

Tailormade Geometric Properties of Chitosan by Gamma Irradiation

F. Elashhab, L. Sheha, R. Fawzi Elsupikhe, A. E. A. Youssef, R. M. Sheltami, T. Alfazani

Abstract—Chitosans, CSs, in solution are increasingly used in a range of geometric properties in various academic and industrial sectors, especially in the domain of pharmaceutical and biomedical engineering. In order to provide a tailoring guide of CSs to the applicants, gamma (γ)-irradiation technology and simple viscosity measurements have been used in this study. Accordingly, CS solid discs (0.5 cm thickness and 2.5 cm diameter) were exposed in air to Cobalt-60 (γ)-radiation, at room temperature and constant 50 kGy dose for different periods of exposer time (t_γ). Diluted solutions of native and different irradiated CS were then prepared by dissolving 1.25 mg cm⁻³ of each polymer in 0.1 M NaCl/0.2 M CH₃COOH. The single-concentration relative viscosity (η_r) measurements were employed to obtain their intrinsic viscosity ($[\eta]$) values and interrelated parameters, like: the molar mass (M_η), hydrodynamic radiuses ($R_{H,\eta}$), radius of gyration ($R_{G,\eta}$), and second virial coefficient ($A_{2,\eta}$) of CSs in the solution. The results show an exponential decrease of η_r , $[\eta]$, M_η , $R_{H,\eta}$ and $R_{G,\eta}$ with increasing t_γ . This suggests the influence of random chain-scission of CSs glycosidic bonds, with rate constant k_r and k_r^{-1} (lifetime $\tau_r \sim 0.017 \text{ min}^{-1}$ and 57.14 min, respectively). The results also show an exponential decrease of $A_{2,\eta}$ with increasing t_γ , which can be attributed to the growth of excluded volume effect in CS segments by t_γ and, hence, better solution quality. The results are represented in following scaling laws as a tailoring guide to the applicants: $R_{H,\eta} = 6.98 \times 10^{-3} M_r^{0.65}$; $R_{G,\eta} = 7.09 \times 10^{-4} M_r^{0.83}$; $A_{2,\eta} = 121.03 M_{\eta,r}^{-0.19}$.

Keywords—Gamma irradiation, geometric properties, kinetic model, scaling laws, viscosity measurement.

1. INTRODUCTION

HIGH molecular weight molecules that are made up of long chains of repeating units are called polymers, while those with electrolyte groups in their repeat units are often referred to as polyelectrolytes [1], [2]. Polymers have been in existence and have played essential roles in life since it began. From the early days, applicants have used polymers in nature (e.g., starch, cotton, gums, etc.) as a source of food, clothes, personal care, medical treatments, and others [2], [3]. These polymers make solutions viscous even at low concentration, making them suitable for be used in items, such as: paints, processed food, and other human requirements [2]. The scarcity of these materials during World War II led to the development of man-made polymers, and hence the growth of

the commercial industry for polymers in the last century [3]. Since then, polymers and their solutions have been increasingly used every day and everywhere. The subject of polymers is discussed in considerable detail in [2].

In diluted solutions, the linear polymers with neutral chains gyrate individually in a randomly coiled fashion, while those with charged chains follow the extended conformational type; nevertheless, the extended chains can be converted to random fashion by adding ionic salt to the solution [4]-[7].

The molar masses M_s of linear polymers in diluted solution are usually connected to their geometric properties, GPs, such as those of their size and shape via the general scaling law (SLs) [4]-[8]:

$$P_{GP} = K_{GP} M_r^{v_{GP}} \quad (1)$$

Here, P_{GP} is the GP parameter of the polymer, like: the intrinsic viscosity $[\eta]$, radius of gyration R_G , hydrodynamic radius R_H , and the second virial coefficient A_2 , which are usually used to probe the polymer size and shape in solution; K_{GP} is the proportionality constant; M_r is the polymer's relative molar mass; and v_{GP} is the scaling coefficient. The practical use of the SL, (1), is that once we know the polymer molar mass we can tailor its GPs, and vice versa [8]. The law can be formulated by calculating K_{GP} and v_{GP} through the plot representation of (2), which would need a range of M_r and P_{GP} as well.

$$\ln P_{GP} = \ln K_{GP} + v_{GP} \ln M_r \quad (2)$$

Carbohydrate polymers, commonly called polysaccharides, are composed of multi repeating monosaccharide units joined together by glycosidic bonds [1]. These polymers offer some unique advantages like biocompatibility, biodegradability, availability, rheological modification, solubility, etc., for use in various aqueous systems, ranging from the classical rheological industry to modern pharmaceutical and biomedical applications [9]-[13].

