



Short communication

Hydroxyl radical-induced crosslinking and radiation-initiated hydrogel formation in dilute aqueous solutions of carboxymethylcellulose



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ARTICLE INFO

Article history:

Received 16 April 2014

Received in revised form 27 May 2014

Accepted 4 June 2014

Available online 11 June 2014

Keywords:

Crosslinking
Polysaccharide hydrogels
Carboxymethylcellulose
Ionizing radiation
Polymer solution

ABSTRACT

Ionizing radiation causes chain scission of polysaccharides in the absence of crosslinking agents. It has been demonstrated before that degradation of carboxyalkylated polysaccharides may be prevented, despite presence of strong electrostatic repulsing forces between chains, at very high polymer concentration in water (paste-like state) when physical proximity promotes recombination of radiation-generated polymer radicals. In such conditions, crosslinking dominates over chain scission and covalent, macroscopic gels can be formed. In an approach proposed in this work, neutralizing the charges on carboxymethylcellulose (CMC) by lowering the pH results in retracting the electrostatic repulsion between chain segments and thus allows for substantial reduction of polymer concentration required to achieve gelation due to domination of crosslinking reactions. Electron-beam irradiation of aqueous solutions of low pH containing 0.5–2% CMC results in hydrogel formation with 70% yield, while both concentration and dose determine their swelling properties. Time-resolved studies by laser flash photolysis clearly indicate strong pH influence on decay kinetics of CMC radicals.

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1. Introduction

Permanent hydrogels based on three-dimensional networks of covalently bound hydrophilic polymer chains, able to swell in aqueous media till equilibrium, have numerous applications, for instance as soft contact lenses, wound dressings and superabsorbents (Funke, Okay, & Joos-Müller, 1998; Gulrez, Al-Assaf, & Phillips, 2011; Hoffman, 2001, 2002; Mathur, Moorjani, & Scranton, 1996; Peppas, 1986; Tanaka, 2003). Among the available methods for synthesizing hydrogels based on synthetic polymers, radiation technique plays an important role, being since long employed on a commercial scale (Rosiak, Rucinska-Rybus, & Pekala, 1988; Rosiak, 1991). Irradiation of aqueous polymer solution leads to the formation of polymer radicals, which recombine to form covalent bond between the polymer chains. As a result, permanent

three-dimensional network is formed, which is hydrophilic and swellable but insoluble (Rosiak & Ulanski, 1999). This method is simple and does not require any added chemicals (initiators, crosslinking agents).

While the radiation method works well for many synthetic polymers, its application for synthesizing hydrogels based on polysaccharides (being very promising materials) is more problematic. Generally, irradiation of polysaccharides induces their degradation, resulting in chains of reduced molecular weight, and no crosslinked structures are formed (Czechowska-Biskup et al., 2007; Ershov, 1998; Ulanski & von Sonntag, 2000; Wasikiewicz, Yoshii, Nagasawa, Wach, & Mitomo, 2005; Zegota & von Sonntag, 1977). Some methods have been elaborated to crosslink polysaccharides by ionizing radiation by using an additive to promote crosslinking process, such as an alkyne gas (Al-Assaf, Phillips, Williams, & Plessis, 2007; Phillips, Plessis, Al-Assaf, & Williams, 2003) or carbon tetrachloride (Ramnani, Chaudhari, Patil, & Sabharwal, 2004). These methods require additives and specific reaction conditions, therefore the processing is rather complex.

Radiation-initiated crosslinking of polysaccharides without additives by a straightforward method – irradiation proceeded in

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so called 'paste-like' state – has been developed in the laboratory of Yoshii (Fei, Wach, Mitomo, Yoshii, & Kume, 2000). Starting from carboxymethylcellulose (CMC) of various degree of substitution (DS), i.e., the average number of functional side groups per one repeating unit of D-glucose, through other derivatives of cellulose, starch, chitin and other water-soluble polysaccharides, the method became widely utilized for formation of polysaccharide hydrogels (Nagasawa, Yagi, Kume, & Yoshii, 2004; Wach, Mitomo, Yoshii, & Kume, 2002; Wach, Mitomo, Nagasawa, & Yoshii, 2003a,b; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003). The essential factor for hydrogel formation was high concentration of the polymer in aqueous solution, when physical proximity of chains facilitated crosslinking. Concentrations over 10%, up to even 60%, until the mixture maintains homogeneity, are commonly used. While this method is effective and can be scaled up, the necessity of preparing the substrate in the form of a highly viscous or solid paste and degassing it (such mixture usually contains air bubbles, which are difficult to remove) before irradiation makes it labor and time consuming.

In the present communication hydrogel formation by radiation-initiated crosslinking of carboxymethylcellulose chains in aqueous solution of low concentration is reported. This innovative approach, conversely to the known methods being applied either in R&D and in the industry, does not require laborious procedures, such as formulation of a paste-like state, nor utilization of additives facilitating crosslinking. Results on gel formation are supported by spectral and kinetic data on recombination of carboxymethylcellulose radicals in oxygen-free acidic aqueous solutions.

Possible applications of polysaccharide hydrogels, for instance based on CMC, include superabsorbents for agriculture and industry, and biomaterials, such as personal care absorbents or components of hydrogel dressings (Yoshii, Kume, & Murakami, 2005). Therefore, radiation technique of polysaccharide manufacturing may be preferred because a product can be sterilized simultaneously. Foremost advantages of polysaccharide hydrogels over synthetic polymers gels are the origin of substrates (sustainable resources) and product biodegradability.

