

RHEOLOGICAL CHARACTERIZATION OF THE THERMAL GELATION OF POLY(N-ISOPROPYLACRYLAMIDE) AND POLY(N-ISOPROPYLACRYLAMIDE) CO-ACRYLIC ACID

FILIPE E. ANTUNES^{*1,2}, LUIGI GENTILE², LORENA TAVANO³, AND CESARE OLIVIERO ROSSI²

¹ Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

² Department of Chemistry, Calabria University, Via P. Bucci, Cubo 14/D,

87036 Arcavacata di Rende, Italy

³ Department of Pharmaceutical Science, Calabria University, Edificio Polifunzionale,
87036 Arcavacata di Rende, Italy

* Email: filipe.antunes@ci.uc.pt

Fax: x351.23.9827703

Received: 26.1.2009, Final version: 7.5.2009

ABSTRACT:

The combined effect of charged addition and molecular weight, M_w , on the thermal gelation and gel dissolution of poly(N-isopropylacrylamide) chains was explored by using Rheological techniques. The synthesized charged derivative is poly(N-isopropylacrylamide co-Acrylic acid). The rheological behavior of the two macromolecules is clearly different: the thermal gelation of the high M_w and charged macromolecule is much more accentuated. This suggests that the gelation at high temperatures only occurs when the inter polymer aggregate distance is sufficiently short to allow polymer bridging; this situation can be achieved by different approaches, such as increasing polymer concentration and increasing polymer persistence length and polymer M_w .

ZUSAMMENFASSUNG:

Der kombinierte Einfluss von geladenen Zusätzen und Molekulargewicht M_w auf die thermische Gelbildung und die Auflösung des Gels von Poly(N-isopropylacrylamid)-Ketten wurde mit Hilfe rheologischer Techniken untersucht. Das synthetisierte geladene Derivat ist Poly(N-isopropylacrylamid-co-acrylsäure). Das rheologische Verhalten dieser zwei Makromoleküle unterscheidet sich deutlich: die thermische Gelbildung des hochmolekularen und des geladenen Makromoleküls tritt in einer wesentlich klareren Weise auf. Diese Beobachtung führt zu der Vermutung, dass die Gelbildung nur dann bei hohen Temperaturen auftritt, wenn der Abstand zwischen den Polymeraggregaten ausreichend kurz ist, um die Bildung von Polymerbrücken zu erlauben. Diese Situation kann durch verschiedene Ansätze erreicht werden, wie z. B. eine steigende Polymerkonzentration, eine höhere Persistenzlänge und ein höheres Molekulargewicht.

RÉSUMÉ:

L'effet combiné de l'addition de charges et de la masse moléculaire sur la gélation thermique et la dissolution de gels de chaînes de poly(N-isopropylacrylamide), a été étudié au moyen de techniques rhéologiques. Le composé dérivé chargé synthétisé est un poly(isopropylacrylamide co-acide acrylique). Le comportement rhéologique des deux composés est clairement différent: la gélification thermique de la macromolécule chargée et de haut poids moléculaire est beaucoup plus accentuée. Cela suggère que la gélification à hautes températures s'effectue quand la distance entre agrégats polymériques est suffisamment courte pour permettre un pontage polymérique; cette situation peut être obtenue en suivant différentes approches telles que une augmentation de la concentration en polymères et l'augmentation de la longueur de persistance et de la masse moléculaire du polymère.

KEY WORDS: thermalgelation, PNIPAA, PNIPAAcoAAC, polymeric networks, rheology

1 INTRODUCTION

Some systems show high miscibility in water at low temperatures while they phase separate at high temperatures. Before the macroscopic phase separation there is a strong turbidity, defined as clouding [1, 2]. At certain circumstances, namely

above a critical concentration, the polymer system stays turbid with a gel-like appearance, without any macroscopic phase separation [3]. Gels defined in terms of rheological characteristics can be considered as two component systems exhibiting a solid-like behaviour under small deformation. Thermal reversible gelation

© Appl. Rheol. 19 (2009) 42064

This is an extract of the complete reprint-pdf, available at the Applied Rheology website