Bioactive polysaccharides are usually used in a range of chain sizes and M_s (e.g., large L, medium M and small sizes) in such applications [14]. For this reason, linear polysaccharide products have been converted into a range of reduced molar masses M_s by several methods, namely: biological, chemical, and irradiation degradation methods; among them, gamma (γ)-irradiation was recommended by several researchers as the most effective and environmentally friendly [15]. In addition, the degradation reaction of this methods occurs in a single step process (Fig. 1), which makes

F. Elashhab, L. Sheha, R. F. Elsupikhe, T. Alfazani, and R. M. Sheltami are with the Department of Chemistry, Benghazi University, Benghazi, Libya. (e-mail: fathi.elashhab@uob.edu.ly, lobna.sheha@uob.edu.ly, randa.elsupikhe@uob.edu.ly, tahnialfazani@gmail.com, rasha.sheltami@uob.edu.ly)

A. E. A. Youssef was with the Department of Chemistry, Sebha University, Sabha, Libya. He is now with the Department of Chemistry, Benghazi University, Benghazi, Libya (corresponding author, phone: +218 94 435 6081; e-mail: abdelallam.youssef@uob.edu.ly).

its rate easily to be controlled during the measurements [15], [16].

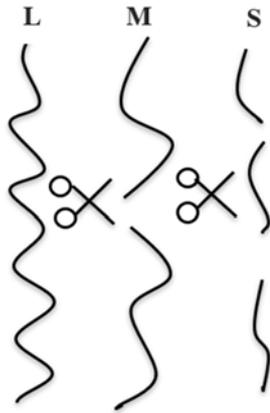


Fig. 1 Single radiation degradation processes of polysaccharides

CS, poly-b-1, 4-linked glucosamine, is a cationic polyelectrolyte that belongs to the bioactive polysaccharide family and has a multitude of applications, including: biomedical, wastewater treatment, fuel cells, packaging of food, textile industries, bioplastics, and nano composite applications [17]-[24].

Tailormade CS polymers (CSs with different molecular masses, sizes, and shapes in solution) are increasingly used in many applications, such as water treatment, the food industry, pharmaceutical and biomedical engineering including vaccine and other drug delivery, etc. [19]-[24].

Investigations with γ -irradiation of CS, e.g. [25], [26], indicated that the polymer has degraded randomly by first order chain scission of its glycosidic bonds. However, neither simple scission characterization nor a tailoring guide for CS have been reported in the literature. Indeed, both are the actual purposes of this paper.

II. MATERIALS AND METHODS

A. Materials

A practical grade of CS powder (Fig. 2) material from shrimp shells, $M = 190000$ to $375000 \text{ g mol}^{-1}$. was supplied by Sigma-Aldrich and used without further purification. The acetic acid (CH_3COOH) and sodium chloride (NaCl) were analytical grade, while the water was prepared by double distillation.

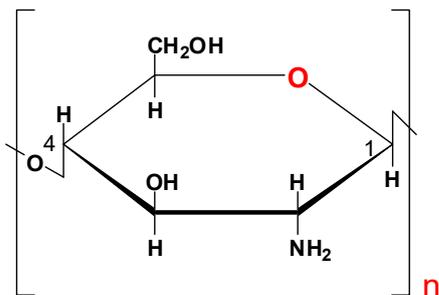


Fig. 2 Monomer unit of totally deacetylated CS

B. Methods

1. Irradiation

CS solid discs (0.5 cm thickness and 2.5 cm diameter) were irradiated in air at room temperature, by a Cobalt-60 gamma source (Theratron 780 treatment unit, Theratronics Ltd, Canada), located in Benghazi Radio Diagnosis & Radiotherapy Center. Each disc was exposed to γ -radiation at a constant 50 kGy for different periods of time. Further details on the irradiation process are shown in Fig. 3.

