



Structure and dynamics of hydrogels and organogels: An NMR spectroscopy approach

Yury E. Shapiro*

Mina and Everard Goodman Department of Life Sciences, Bar-Ilan University, Ramat-Gan 52900, Israel

ARTICLE INFO

Article history:

Received 23 September 2010
 Received in revised form 7 April 2011
 Accepted 7 April 2011
 Available online 19 April 2011

Keywords:

Hydrogels
 Organogels
 NMR spectroscopy
 Network structure
 Morphology and mobility

ABSTRACT

Hydrogels and organogels are semi-solid systems, in which a liquid phase is immobilized by a three-dimensional network composed of self-assembled, intertwined polymer/gelator fibers. Investigations pertaining to these systems have only picked up speed in the last few decades. Consequently, many burning questions regarding these systems, such as the specific molecular requirements guaranteeing gelation, still await definite answers. Nonetheless, the application of different hydrogels and organogels to various areas of interest, i.e., as drug delivery devices, has been quick to follow their discoveries.

The use of NMR spectroscopy for the characterization of polymer hydrogels and organogels has recently seen enormous growth. The NMR measurements involving magic angle spinning (MAS) in the solid-state NMR, spin relaxation times, nuclear Overhauser enhancements (NOE), or multiple-quantum (MQ) spectroscopy, the pulse field gradient (PFG) technique and magnetic resonance imaging (MRI) allow obtaining the detailed information on morphology, molecular organization, specific interactions and internal mobility of constituents.

This review aims at providing a global view and capabilities all of these NMR methods in comprehensive studies of hydrogels and organogels, with special emphasis on the interplay between the morphology and molecular mobility of constituents and the intermolecular interactions.

© 2011 Elsevier Ltd. All rights reserved.

Contents

| | |
|---|------|
| 1. Introduction | 1185 |
| 1.1. Hydrogels and organogels: definition and history | 1185 |
| 1.1.1. Hydrogels | 1186 |
| 1.1.2. Organogels | 1186 |
| 1.2. Properties of hydrogels and organogels | 1186 |
| 1.3. NMR spectroscopy of gels | 1188 |
| 1.3.1. General experimental approaches | 1188 |
| 1.3.2. Spin–lattice and spin–spin relaxation | 1190 |
| 1.3.3. Chemical shift and its anisotropy | 1190 |
| 1.3.4. Self-diffusion | 1190 |
| 1.3.5. Concepts of the nuclear Overhauser enhancement (NOE) | 1190 |

* Tel.: +972 3 5317926; fax: +972 3 7384058.
 E-mail address: shapiro@nmrsg4.ls.biu.ac.il

