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Cryogels of cellulose derivatives prepared via UV irradiation of moderately frozen systems

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Abstract

Cryogels of non-ionic (hydroxypropyl)methylcellulose, 2-hydroxyethylcellulose, methylcellulose and cationic hydroxyethylcelluloses were prepared for the first time via UV irradiation of moderately frozen systems. The influence of the irradiation time, the concentration of the photo-initiator (4-benzoylbenzyl)trimethylammonium chloride, and the concentration of the polymer solution on the efficiency of the cross-linking process in moderately frozen systems was investigated. It was found that 2-min irradiation at an irradiation dose rate of 5.7 J/cm^2 min is adequate for cross-linking of 3 wt.% polymer solutions resulting in high quality cryogel.

Keywords: Cryogels; Cellulose derivatives; UV irradiation

1. Introduction

Hydrogels based on both natural and synthetic polymers have found various applications in medicine and pharmacy as drug and cell carriers, tissue engineering matrices, membranes for biosensors, contact lenses, etc. [1,2]. Cellulose derivatives have received considerable attention because of their water solubility, easy biodegradation and low costs. Hydrogels of cellulose derivatives can be obtained either by reaction with chemical reagents or by ionizing radiation [3–8]. Wach et al. have demonstrated that two processes, degradation and cross-linking, are in competition at high-energy irradiation with either electron beam or gamma rays of numerous cellulose derivatives [4,5,7]. The authors have found that when exposed to ionizing radiation at ambient temperature in solid state and in aqueous solutions of low concentration (less than 10 wt.%) the examined polymers undergo degradation, while the best results of cross-linking have been obtained at paste-like conditions (25–40 wt.% depending on the polymer). It is noteworthy that in the case of highly concentrated polymer solutions several days are required for complete dissolution of the cellulose derivative in water [4].

Recently, Doycheva et al. [9] obtained hydrogels of high molecular weight poly(ethylene oxide) by UV irradiation of both aqueous solutions and moderately frozen aqueous systems. The process of gel formation, which takes place in a frozen system, and the subsequent thawing are named cryotropic gelation and the materials obtained – cryogels [10]. The advantages of the UV irradiation are the very low capital outlay and the extremely short time for efficient gel formation.

The present paper aims at reporting on the first results for effective cross-linking of various cellulose derivatives via UV irradiation of moderately frozen systems on the basis of semidilute aqueous solutions of the polymers.

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2. Experimental part

2.1. Materials

(Hydroxypropyl)methylcellulose (HPMC), 2-hydroxyethylcellulose (HEC), methylcellulose (MC), (4-benzoylbenzyl)trimethylammonium chloride (BBTMAC), N,N'-methylenebisacrylamide, and poly(ethylene glycol) diacrylate (M_n ca. 700) were purchased from Aldrich and used as received. Cationic hydroxyethylcelluloses (Ucare polymer JR-30M and Quatrisoft polymer LM-200) were obtained from Union Carbide Chemicals and Plastics Co.

2.2. Cryogels preparation

Each polymer (Table 1) was dissolved in an appropriate amount of distilled water to obtain semidilute solution (0.5–4 wt.%) and the sample was kept for 24 h at 5 °C to ensure complete dissolution and homogeneity. Given amount of photoinitiator, BBTMAC, (0.5–15 wt.% with respect to the polymer) dissolved in 2 ml water was added under stirring at room temperature. The resulting homogeneous solution was poured into 8 Teflon dishes (20 mm diameter) forming a 2.5 mm thick layer, which was then kept in a freezer at −30 °C for 2 h. The dishes were then quickly placed in a thermostated open chamber connected with a cryostat apparatus (“Julabo”). The frozen system was irradiated with full spectrum UV–vis light at −30 °C with a Dymax 5000-EC UV curing equipment with 400 W metal halide flood lamp for 1–5 min (input power = 93 mW/cm^2).

In some experiments cross-linking agent, N,N'-methylenebisacrylamide or poly(ethylene glycol) diacrylate (3 wt.% with respect to the polymer) was used. In this case, the concentration of the polymer solution was 3 wt.% and the amount of the photoinitiator was 2 wt.% (to the polymer mass).

