 kHz was achieved. The dilutions were also convenient to avoid. particle interactions. The pH of the solutions was adjusted by adding few drops of NaOH or HCl. The scattered light intensity was detected at a 90° angle and measurements were run for at least 10 min. The volume-weighted hydrodynamic mean diameters were reported to know the size contributing the most volume. The polydispersity index (PDI) (the square of the coefficient of variation) which is a measure of the size distribution breadth was also calculated.

2.4. FT-IR spectrum analysis

FT-IR spectra of PVP, PAAc and freeze-dried PVP/PAAc nanogel as KBr pellets were recorded by a JASCO FT/IR-6300 spectrometer in the range of 400–4000 cm^{-1}.

2.5. UV–Vis measurements

To follow the formation of PVP/PAAc complexes, solutions were analyzed by measuring the change in transmittance at 500 nm using a JASCO UV/VIS spectrophotometer V-560.

2.6. Viscosity measurements

Viscosity measurements were conducted at 30.0 ± 0.5 °C using Ubbelohde viscometer. The pH of the solutions was adjusted by adding few drops of NaOH or HCl. Deionized water was used as a reference solvent.

2.7. Morphology study

Transmission electron microscopy (TEM; JEOL JEM-100CX, Japan) and atomic force microscopy (AFM; Agilent AFM 5500, USA) were used to observe the morphology of nanogel particles. For TEM observations, the nanogel suspension was properly diluted and dripped onto carbon-coated copper grid and then dried at room temperature.