| | | |
|---------|---|------|
| 1.3.6. | Main sources of NMR signal broadening in gels and solids..... | 1191 |
| 1.3.7. | Experimental tools for NMR spectroscopy in hydro-/organogels..... | 1191 |
| 1.3.8. | (¹ H)- ¹³ C cross-polarization under MAS conditions..... | 1192 |
| 1.3.9. | The solid-state ² H NMR..... | 1192 |
| 1.3.10. | Relaxation of I = 1/2 nuclei in the rotating frame..... | 1192 |
| 1.3.11. | Magnetic resonance imaging (MRI)..... | 1192 |
| 2. | NMR spectroscopy on the mechanisms of gelation..... | 1193 |
| 2.1. | Gelation and gelators..... | 1193 |
| 2.2. | Sol and gel phases as detected by NMR spectroscopy..... | 1193 |
| 2.3. | Self-assembly of fibrils and morphology of gels..... | 1197 |
| 2.3.1. | Self-assembly of hydrogel network from polymers and oligomers..... | 1197 |
| 2.3.2. | Self-assembly of LMWG networks..... | 1198 |
| 2.3.3. | Networks based on the inclusion complexes..... | 1199 |
| 2.3.4. | Stereochemical control of the self-assembly..... | 1201 |
| 2.3.5. | Thermodynamics of gelation..... | 1202 |
| 2.4. | Hydration and hydrogen bonding in gels..... | 1203 |
| 2.5. | π-π stacking and van der Waals interactions..... | 1208 |
| 2.6. | Chemical crosslinking..... | 1211 |
| 2.6.1. | Model studies of the initial stage of crosslinking..... | 1211 |
| 2.6.2. | Estimation of the crosslinking degree..... | 1211 |
| 2.6.3. | Mechanisms of crosslinking by gelation..... | 1215 |
| 2.6.4. | Swelling and deswelling..... | 1218 |
| 3. | NMR spectroscopy on the molecular dynamics of hydrogels and organogels..... | 1219 |
| 3.1. | NMR relaxometry and gel dynamics..... | 1219 |
| 3.1.1. | General consideration..... | 1220 |
| 3.1.2. | ¹ H T ₂ relaxation affected by an exchange..... | 1221 |
| 3.1.3. | Anisotropic molecular motion..... | 1221 |
| 3.1.4. | ¹ H T ₁ relaxation affected by an exchange..... | 1221 |
| 3.1.5. | ¹ H T ₁ for polymers with no exchangeable protons..... | 1222 |
| 3.2. | NMR relaxometry on discrimination and self-assembly of species with different mobility..... | 1222 |
| 3.3. | NMR relaxometry on network structure and crosslinking reactions..... | 1226 |
| 3.4. | Detection of slow mobility in gels with one-dimensional exchange NMR experiments..... | 1228 |
| 3.5. | PFG-NMR on self-diffusion of constituents of hydro-/organogels..... | 1229 |
| 3.5.1. | Pulsed field gradient spin-echo experiments..... | 1230 |
| 3.5.2. | Diffusion models in gels..... | 1231 |
| 3.5.3. | Self-diffusion of a solvent in hydro-/organogels..... | 1231 |
| 3.5.4. | Self-diffusion of low- and high-molecular weight compounds in hydro-/organogels..... | 1234 |
| 3.5.5. | Self-diffusion of the hydro-/organogel network..... | 1237 |
| 4. | NMR spectroscopy on the morphology of hydrogels and organogels..... | 1237 |
| 4.1. | NOE measurements for study of hydro-/organogel morphology..... | 1237 |
| 4.2. | NMR diffusometry on morphology of hydro-/organogels..... | 1239 |
| 4.3. | NMR cryoporometry..... | 1242 |
| 4.4. | ¹²⁹ Xe NMR in the porosity studies..... | 1242 |
| 4.5. | MRI of hydrogels and organogels..... | 1243 |
| 5. | Conclusions..... | 1244 |
| | References..... | 1245 |

1. Introduction

A recent issue in supramolecular chemistry of smart materials is the focus on the organization of monomer and polymer species into desired superstructures. Hydrogels and organogels belong to these materials and are characterized by more than one length scale through crosslinks formed by covalent bonds or physical (hydrogen bonding, solvophobic, charge transfer and van der Waals) interactions.

NMR spectroscopy in combination with FTIR, X-ray, electron microscopy and others, is rewarding in study of morphology, molecular structure and component dynamics of gel networks. For example, the chemical shifts and intensities of peaks in the NMR spectra allow structural quantities such as polymer composition, micro-

tacticity, sequence distribution, branching, crosslinking and molecular weight to be measured [1–4], while the more sophisticated experiments, i.e., magic angle spinning (MAS), measurements of spin relaxation times, nuclear Overhauser enhancements (NOE), or multiple-quantum (MQ) spectroscopy, as well as pulse field gradient (PFG) technique and magnetic resonance imaging (MRI) can provide detailed information about molecular organization, specific interactions and internal mobility of constituents [5,6].

1.1. Hydrogels and organogels: definition and history

We begin with definitions of a few terms used throughout this review [7].

Download English Version:

<https://daneshyari.com/en/article/5208704>

Download Persian Version:

<https://daneshyari.com/article/5208704>

[Daneshyari.com](https://daneshyari.com)