Polymer 54 (2013) 54–64

Contents lists available at SciVerse ScienceDirect

Polymer

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

Structure of e-beam sculptured poly(N-vinylpyrrolidone) networks across different length-scales, from macro to nano

Maria Antonietta Sabatino [a], Donatella Bulone [b], Miklos Veres [c], Alberto Spinella [d], Giuseppe Spadaro [a], Clelia Dispenza [a,b,*]

[a] Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze Ed. 6, 90128 Palermo, Italy
[b] CNR – Istituto di Biofisica (IBF) UOS Palermo, Via U. La Malfa 153, 90146 Palermo, Italy
[c] Institute for Solid State Physics and Optics, Wigner RCP, Hungarian Academy of Sciences, P.O. Box 49., H-1525 Budapest, Hungary
[d] Centro Grandi Apparecchiature-UniNetLab, Università degli Studi di Palermo, Via F. Marini 14, 90128 Palermo, Italy

ARTICLE INFO

Article history:
Received 27 August 2012
Received in revised form
6 November 2012
Accepted 12 November 2012
Available online 20 November 2012

Keywords:
Nanogels
Irradiation
Poly(N-vinylpyrrolidone)

ABSTRACT

Study of macromolecular structure and dynamics of networks formed by pulsed electron-beam irradiation of poly(N-vinyl pyrrolidone) (PVP) aqueous solutions, at relatively low energy per pulse and across different concentration regimes, provides the basis for the understanding of a new generation of functional nanostructures. Networks are the result of the follow–up reactions initiated by a continuous series of electron pulse-generated hydroxyl radicals, which may have a different fate at the variance of polymer concentration. Different spectroscopic techniques, FT-IR, ^{13}C {^{1}H} CP-MAS NMR and Raman, applied to characterize the formed networks, describe a profound modification of the chemical structure when network size is approaching the nanoscale. Static light scattering measurements provide further information on the average weight molecular weight modification of PVP when forming nanogel particles. From the simultaneous control of network size and modification of chemical functionality stems also an intrinsic fluorescence of these nanogels never observed before. Altogether the obtained radiation-sculptured nanogels exhibit interesting multifunctionality that, coupled with the already proven biocompatibility, can be exploited in the biomedical field.

1. Introduction

Among the different synthetic methodologies for the production of hydrogels much interest has been paid to the use of high energy radiation processing, as it generally yields highly pure materials through environmentally friendly and economically viable processes [1–6]. It is also well known that one of the most appealing features of radiation crosslinking is the possibility of tuning structure and properties of networks obtained from the same feedstock materials through an apt choice of processing parameters, limiting the number of compounds present in the system [7–10]. When the target is the formation of nanoscalar "finite" networks, or nanogels, suitable for biomedical application, e-beam irradiation may become the elective technology, as nanogels directly form from irradiation of dilute aqueous solutions of suitable polymers and monomers, with no recourse to surfactants for the control of particle size. As-born sterile materials are formed, depending on the irradiation dose applied. Production process can be easily scaled-up with high yields and interesting through-put [11–13]. In deoxygenated aqueous solutions of PVP, carbon centred PVP radicals are promptly formed by the rapid H-abstraction reaction by water radiolysis products: hydroxyl radicals, (•OH, 0.29 μmol J^{-1}), hydrated electrons (e^-_{aq}, 0.29 μmol J^{-1}) and protons (H•, 0.06 μmol J^{-1}) are quantitatively formed (numbers in parentheses indicate the radiolytic yields or G values), together with H_2O_2, H_2, H^+, OH^-. Irradiating in N_2O saturated solutions makes hydroxyl radicals (•OH, μmol J^{-1}) the predominant radical species (ca. 90%), through conversion of e^-_{aq} to •OH [14]. Therefore, instantaneous concentration of carbon centred PVP radicals can be estimated from the knowledge of dose per pulse and hydroxyl radicals radiation yield. The distribution of these radicals along the different polymer chains, which depends on polymer concentration in solution and polymer molecular weight, will affect the way they evolve through the many possible competitive reactions: intra and inter-molecular recombination, disproportionation, chain scission, radical transfer though H-abstraction, recombination with other radicals, etc.

---

[*] Corresponding author. Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze Ed. 6, 90128 Palermo, Italy. Tel.: +39 091 23863710; fax: +39 091 23860841.
E-mail address: clelia.dispenza@unipa.it (C. Dispenza).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.11.031

In this work we attempt a description of chemical structure and molecular architecture of radiation-sculptured both “finite” and “infinite” PVP networks as obtained from multiple low-dose electron pulses, by applying several complementary analyses: static light scattering measurements, FTIR, Raman and {^{1}H} CP-MAS NMR. Interesting differences in the structure and dynamics of the networks formed at a fixed dose per pulse, pulse length, pulse frequency and integrated dose (40 kGy), only by varying the polymer concentration, can be appreciated. The process is represented in Scheme 1. In particular, significant modification of pyrrolidone ring occurs when nanoscalar networks are formed. An increase of average molecular weight of PVP is always observed. These evidences suggest a competition of inter-molecular recombination with recombination reactions of macroradicals with hydroxyl radicals and further evolution of the formed PVP—OH toward other oxidized forms. ^{1}H spin lattice relaxation times in the rotating frame, $T_{1\rho}H$, and cross-polarization times, T_{CH}, have been determined to highlight differences in rigidity. Unexpected intrinsic fluorescence will be also reported that, in conjunction with the already proven biocompatibility [13,15], prospect interesting application in the biomedical field.

