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The effect of environmental humidity on radiation-induced degradation of carrageenans

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ABSTRACT

Better understanding of the chemistry of radiation-induced degradation is becoming of increasing importance on account of the utilization of polymeric materials in a variety of radiation environments as well as beneficial uses of degraded polymers. In this report the importance of environmental humidity on the degrading effect of radiation has been considered from the point of view of controlling the molecular weights of kappa- and iota-carrageenans. These two polysaccharides were irradiated in solid form under strictly controlled environmental humidity conditions by incubating and later irradiating the samples over saturated aqueous salt solutions of NaCl, $NaNO_3$ and $MgCl_2$. The degradation was followed in detail by a careful gel permeation chromatographic analysis of their respective molecular weights before and after irradiation. The chain scission yield values $G(S)$ were found to decrease with the water adsorbed from environment at every absorbed dose in the range of 5–100 kGy. On the other hand at very high water uptakes the yield of chain scission again increases especially at low doses. The decrease in degradation yield was attributed to the plastifying effect of water trapped in between the polymer chains facilitating the macroradical recombinations thus reducing the extent of chain scission. This study showed that although carrageenans were irradiated in solid form, the difference in their water uptake from changing environmental humidity has a profound effect in controlling their molecular weights by irradiation with ionizing radiation.

1. Introduction

Among various techniques used for the modification of polymer properties the use of ionizing radiation either in photonic (gamma rays, X-rays) or particulate forms (accelerated electrons, ion beams) has proven to be very convenient and versatile for large scale applications. Since the ultimate properties of polymers are generally controlled by their molecular weights, the control of molecular weight and its distribution is of great importance in determining the technical specifications required for a particular end-use. The polymers find their wide utilization in everyday life due to their light weights, relative ease of fabrication in the final form and unequalled mechanical properties based on performance vs. weight. The improvement in mechanical properties is mostly achieved by increased molecular weights and/or cross-linking of polymer chains. The increased resistance to heat, deformation and mechanical stresses obtained through radiation-induced cross-linking has long been the main reason for the use of high energy radiations in polymer processing (Haji-Saeid, Sampa, Ramamoorthy, Güven, & Chmielewski, 2007).

The opposite effect of radiation, in other words chain scissioning or degradation of polymers has not found great industrial interest until recently (Hien et al., 2000; Relleve et al., 2005; Şen, Yolaçan, & Güven, 2007). The degradation effect of ionizing radiation has been generally connected with the chemical structure of polymer chains, presence or absence of some additives and irradiation atmosphere, presence of oxygen or air leading mostly to radiation-induced oxidation with eventual chain scission. In recent years, there has been growing interest in understanding the effect of ionizing radiation on the chemical structure of polysaccharides such as chitin, chitosan, sodium alginate, and kappa carrageenan due to their versatile food and non-food applications (Choi, Ahn, Lee, Byun, & Park, 2002; Nagasawa, Mitomo, Yoshii, & Kume, 2000). The research in this field is mostly concentrated on the degradative effect of radiation to produce polysaccharides with desired low molecular weight ranges. The main effect of ionizing radiation on polysaccharides is chain scission of C—O bond connecting the glycoside groups on the main chain.

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Table 1
Water uptake of carrageenans incubated for 3 days in different humidity conditions.

Saturated solution (30 °C)	Atmospheric humidity (%)	Water adsorbed by KC (w%)	Water adsorbed by IC (w%)
$MgCl_2$	50	5	2
NaCl	75	21	17
KNO_3	90	40	31
Water	100	230	150

The three well known marine based polysaccharides namely, carrageenans, alginate and chitin/chitosan are known to be susceptible against ionizing radiation and degrade when irradiated in dry form or in solution. Some studies on irradiation of highly concentrated (>10%) solutions of carboxylate–polysaccharides in paste-like conditions have shown that chain scission is reduced in favor of crosslinking to from insoluble gels (Yoshii et al., 2003). The dependence of effect of radiation on the concentration of aqueous polysaccharide solutions prompted us to consider the effect of environmental humidity which may change from 0 to 100% depending on the climatic conditions, on radiation-induced degradation of this group of natural polymers.

2. Experimental

Commercially available kappa-carrageenan (KC) and iota-carrageenan (IC) were obtained from Aldrich and used as received. The CAS number of kappa-carrageenan (Type III) is 11114-20-8 and it is a mucopolysaccharide obtained from the cell walls of the red algae *Eucheuma cottonii*. The CAS number of iota-carrageenan (Type II) is 9062-07-1. The ion concentrations of KC used in this study are as follows: K^+, 11.3%; Na^+, 1.0%; Ca^{2+}, 2.2% (Aldrich Data Sheet, Lot (17327JI) results). The ion concentrations of IC are given as K^+, 4–6%; Na^+, 1–2%; Ca^{2+}, 2–4% (Sigma-Aldrich C1138 Specification Sheet).