In control experiments, 3 wt.% polymer solutions were irradiated with UV–vis light at room temperature.

2.3. Measurements of gel fraction yield and equilibrium degree of swelling

Gel fraction (GF) yield and equilibrium degree of swelling (ES) of the cryogels were determined gravimetrically. GF content in the dried sample was estimated by weighing the insoluble part after extraction in distilled water for 7 days at room temperature. GF yield [%] = (wt. of dried sample/initial wt. of polymer) × 100. ES was determined at room temperature. Disks of dried cryogel were immersed in distilled water and an equilibrium water uptake was reached (at least 72 h). The surface of the cryogel was blotted by filtration paper prior to weighing. ES = wt. of swollen sample/wt. of dried sample.

Table 1
Characteristics of non-ionic and cationic cellulose derivatives as specified by the suppliers

Cellulose derivative	DS[a]	MS[b]	DQ[c]	Approximate mol. weight (g/mol)
HEC	1	2	–	250,000
HPMC	1.1–1.6	0.1–0.3	–	120,000
MC	1.5–1.9	–	–	88,000
JR-30M	–	–	0.4	900,000
LM-200	–	–	0.08	250,000

[a] Degree of substitution.
[b] Molar degree of substitution.
[c] Molar degree of substitution of quaternary ammonium moiety.

2.4. Dynamic rheological measurements

Dynamic rheological measurements of the cryogels were performed on a Haake RheoStress 600 rheometer with a parallel plate sensor system (20 mm diameter) and Peltier temperature controller. Disks of the cryogels were extracted for 7 days and the dynamic storage (G') and loss (G'') moduli were measured in the 0.1–10 Hz frequency range at 25 °C in CD-mode ($\gamma = 0.005$).

3. Results and discussion

Semidilute solutions of non-ionic (hydroxypropyl)methylcellulose, 2-hydroxyethylcellulose, methylcellulose and cationic hydroxyethylcellulose (JR-30M), and hydrophobically modified cationic hydroxyethylcellulose (LM-200) were irradiated with UV–vis light in both frozen state (−30 °C) and at room temperature. The frozen-thawed samples were opaque spongy materials, while all samples irradiated at RT were still liquid. Fig. 1 shows the storage and loss moduli in the 0.1–10 Hz frequency range of 3 wt.% aqueous HEC solutions irradiated at the above mentioned conditions. The apparent values of G' and G'' of the sample obtained by UV irradiation of the frozen aqueous systems exhibit little dependence on the frequency (f) and $G' > G''$ over the entire f range explored. The observed results are consistent with the typical behavior of a polymer gel [11] and indicate that cross-linking reactions

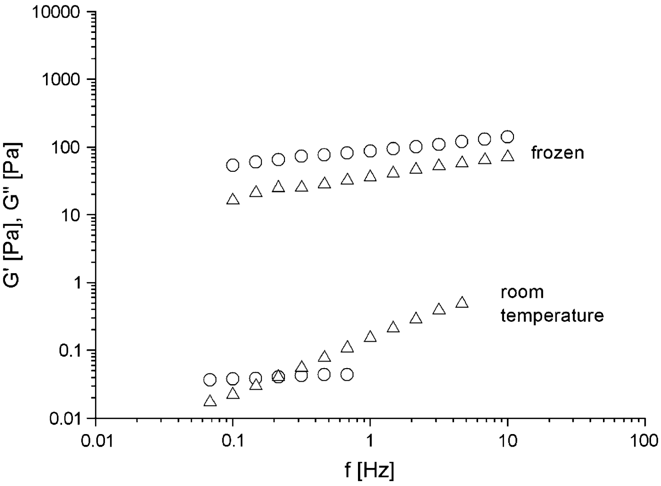

Fig. 1. Variation of elastic (○) and loss (△) moduli in the 0.1–10 Hz frequency range of 3 wt.% aqueous HEC solutions irradiated with UV–vis light at room temperature and in frozen state; 5 wt.% BBTMAC; irradiation time: 2 min.