Polymer 128 (2017) 363–372

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Physical gelation of supramolecular hydrogels cross-linked by metal-ligand interactions: Dynamic light scattering and microrheological studies

Hiroto Ozaki [a], Tsutomu Indei [b], Tsuyoshi Koga [a], Tetsuharu Narita [c, d, *]

[a] *Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan*

[b] *Department of Chemical and Biological Engineering, and Center for Molecular Study of Condensed Soft Matter, Illinois Institute of Technology, 3440 S. Dearborn Street, Suite 150, Chicago, IL 60616, United States*

[c] *Laboratoire Sciences et Ingénierie de la Matière Molle, PSL Research University, UPMC Univ Paris 06, ESPCI Paris, CNRS, 10 rue Vauquelin, 75231, Paris Cedex 05, France*

[d] *Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan*

ARTICLE INFO

Article history:
Received 10 December 2016
Received in revised form
26 January 2017
Accepted 30 January 2017
Available online 15 February 2017

Keywords:
Associating polymer
Physical gel
Hydrogel
Metal-ligand bond
Viscoelasticity
Dynamic light scattering
Diffusing-wave spectroscopy microrheology

ABSTRACT

Microrheology based on diffusing-wave spectroscopy, dynamic light scattering (DLS), and macrorheology were performed on solutions of polyacrylamide-derivative associating polymer containing imidazole groups. By adding Ni ion, the physical gel is formed by metal-ligand bond. The physical gel point, where the percolation of a transient network is supposed to occur, was microrheologically determined. In the DLS measurement showing ergodicity at all the conditions studied, we observed three modes in the autocorrelation functions: fast, intermediate, and slow modes. The fast mode is the collective diffusion (gel mode), while the slow mode is attributed to the diffusion of clusters. For the intermediate mode, with increase in Ni ion concentration, the transition from diffusive mode to relaxation mode was observed near the microrheologically determined physical gel point. In postgel regime, intermediate mode can be attributed to the macroscopic relaxation since the activation energies are comparable with the relaxation energy estimated by macrorheology.

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1. Introduction

Hydrogels are cross-linked polymer chains swollen in water. Due to biocompatibility, permeability and deformability, hydrogels are often used in biomedical applications in forms of films as wound care dressings, nanoparticles as drug delivery systems, and complex coacervates as tissue engineering matrices [1–4]. Control and improvement of rheological properties of hydrogels are crucially important to achieve better performance in these applications.

Hydrogels can be classified into two categories depending on the strength of the cross-linking interactions: chemical gels and physical gels. Chemical gels are networks formed by covalent bonds. The material is percolated by the network spanning the whole sample [5]. The obtained permanent cross-links preserve the topological structures of the networks, making them elastic but brittle. On the other hand, physical gels are formed by noncovalent physical bonds, e.g., hydrophobic interaction, hydrogen bond, electrostatic interactions and metal-ligand bond. The obtained transient networks are elastic at shorter time scales than the lifetime of elastically active chains and viscous at longer time scales.

Recently, the physical cross-linking attracts attention since such transient cross-links reversibly break and reform enabling the gels to dissipate a large quantity of energy and to self-heal under deformation [6–8]. Hydrogels that include both physical and chemical cross-links have been made to improve mechanical reinforcement of the hydrogels [7,8]. In terms of the reversibility of cross-links, the supramolecular dynamic cross-links, a kind of physical cross-links, have also attracted attention in the context of tough hydrogels [9]. In order to design tough self-healing hydrogels based on supramolecular cross-linking, better physical

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* Corresponding author. Laboratoire Sciences et Ingénierie de la Matière Molle, PSL Research University, UPMC Univ Paris 06, ESPCI Paris, CNRS, 10 rue Vauquelin, 75231, Paris cedex 05, France.
E-mail address: tetsuharu.narita@espci.fr (T. Narita).

http://dx.doi.org/10.1016/j.polymer.2017.01.077
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understanding dynamic properties of the supramolecular cross-linking is essential. By changing the amount of supramolecular cross-linking, the system can show various viscoelastic behaviors from those of dilute and semidilute polymer solutions to those of viscoelastic gels because the cross-linking is reversible.

In general, the rheological properties of physical gels are different from those of chemical gels due to the reversible nature of physical cross-links. Meanwhile, even physical gels do not flow in observation time if the lifetime of the transient physical cross-link is sufficiently long, that is, they rheologically behave similarly to chemical gels. For such permanent physical gels, signatures of the gelation, or the percolation of the polymer chains to the infinite size (sample size) are the divergence of the zero-shear viscosity to infinity and the power-law behavior of the viscoelastic modulus for a wide range of time. The appearance of this Winter–Chambon (WC) law is a strong evidence of the gelation due to a percolation transition of connectivity [10–13].

On the other hand, when the lifetime of the transient cross-link is shorter than the observation time scales, the physical gels flow thus the divergence of the viscosity cannot be observed, even though the transient percolated networks are formed. It is plausible to expect that the WC law appears for such flowable physical gels in the time range shorter than this lifetime. However, it is not easy to access this time range with conventional rheological methods. Recently, high-frequency passive microrheology based on diffusing-wave spectroscopy, DWS, was successfully applied to a model flowable physical gel of poly(vinyl alcohol)–borax [7,14]. This modern optical rheological technique allows us to measure the linear viscoelastic properties of a sample in a wide frequency regime ($10^1 \sim 10^5$ Hz) from the mean-square displacement (MSD) of micron-sized probe particles embedded into the sample [15–17]. By using the DWS microrheology, the physical gel point of the model physical gel was determined in terms of WC criterion [14]: the power-law behavior was observed only in the high frequency range, or the shorter time scale than the network relaxation due to the transient bond dissociation.