In order to irradiate the polysaccharides mentioned above under controlled humidity conditions, saturated aqueous salt solutions were prepared from NaCl, $NaNO_3$ and $MgCl_2$ whose vapor pressures provide a certain constant humidity. In Table 1 given below relative humidity of the atmosphere above respective salt solutions are listed. The polysaccharide samples in powder form first dried in a vacuum oven at 40 °C and then placed in small baskets suspended over the saturated salt solutions all together kept in closed containers. The powders kept for three days in various constant relative humidity were thus allowed to absorb corresponding amounts of water by reaching equilibrium, all at room temperature. Water uptake of polymers determined gravimetrically corresponding to different environmental humidity levels was also indicated in Table 1.

The carrageenan samples equilibrated under different relative humidity of surrounding atmospheres and kept suspended over the salt solution were placed in tightly closed containers and irradiated to various doses (2.5, 5, 10, 20, 50 and 100 kGy) in a Gammacell 220 type ^{60}Co-gamma irradiator at room temperature in air at a dose rate of 0.18 kGy/h.

Irradiated and unirradiated samples were analyzed by a Waters Breeze model Gel Permeation Chromatograph equipped with an inline degasser (Waters AF) and a refractive index detector (Waters 2414). The mobile phase was 0.1 M $NaNO_3$ at a flow rate of 0.8 mL/min, and the columns were operated at 40 °C. The injection volume and concentration of injected polymer were 200 μL and 0.01 g/mL, respectively. 2000–1000–500 waters hydrogel columns were used to provide separation within a molecular weight range of 20,000–600,000. Universal calibration was constructed by using narrow molecular weight (20,600–553,000) PDI ≤ 1.04 standard samples of poly(ethylene oxide) obtained from PSS company. The Mark–Houwink constants used for PEO were $K = 6.9 \times 10^{-5}$ dL/g and $a = 0.81$ (Brandrup & Immergut, 1989). Corresponding constants for carrageenans were taken as $K = 5.98 \times 10^{-5}$, $a = 0.90$ (Zhou, Yao, & Wang, 2006) for use in universal calibration. The K and a constants of carrageenans used in this study was reported by Zhou et al. for 0.1 M KCl solution. The mobile phase used in GPC was however, 0.1 M $NaNO_3$ therefore we checked the elution behavior of KC in 0.1 M KCl and 0.1 $NaNO_3$ solutions and obtained the same chromatograms. Therefore we were confident to use these constants as the K and a constants of carrageenans of the eluting solvent of GPC i.e. 0.1 M $NaNO_3$ solution.

3. Results and discussion

3.1. Controlling the molecular weight of polysaccharides

It is very well known that polysaccharides in dry form or in solution degrade when exposed to ionizing radiation (Choi et al., 2002; Wasikiewicz, Yoshii, Nagasawa, Wach, & Mitomo, 2005). The results reported so far on the radiation-induced degradation of polysaccharides indicated that chain scission yield strongly depends on the concentration of polymer. In dilute aqueous solutions with polymer concentration less than 4% (w/v) the dominating effect is chain scission. The same applies to polysaccharides irradiated in solid state where radiation induced degradation yield, $G(S)$ defined as number of chain scissions per Joule of absorbed dose, reported for kappa-, iota- and lambda-carrageenans irradiated in solid form are within 0.104 μmol/J to 0.135 μmol/J range whereas for 4% solution the $G(S)$ values change from 0.83, to 1.24 and 1.35 μmol/J, respectively, for the three carrageenans mentioned above (Relleve et al., 2005). Since different units for the yield values are used in the literature, the $G(S)$ values given above were converted to μmol/J by multiplying the scission/eV(sc/eV) values by 0.10364, and concentration of the solution was also considered in the equations (Woods & Pikaev, 1994). In the study of Nagasawa et al. (2000), alginates were claimed to be more sensitive to degradation by irradiation though the $G(S)$ value for solid state irradiation was found to be similar to that of carrageenans, 0.2 μmol/J (1.9 sc/eV), in 1% aqueous solution the chain scission yield increased to 5.7 μmol/J (55 sc/eV), which reduced to 1.9 μmol/J (18 sc/eV) as a result of raising the solution concentration from 1 to 4%. In the calculation of G values reported above; however, the concentration of the solution was not considered. Taking into account the concentration effect as described by Janik, Kasprzak, Al-Zier, and Rosiak (2003) the corrected $G(S)$ values were recalculated in the recent study of Duy, Phu, Anh, and Hien (2011). As a result of recalculations, it was found that the $G(S)$ values should be 0.057 and 0.076 μmol/J for 1 and 4% alginate concentrations, respectively. These results clearly indicated that the $G(S)$ value increased with increasing polymer concentration in dilute regime. The effect of concentration on the radiation-induced degradation of chitosan, was explained in the recent paper of Duy et al. (2011) in detail. On the other hand, it has been shown that when the concentration of chemically modified polysaccharides, such as carboxymethylstarch, carboxymethylcellulose, carboxymethylchitin, and carboxymethylchitosan is increased beyond viscous solution to a paste-like condition, the crosslinking effect starts to dominate and typically chitosan a predominantly scissioning type of polysaccharide behaves like a crosslinking type upon carboxymethylation exhibiting approximately 60% gelation. (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Yoshii et al., 2003; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003).

It is very well known that the difference observed on the effect of radiation on polymers irradiated in dry or solution form is due