2. Experimental

2.1. Materials and ionizing irradiation process

PVP k60 (Aldrich, $M_w = 4{,}1 \times 10^5$ g/mol and $R_g = 27 \pm 5$ nm from static light scattering measurements, $R_h = 20 \pm 10$ nm from dynamic light scattering measurements both carried out in water at 20 °C), was supplied as 45 wt% aqueous solution [9]. PVP critical chain overlapping concentration in water, ~1 wt%, was determined by laser light scattering measurements (calculated as $c^* = 3M/4\pi R_g^3$) [16].

All solutions were carefully deoxygenated by gaseous nitrogen and bottled in hermetically closed 15 ml glass vials. Solutions at 0.5, 0.25, 0.1 and 0.05 wt% were also saturated by N_2O (99.99%) prior to irradiation. Electron beam irradiation was performed using LAE 13/9, a 10 MeV linear accelerator of the ICHTJ of Warsaw (Poland) at 0–4 °C. Irradiation conditions were set to have an average current of 0.08 μA, pulse duration and frequency of 10–12 μs and 37.5 Hz, respectively, corresponding to 0.74 Gy per pulse. The homogeneous dose distribution in the sample was measured using polyvinyl chloride film dosimeters on the basis of absorbance at 396 nm.

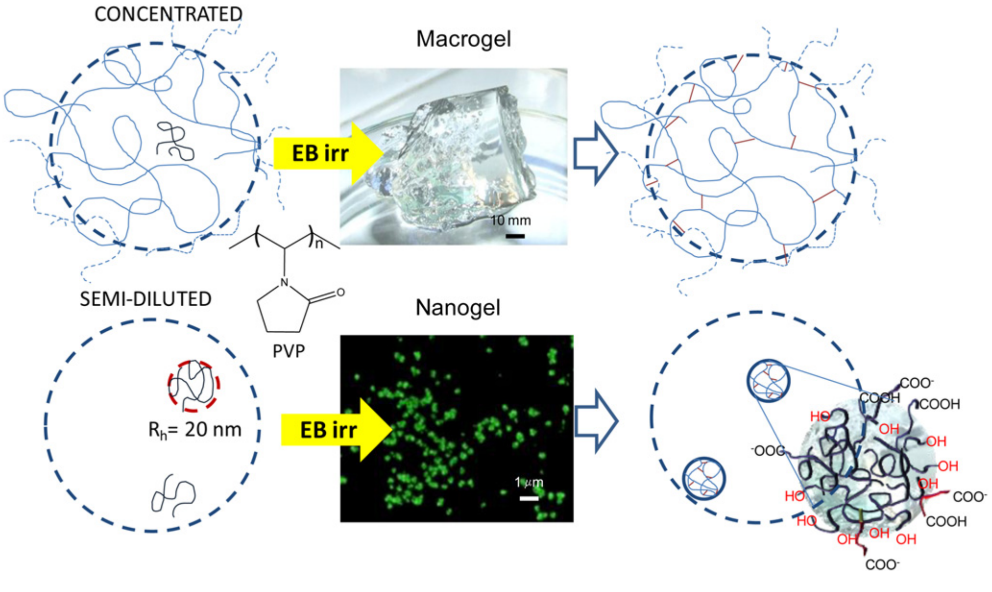
Macroscopically gelled systems were separated from their soluble portions by immersion for 72 h in excess double-distilled water at 40 °C and filtration with filter paper. Samples at 0.25, 0.1 and 0.05 wt % were dialysed against distilled water for 48 h using dialysis tubes of 12 and 100 kDa cut-off (Aldrich) [13]. The system at 0.5 wt% system, which consists of macrogel flakes floating in an aqueous phase, was separated in the sol and gel fractions through filtration. Each phase, sol or gel, was then treated as the other nano or macro-systems, respectively.

2.2. Light scattering measurements

The hydrodynamic radius (R_h) of particles dispersion ($C_{\mathrm{polym}} < 0.5\%$), measured by dynamic light scattering (DLS) was the subject of a previous investigation [9]. Weight average molecular weight (Mw) and radius of gyration (R_g) of PVP nanogels obtained from 0.25 wt% polymer solutions were estimated from multi-angle static light scattering measurements at 25 °C ± 0.1 °C in aqueous solution. The refractive index increment (dn/dc) of PVP in aqueous solution was measured by using a Brookhaven Instruments differential refractometer at $\lambda = 620$ nm. Data were analysed according to the Zimm plot method. When attempting to draw a Zimm plot with scattered light data collected on nanogels samples obtained from 0.1 wt%, a downward curvature in the scattering angle dependence was observed, probably due to polydispersity and/or inter-particles interactions. This occurrence prevented a reliable determination of extrapolated light scattered values at zero scattering angle. However, an estimate of the molecular weight was obtained consistently by averaging the values obtained through Debye's plots for each different scattering angle [13].

2.3. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was carried out with Perkin Elmer-Spectrum 400 apparatus by dispersing the solids in potassium bromide and compressing them into pellets. Spectra were recorded at 30 scans per spectrum and 1 cm^{-1} resolution in the 4000–400 cm^{-1} range. All spectra have been normalized with respect to the peak correspondent to the stretching of methylene groups (2956 cm^{-1}).



Scheme 1. Representation of the process which leads to either PVP macrogels or nanogels, depending on the different polymer concentration regimes. Irradiation of semi-diluted solutions leads to significant modification of the polymer structure.