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Nonionic gelation agents prepared from hydroxypropyl guar gum

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ABSTRACT

Nonionic gels were prepared from hydroxypropyl guar gum (HPG) with different molar substitution degrees by crosslinking with ethylene glycol diglycidyl ether (EGDE). FTIR and solid-state NMR spectroscopy revealed that the crosslinking degree of HPG gels increased with the amount of EGDE used during the reaction; this result was also confirmed by the water mobility in the swollen gels. Rheological characterization revealed behaviors typical of true gels, and their viscoelastic behaviors strongly depended on the crosslinking degree. The HPG gels absorbed buffers, aqueous saline, and water, and the absorption was not affected by the ionic strength or pH of the solution. In addition, HPG gels with high crosslinking degrees and molar substitution degrees exhibited gelation ability toward protic organic solvents such as methanol, ethanol, and 1-propanol. These HPG gels may find application as gelation agents for many industrial uses.

1. Introduction

Hydrogels may generally be described as crosslinked hydrophilic polymers that are capable of absorbing large amounts of water, often as much as 100–500 times their own weight. These crosslinked polymers are widely used in many applications such as disposable diapers, sanitary napkins, and as soil additives in agriculture (Buchholz, 1998a). Among the many commercially available hydrogels, crosslinked sodium polyacrylates, synthesized by the copolymerization of acrylic acid with various monomers, are the most widely used superabsorbent polymers. A major drawback of crosslinked sodium polyacrylates is the drastic decrease or disappearance of absorption ability in acidic and ionic solutions, as well as in aqueous or neat organic solvents, because the ionization state of the sodium carboxylate groups in these materials has an important part to play in the absorption ability. The release of free sodium cations from the crosslinked polyacrylates in solution drives the osmotic pressure between the gel and solution, causing the gel to swell, while the electrostatic repulsion between the carboxylate anions increases the volume expansion of the gel, prompting further swelling (Buchholz, 1998b). In acidic solutions, however, the carboxylate anions are protonated, diminishing the electrostatic repulsion and thereby resulting in gel shrinkage. At higher ion concentrations, the osmotic pressure that arises from the difference in ionic concentration between the gel and medium is suppressed, which results in a drastic decrease in absorbency (Peppas & Hariharan, 1994). In pure or aqueous solutions of organic solvents, dissociation of the sodium cations and carboxylate anions does not occur, and the crosslinked sodium polyacrylates do not exhibit any absorption ability (Horkay, Basser, Hecht, & Geissler, 2000).

Guar gum (GG) is a polysaccharide consisting of a backbone of 1,4-linked β-D-mannopyranosyl units (Man) with branches of 1,6-linked α-D-galactopyranosyl units (Gal) (Dea & Morrison, 1975; Dey, 1980; Dierckx & Dewettinck, 2002; Maier, Anderson, Karl, Magnuson, & Whistler, 1993; Scherbukhin & Anulov, 1999). The Man-to-Gal ratio has been estimated at 1.5:1 to 2:1 (Crescenzi et al., 2004; Gamal-Eldeen, Amer, & Helmy, 2006). The molecular weight of GG has been reported as $\sim 2.8 \times 10^7$ g mol^{-1} (Barth & Smith, 1981; Vijayendran & Bone, 1984). Due to its low cost, nontoxicity, high viscosity, and high water-solubility, GG is now used in many industries as thickening, emulsifying, and stabilizing additives (Chudzikowski, 1971; Wang, Ellis, & Ross-Murphy, 2000). The various derivatives of GG, manufactured by reacting the hydroxyl groups with various chemicals, exhibit improved physical and chemical properties (Bahamdan & Daly, 2007; Das, Ara, Dutta, & Mukherjee, 2011; Kautharapu et al., 2009; Sinha & Kumria, 2001).

Among the derivatives of GG, hydroxypropyl guar gum (HPG) has drawn attention as an essential additive to fracturing fluids,

Abbreviations: HPG, hydroxypropyl guar gum; EGDE, ethylene glycol diglycidyl ether; GG, guar gum; DDMAS, dipolar-decoupled/magic angle spinning; SR, swelling ratio; CR, crosslinking degree; MS, molar substitution.

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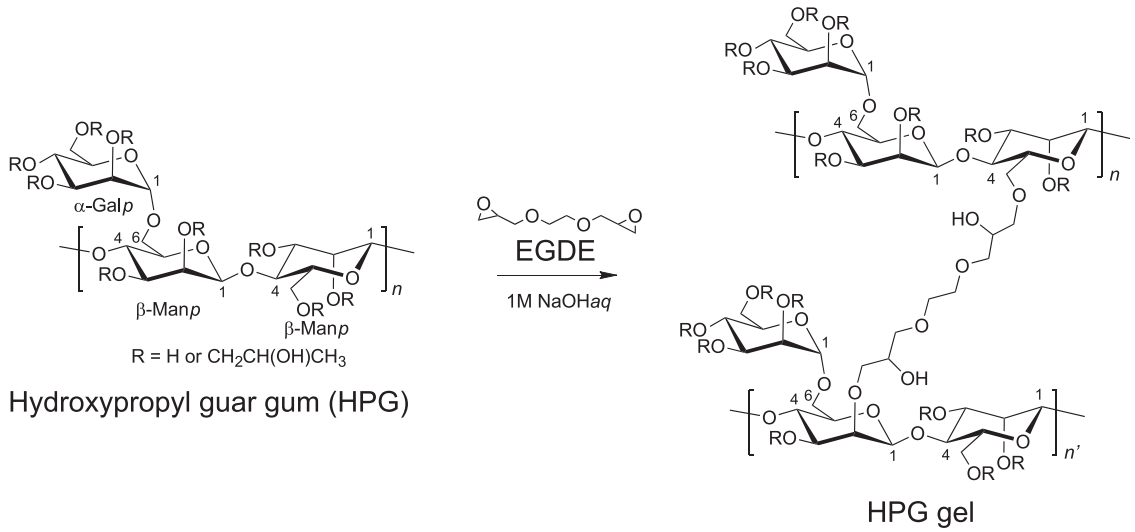