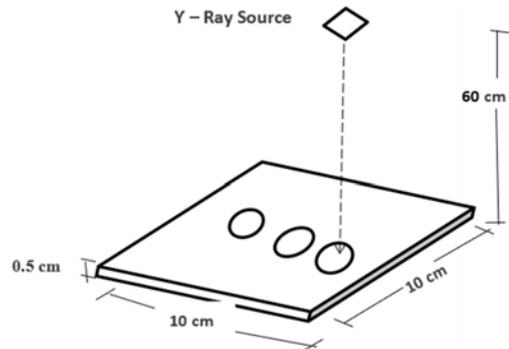


Fig. 3 Method of gamma irradiation

2. Relative Viscosity Measurements

The solvent was 0.1 M $\text{NaCl}/0.2 \text{ M CH}_3\text{COOH}$. The concentration (C) of the native and different irradiated CS solutions was 1.25 mg cm^{-3} . The relative viscosity, η_r , of diluted CS solutions was obtained at $25 \pm 0.5 \text{ }^\circ\text{C}$ by applying (3) [27]:

$$\eta_r = t_s / t_o \quad (3)$$

t_s and t_o are the solution and solvent efflux times, respectively. The efflux time measurements have been discussed in considerable detail in [28].

3. Data Treatments

The $[\eta]$ of CS solutions was determined via (4) [29], [30]:

$$[\eta] = e^C \eta_r \quad (4)$$

The degradation rate constant (k_r) of CSs is expected to obey the first order reaction kinetics as [16]:

$$\frac{1}{[\eta]_t^{1/a}} = \frac{1}{[\eta]_0^{1/a}} + k_r t, \quad (5)$$

$$k_r = k^{-1} (216 \text{ g mol}^{-1}) (1.81 \times 10^{-3} \text{ g}^{-1} \text{ cm}^3)^{1/0.93} \quad (6)$$

$[\eta]_t$ and $[\eta]_0$ are $[\eta]$ at exposure time t and 0, respectively.

The native and degraded M_s of CS were determined by applying the Mark-Houwink equation [31]-[33]:

$$\ln[\eta] = \ln 1.81 \times 10^{-3} + 0.93 \ln M_{\eta,r} \quad (7)$$

where the subscript η indicates viscometric measurement.

The P_{GPs} of CSs were computed by applying (8) and (9) for

size prediction [27], [34], [35] and (10) and (11) for the polymer shape [36], [37]:

$$R_{H,\eta} = \left(\frac{3[\eta]M_\eta}{10\pi N_A} \right)^{1/3} \quad (8)$$

$$R_{G,\eta} = \frac{[\eta]}{(4.17 \times 10^{24} \text{ mol}^{-1})^{1/3}} M_\eta^{1/3} \quad (9)$$

$$A_{2,\eta} = \frac{[\eta] - [\eta]_\theta}{5 \times 10^{-5} M_\eta} \quad (10)$$

where the intrinsic viscosity at theta condition $[\eta]_\theta$ is given by [38]-[40]:

$$[\eta]_\theta = \frac{[\eta][1 - \exp(-\frac{c}{0.77/[\eta]})]}{\frac{0.77^3 \times 2.5/[\eta]}{0.77/[\eta]} - \exp(-\frac{c}{0.77/[\eta]})} \quad (11)$$

III. RESULTS AND DISCUSSION

A. Characterization of Scission

The plots in Fig. 4 demonstrate, in the same fashion, the influence of t_γ on the macroscopic property η_r and microscopic property $[\eta]$ of CS solution, respectively. Both are an indication for the chain scission on β -(1 \rightarrow 4) glycosidic bonds of solid CS by γ -rays, which is very common in the degradation processes of CS and other linear polysaccharides, e.g. [16], [25], [26], [41], [42]. As one can see in Fig. 4, $[\eta]$ and η_r of irradiated CS samples were rapidly decreased until $t_\gamma = 60$ min, and then slowly decreased with the increase of t_γ up to 100 min. Thus, short chain CSs are expected to be produced below $t_\gamma = 60$ min, while those of medium length should be in the range of $t_\gamma = 60$ min.

Fig. 5 illustrates the first-order degradation kinetics of CS by γ -rays, which is an indication on the random chain scission of the CS glycosidic linkages [16], [25], [26], [41], [42]. The scission was with rate constant k_r and k_r^{-1} (lifetime $\tau_r \sim 0.017 \text{ min}^{-1}$ and 57.14 min, respectively). Consequently, it would be unsurprising if applicants have used such rate and time to tailor medium and small CSs at $t_\gamma = 30$ and 100 min, respectively.