Dynamic light scattering (DLS) is commonly used to characterize the dynamics of polymer solutions and gels at short time scales. DLS has been used not only to characterize the collective diffusion dynamics related to the correlation length of the entangled or cross-linked polymer chains, but also to characterize gelation of chemical gels [18,19]. A gel point can be determined by the following two signatures. (1) A power-law behavior of the autocorrelation function is observed near the gel point, since the structure is self-similar and no characteristic size and time exist (i.e., any size between the single chain and the sample exists). (2) The scattering light signals become non-ergodic in the postgel region since the concentration gradient is topologically fixed in the chemical network and therefore a part of the scattered light does not fluctuate with time. The portion of the frozen-in intensity depends on the position of the measurement in the gel [20,21]. Similarly, for permanent physical gels, the scattering signal can be no longer ergodic in the observation time scale, and the power-law behavior is observed [22].

On the other hand, it is not evident to apply these criteria to the flowable physical gels; the ergodicity holds because the network structure constantly changes due to the nature of physical cross-links, and the system flows, thus the transition to non-ergodicity cannot be used as a signature of gelation. As far as the authors know, no systematic study on the power-law behavior of the autocorrelation function at the gel point has been reported. Since there coexist different dynamic modes having different q–dependence with the power-law mode, detailed multiangle studies are needed [23].

In the present study, we investigate dynamical properties of physical gels with metal-ligand bond around the physical gel point by DLS and microrheology based on DWS, complemented by macrorheology. The supramolecular physical gels consist of polyacrylamide-derivative associating polymers containing imidazole groups which can form metal-ligand bonds in the presence of transition metal ions, Ni^{2+}. Although similar physical gels formed by metal-ligand coordination bonds have been recently reported by Fullenkamp et al., the Winter–Chambon criterion has not been applied to determine a physical gel point [24]. Here, we first show that the physical gel point can be microrheologically determined by DWS for physical gel cross-linked by the metal-ligand bonds. Then we characterize the dynamics of three modes found by DLS in pregel and postgel regimes. We discuss how the transient nature of physical cross-links alters dynamical properties of the flowable gel before and after gelation.

2. Experimental section

2.1. Synthesis of poly(acrylamide-co-1-vinylimidazole)

1-Vinylimidazole, acrylamide, sodium formate were purchased from Sigma-Aldrich (Lyon, France). 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was purchased from Wako Chemicals GmbH (Neuss, Germany). $NiCl_2 \cdot 6H_2O$ was purchased from Prolabo (Paris, France).

Poly(acrylamide-*co*-1-vinylimidazole) was synthesized by free radical polymerization in water. In order to minimize secondary reactions (chain branching, hydrolysis etc), the polymerization was conducted at 30 °C in the presence of a chain-transfer agent, sodium formate, following the procedure detailed in Ref. [25]. In a flask containing 435 ml of water, acrylamide (12.8 g), 1-vinylimidazole (1.88 g) and sodium formate (3.40 g) were dissolved. The solution was stirred under a nitrogen atmosphere at 30 °C. A solution of the initiator VA-044 (0.0646 g in 3 ml of water) separately prepared under a nitrogen atmosphere was added to the flask. The polymerization reaction was kept for 5 h under a nitrogen atmosphere. The obtained viscous solution of the copolymer was dialyzed for 1 week in milli-Q water. The dry copolymer was obtained by lyophilization. Static light scattering was used to determine the molecular weight. With a literature value of dn/dc for polyacrylide ($0.183\ \mathrm{ml\ g^{-1}}$ [26]), the molecular weight was estimated as $1.1 \times 10^5 \mathrm{g\ mol^{-1}}$. The chemical structure of poly(-acrylamide-*co*-1-vinylimidazole) is shown in Fig. 1.

2.2. Diffusing-wave spectroscopy microrheology

We performed microrheological measurements based on diffusing-wave spectroscopy (DWS) using a laboratory-made setup. As the coherent source, a Spectra-Physics Cyan CDRH laser ($\lambda = 488$ nm) with an output power of 50 mW was used. The laser beam diameter was increased up to approximately 1 cm using a beam expander. The diffused light was collected by an optical fiber with a photon counter (ALV, Langen, Germany) placed in the transmission geometry.

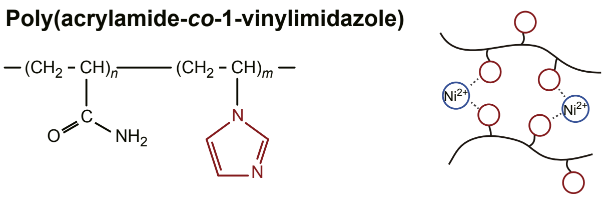

Fig. 1. Structure of poly(acrylamide-*co*-1-vinylimidazole) and a schematic figure of the complex cross-linked by metal-ligand bonds.

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