Fig. 1. Gel synthesis via crosslinking of HPG with EGDE. Although crosslinking can potentially occur at any hydroxyl group of GG, these possibilities were omitted in the figure for simplicity.

serving as a thickening agent to form concentrated muddy water in hydraulic fracturing for shale gas, tight gas, tight oil, and coal seam gas (Goel, Shah, & Grady, 2002). HPG is prepared from native guar gum via irreversible alkylation with propylene oxide in the presence of an alkaline catalyst (Prabhanjan, Gharia, & Srivastava, 1989). Compared to native guar gum, HPG shows better solubility toward alcohols such as methanol as well as water, and is thermally and chemically stable in solution (Prabhanjan, Gharia, & Srivastava, 1990). In the oil industry, for example, HPG can be easily dissolved in fracturing fluids, which normally contain many other chemical substances such as methanol, ethylene glycol, borate salts, and glutaraldehyde (Goel et al., 2002). Since HPG is soluble in various solvents, it was expected that chemically crosslinked HPG could potentially act as a versatile gelling agent for a variety of applications.

In this study, we prepared a series of gelling agents from HPG with various molar substitution (MS) values using ethylene glycol diglycidyl ether (EGDE) as a crosslinking agent (Kono, Onishi, & Nakamura, 2013). Structures of the obtained HPG gels were precisely determined through FTIR and solid-state ^{13}C NMR spectroscopies. The mobility of water in the swollen gels was investigated by analyzing the ^{1}H spin–spin relaxation time (T_2) of water, obtained by time-domain NMR spectroscopy. The viscoelastic behavior of the swollen HPG gels was characterized by rotational rheometry. Finally, the swelling behaviors of the crosslinked gels in various pH buffers, salines, and some organic solvents were investigated to determine their viability as gelling agents in different media. In addition, we discuss the relationship between the swelling behaviors and the structural parameters of the HPG gels.

2. Experimental

2.1. Materials

Three kinds of HPG with viscosity-average molecular weights of 1.9×10^5, 1.8×10^5, and 1.6×10^5 g mol^{-1} (the data of the molecular weights were provided from a manufacturer) and MS values of 1.2, 2.1, and 4.4 (described in Section 3.1), respectively, were kindly provided by Sansyo Co. Ltd., Japan. These HPGs are denoted as HPG1, HPG2, and HPG3, in order of sitincreasing MS value. EGDE was purchased from Tokyo Chemical Industry Co. Ltd., Japan. Deuterium oxide (99.9% isotopic purity) containing 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) was purchased from Sigma-Aldrich Co., US. All other reagents were of analytical grade and were purchased from Kanto Chemicals, Japan.

2.2. Preparation of HPG gels

As shown in Fig. 1, a series of HPG gels was prepared from HPG1, 2, and 3 with EGDE in an organic synthesizer Process Station PPS-2511 with a Teflon stirring impeller (Tokyo Rikakikai Co., Ltd.). HPG gels were typically prepared as follows: HPG1 (2.0 g, 4.1 mmol per repeating unit of HPG) was completely dissolved in 1 mol L^{-1} NaOH solution (20 mL) at 4 °C using the Teflon impeller at 300 rpm. EGDE (4.1 g, 24 mmol) was added to the HPG solution, and the crosslinking reaction was carried out at 60 °C for 3 h with continuous stirring. Acetone (100 mL) was added to the reaction mixture to precipitate the gel. The gel was washed twice in 1:2 (v/v) water and acetone, dialyzed using dialysis tubing (Mw 1.2–1.3 × 10^4 cut-off, Thermo Fisher Scientific Inc., US) for 3 days until neutral, and then precipitated with acetone. The precipitate was dried under reduced pressure at 60 °C. The resultant solid particles were cut and screened through a 40 mesh filter using a PLC-2M plastic cutting mill (Osaka Chemical Co., Japan) to obtain a white granular product **1a**. The other HPG gels **1b**–**3c** were obtained using a similar method. The initial feed amounts of EGDE and the various HPGs used for the preparation of the HPG gels are listed in Table 1. All the gels were stored in a vacuum desiccator until further use.

2.3. Structural characterization

FTIR spectroscopy was carried out using a Spectrum Two spectrometer (PerkinElmer Inc., US) by the KBr disc method, as previously reported (Kono et al., 2013).

All NMR spectra were recorded on a Bruker AVIII 500 MHz spectrometer (Bruker BioSpin GmbH, Germany). ^{1}H NMR spectra were obtained by use of a 2-channel, 5 mm broadband observe probe incorporating a z-gradient coil at 353 K. The excitation pulse length (flip angle of 30°), data acquisition time, and repetition time were set to 4.5 μs, 3.17 s, and 6 s, respectively, and 16 scans were accumulated. The ^{1}H chemical shifts were calibrated by assigning the methyl peak of DSS as 0 ppm. Solid-state dipolar-decoupled/magic angle spinning (DDMAS) ^{13}C NMR spectra were recorded at 25 °C using a 4 mm dual-tuned MAS probe at a MAS frequency of 10 kHz. The details of the experimental conditions used for obtaining the solid-state ^{13}C NMR spectra were reported in our previous paper