B. Tailoring the Parameter

Figs. 6 (a)-(c) reflect the effect of γ -scission on the mass, size, and shape of CS in the given solution, respectively. It is clearly shown that the mass and size parameters of CS, Figs. 6 (a) & (b), are decreased with increasing t_γ in similar fashion and reason to the plot in Fig. 4, while, the opposite is true for the plot in Fig. 5, as was expected from (10). Furthermore, consideration of Fig. 5 indicates the growth of excluded volume effect in CS segments by t_γ which leads to chain rigidity and better solvation of the polymer in solution [43], [44].

The data in Figs. 6 (a)-(c) are represented in Fig. 7 to deduce the respective coefficients that are expressed in the following SL:

$$R_{H,\eta} = 6.98 \times 10^{-3} M_r^{0.65}$$

$$R_{G,\eta} = 7.09 \times 10^{-4} M_r^{0.83}$$

$$A_{2,\eta} = 121.03 M_{\eta,r}^{-0.19}$$

The above performed SLs can be used as tailoring guide, to tailor particular M or GP to the CS applicants by applying in Fig. 6.

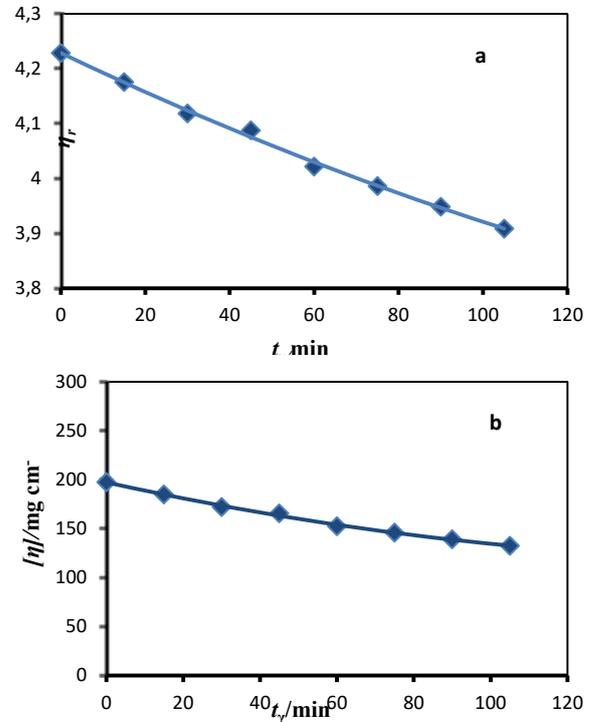


Fig. 4 Progress of CS degradation. (a) relative viscosity η_r , (b) intrinsic viscosity $[\eta]$ of 1.25 mg cm^{-3} CS solution versus γ -rays exposure time t_γ of solid CS; solvent: 0.1 M NaCl/0.2 M CH_3COOH

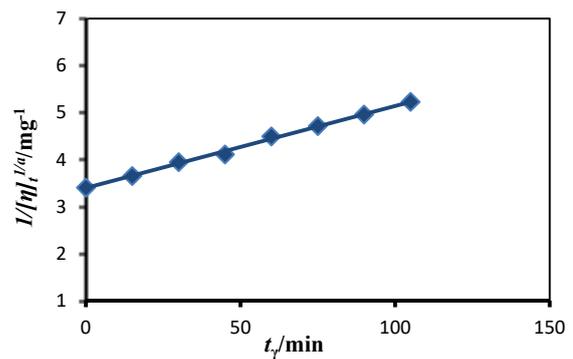


Fig. 5 Rate of CS degradation. The reciprocal of intrinsic viscosity $1/[\eta]$ of 1.25 mg cm^{-3} CS solution versus t_γ of solid CS; solvent: 0.1 M NaCl/0.2 M CH_3COOH