2. Materials and methods

Sodium salt carboxymethylcellulose, CMC (Daicel Co., Ltd., Japan) of the degree of substitution 2.34, and $M_w = 7.4 \times 10^5 \text{ mol g}^{-1}$ was used as received. Solutions were made up with ultrapure water (Milli-Q, Millipore), pH was adjusted with HClO_4 . Prior to irradiation solutions were saturated with N_2O in order to eliminate oxygen and convert hydrated electrons into $\cdot\text{OH}$ radicals (Schuler, Patterson, & Janata, 1980).

Irradiation was conducted using a 6MeV electron accelerator (ELU-6, Eksma, Russia), yielding an average dose rate of 5 kGy/min. Gel fraction (GF = mass of insoluble part per mass of initial sample) and equilibrium degree of swelling of hydrogels (EDS = mass of absorbed water divided per mass of dry gel) were evaluated in water by a method described elsewhere (Wach, Mitomo, Nagasawa, & Yoshii, 2003a,b).

Laser flash photolysis was used to study the kinetics of macroradicals decay, due to its simplicity comparing to the classical pulse radiolysis technique. An excimer laser (Lambda Physik) operated at 248 nm (KrF) with a pulse duration of 20 ns at an energy of 55 mJ/pulse was used. Aqueous solutions of CMC were filtered through a Sartorius 0.45 μm membrane and saturated with N_2O to remove oxygen. H_2O_2 (10 mM) was used as the source of hydroxyl radicals in kinetic experiments (Wach, Kudoh, Zhai, Muroya, & Katsumura, 2005). Time-resolved absorbance was followed at $\lambda = 320 \text{ nm}$, as a representative wavelength to follow the decay of the sum of CMC-derived macroradicals.

3. Results and discussion

Radiolysis of water yields reactive transient species: hydroxyl radicals, hydrogen atoms and hydrated electrons. Hydroxyl radicals react with polysaccharides in dilute aqueous solution at a relatively high rate. Second-order rate constant for reaction of CMC ($M_w = 5.3 \times 10^5 \text{ kDa}$) with $\cdot\text{OH}$, dependent on the pH that governs the ionic state of the carboxylic moieties and the conformation of macromolecules, was determined to be $0.5\text{--}1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (where mol refers to mol of repeating units) (Wach et al., 2005). At low pH in N_2O -saturated solutions a part of hydrated electrons is converted to $\cdot\text{OH}$ radicals, while the rest reacts with protons to yield hydrogen atoms (Schuler et al., 1980; von Sonntag, 1987). Both hydroxyl radicals and hydrogen atoms abstract hydrogen from carbon atoms in either D-glucose repeating unit or a side chain. This leads to the formation of polysaccharide-based radicals.

Among several radicals found on carboxymethylated polysaccharides irradiated in solution, the most stable ones present on side chains, i.e. on alpha carbon with respect to carboxymethyl group, are essential for recombination reactions that may occur in a favorable environment (Saiki et al., 2011; Wach et al., 2004, 2005). Polysaccharide-based radicals typically display a broad, featureless absorption spectrum in UV. Their decay, which may involve recombination, can be followed by pulse radiolysis or laser flash photolysis with time-resolved spectrophotometric detection.

Electrostatic repulsion of ionized carboxylic groups is the major barrier for recombination of CMC radicals. Therefore recombination at neutral or basic pH is very slow, and thus inefficient in competition with single-radical-initiated scission of glycosidic bonds. This competition and other side reactions may lead to a complex kinetic pattern, involving mixed-order kinetics followed by slow first-order decay (Wach et al., 2004). Since at such conditions the yield of scission exceeds the yield of crosslinking, the observed macroscopic result of irradiation is a low-viscosity solution of degraded polymer chains.

Protonation of the carboxyl groups, by removing the barrier of electrostatic repulsion between macromolecules, may change the dominating mechanism and kinetics of radicals decay. Indeed, as shown in Fig. 1a, the time-dependent absorbance of the radicals varies with pH. A very slowly decaying signal is recorded within several millisecond time-range at neutral pH. By lowering the pH, resulting in increasing protonation of carboxylic groups – pK_a of carboxyl groups of CMC is above 3.5 (Hoogendam et al., 1998) – an increase of the termination rate is observed. Second-order kinetics takes part in overall decay at lower pH and eventually at pH 1 the kinetics follows strictly second order. Solid line representing second-order reaction fits well to the experimental data (see the straight line in Fig. 1b). Calculated $2k = 4.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is relatively low when compared to radicals on flexible, uncharged polymer chains. It is known that recombination rate of radicals on polyelectrolyte depends strongly on the protonation state, and decreases significantly with even small number of ionized units (Görllich & Schnabel, 1973). This is a representation of bimolecular reactions, which can be either disproportionation or recombination. Since formation of macroscopic gel in the cuvette was perceptible after the photolysis, it evidenced a significant yield of the latter reaction.

In order to find out if the fast and efficient recombination of CMC radicals at low pH can lead to hydrogel formation even at low polymer concentrations, CMC solutions of 0.5, 1 and 2% wt/vol (approximately 15, 30 and 60 mM of repeating units, respectively; it should be noted that at such low concentrations CMC does not form a physical gel in acidic media) were adjusted to pH 2 with HClO_4 , saturated with N_2O , sealed in glass ampoules and subjected to irradiation by electron beam at various doses. Formation of a gel

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