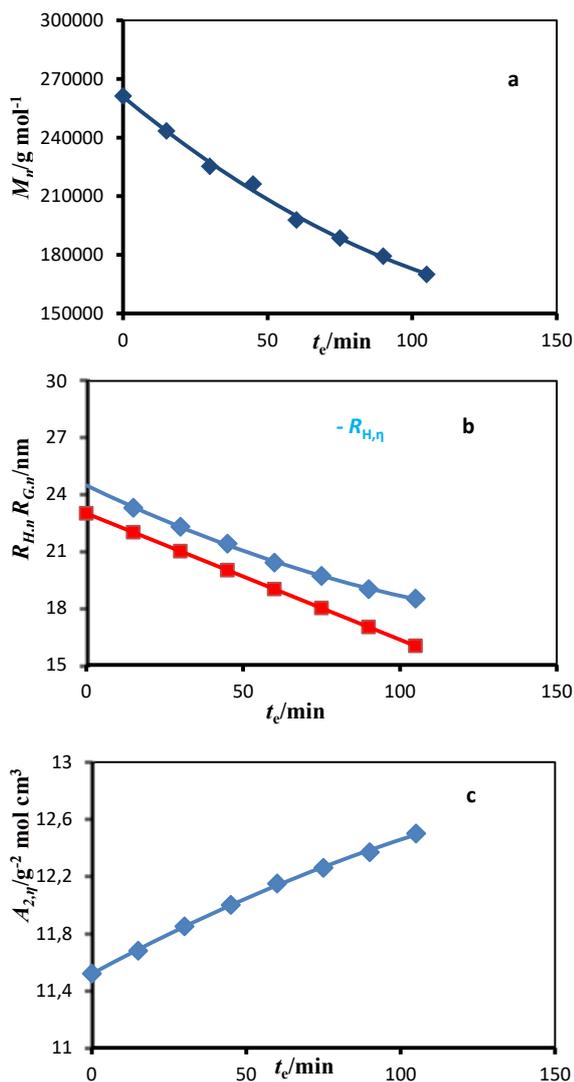


Fig. 6 Controlling the scission of CS. (a) viscosity molar mass M_w , (b) radius of gyration R_G & hydrodynamic radius R_H , and (c) second virial coefficient $A_{2,\eta}$ of 1.25 mg cm^{-3} CS solution versus t_γ of solid CS; solvent: $0.1 \text{ M NaCl}/0.2 \text{ M CH}_3\text{COOH}$

IV. CONCLUSION

The determination of $[\eta]$ via one point method of relative viscosity measurement can be, effectively, used to obtain the progress and rate of degraded CS by γ -irradiation technology, which is an efficient method to tailor the molecular mass, size, and shape of CS in the diluted solution to the applicants. The SLs of CS can be used as a tailoring guide to tailor, in particular, M and GP to the applicants' need. In this regard, it is worth to mention that the CSs with smaller molecular masses and sizes have better solution quality than those of higher one.

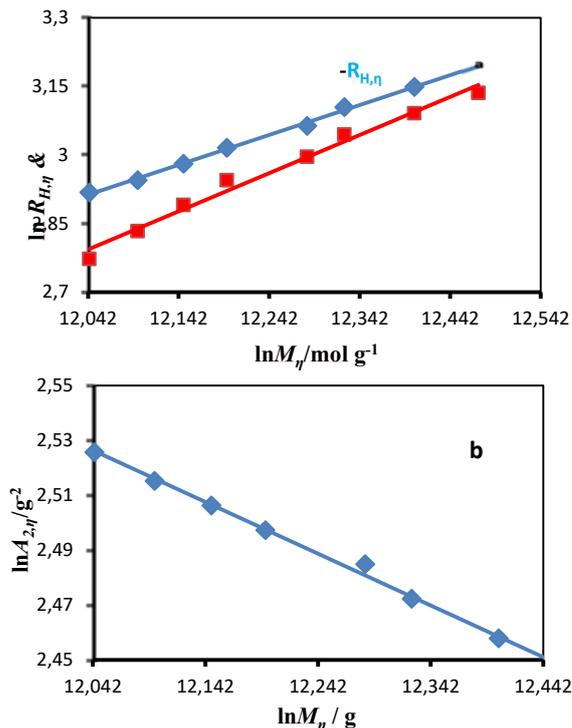


Fig. 7 Logarithmic SLs of CS. (a) $\ln R_{H,\eta}$ & $R_{G,\eta}$ and (b) $\ln A_{2,\eta}$ of CS in 1.25 mg cm^{-3} solution versus t_γ of solid CS; solvent: $0.1 \text{ M NaCl}/0.2 \text{ M CH}_3\text{COOH}$

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