<http://www.appliedrheology.org>

Applied Rheology

Volume 19 · Issue 4

<http://www.appliedrheology.org>

- hydroxypropylmethyl cellulose aqueous solutions, *J. Coll. Int. Sci.* 327 (2008) 333–340.
- [6] Xu X M, Song Y M, Ping Q N, Wang Y, Liu X Y: Effect of ionic strength on the temperature-dependent behavior of hydroxypropyl methylcellulose solution and matrix tablet, *J. Appl. Polym. Sci.* 102 (2006) 4066–4074.
- [7] Sammon C, Bajwa G, Timmins P, Melia C D: The application of attenuated total reflectance Fourier transform infrared spectroscopy to monitor the concentration and state of water in solutions of a thermally responsive cellulose ether during gelation, *Polymer* 47 (2006) 577–584.
- [8] Sarkar N: Thermal gelation properties of methyl and hydroxypropyl methylcellulose, *J. Appl. Polym. Sci.* 24 (1979) 1073–1087.
- [9] Haque A, Richardson R K, Morris E R, Gidley M J, Caswell D C: Thermogelation of methylcellulose. Part II: effect of hydroxypropyl substituents, *Carbohydr. Polym.* 22 (1993) 175–186.
- [10] Kjoniksen A L, Zhu K, Pamies R, Nystrom B: Temperature-Induced Formation and Contraction of Micelle-Like Aggregates in Aqueous Solutions of Thermoresponsive Short-Chain Copolymers, *J. Phys. Chem. B Letters* 112 (2008) 3294–3299.
- [11] Han C K, Bae Y H: Inverse thermally-reversible gelation of aqueous N-isopropylacrylamide copolymer solutions, *Polymer* 39 (1998) 2809–2814.
- [12] Jeong B, Kim S, Bae Y H: Thermosensitive sol-gel reversible hydrogels, *Adv. Drug Deliv. Rev.* 54 (2002) 37–51.
- [13] Yoshida R, Uchida K, Kaneko Y, Sakai K, Kikuchi A, Sakurai Y, Okano T: Comb-type grafted hydrogels with rapid deswelling response to temperature changes, *Nature* 374 (1995) 240–242.
- [14] Kaneko Y, Nakamura S, Sakai K, Aoyagi T, Kikuchi A, Sakurai Y, Okano T: Rapid Deswelling Response of Poly(N-isopropylacrylamide) Hydrogels by the Formation of Water Release Channels Using Poly(ethylene oxide) Graft Chains, *Macromol.* 31 (1998) 6099–6105.
- [15] Zhu K, Jin H, Kjoniksen A L, Nystrom B: Anomalous Transition in Aqueous Solutions of a Thermoresponsive Amphiphilic Diblock Copolymer, *J. Phys. Chem. B* 111 (2007) 10862–10870.
- [16] Durand A, Hourdet D: Thermoassociative graft copolymers based on poly(N-isopropylacrylamide): Relation between the chemical structure and the rheological properties, *Macromol. Chem. Phys.* 201 (2000) 858–868.
- [17] Lebon F, Caggioni M, Bignotti F, Abbate S, Gangemi F, Longhi G, Mantegazza F, Bellini T: Coil-to-Globule Transition of Poly(N-isopropylacrylamide) Doped with Chiral Amino Acidic Comonomers, *J. Phys. Chem. B* 111 (2007) 2372 – 2376.
- [18] Wanka G, Hoffman H, Ulbricht W: Phase Diagrams and Aggregation Behavior of Poly(oxyethylene)-Poly(oxypropylene)-Poly(oxyethylene) Triblock Copolymers in Aqueous Solutions, *Macromol.* 27 (1994) 4145–4159.
- [19] Alexandridis P, Hatton T A: Poly(ethylene oxide) poly(propylene oxide)-poly(ethylene oxide) block copolymer surfactants in aqueous solutions and at interfaces: thermodynamics, structure, dynamics, and modeling, *Coll. Surf. A* 96 (1995) 1–46.
- [20] Zhou Z, Chu C: Light-scattering study on the association behavior of triblock polymers of ethylene oxide and propylene oxide in aqueous solution, *J. Coll. Int. Sci.* 126 (1988) 171–180.
- [21] Attwood D, Collett J H, Tait C J: The micellar properties of the poly(oxyethylene) – poly(oxypropylene) copolymer Pluronic F127 in water and electrolyte solution *Int. J. Pharm.* 26 (1985) 25–33.
- [22] Alexandridis P: Amphiphilic Copolymers and their Applications, *Curr. Opin. Colloid Interface Sci* 1 (1996) 490–501.
- [23] Yang Z, Zhang W, Zou J, Shi W: Synthesis and thermally responsive characteristics of dendritic poly(ether-amide) grafting with PNIPAAm and PEG, *Polymer* 48 (2007) 931–938.
- [24] Schild H G: Poly(N-isopropylacrylamide): Experiment, theory and application, *Prog. Polym. Sci.* 17 (1992) 163–249.
- [25] Gariepy E, Leroux J: In situ-forming hydrogels—review of temperature-sensitive systems, *Eur. J. Pharm. Biopharm.* 58 (2004) 409–426.
- [26] Chang C, Wei H, Quan C, Li Y, Liu J, Wang Z, Cheng S, Zhang X, Zhuo R: Fabrication of thermosensitive PCL-PNIPAAm-PCL triblock copolymeric micelles for drug delivery, *J. Polym. Sci. A* 46 (2008) 3048–3057.
- [27] Osada Y, Okuzaki H, Hori H: A polymer gel with electrically driven motility, *Nature* 355 (1992) 242–244.
- [28] Xu X D, Wei H, Zhang X Z, Cheng S, Zhuo R: Fabrication and characterization of a novel composite PNIPAAm hydrogel for controlled drug release, *J. Biomed. Mater. Res. A* 81 (2007) 418–426.
- [29] Chen G, Hoffman H: Graft copolymers that exhibit temperature-induced phase transitions over a wide range of pH, *Nature* 373 (1995) 49–52.
- [30] Shibayama M, Fujikawa Y, Nomura S: Dynamic Light Scattering Study of Poly(N-isopropylacrylamide-co-acrylic acid) Gels, *Macromol.* 29 (1996) 6535–6540.
- [31] Chen H, Hsieh Y: Ultrafine hydrogel fibers with dual temperature- and pH-responsive swelling behaviors, *J. Polym. Sci. A* 42 (2004) 6331–6339.
- [32] Wang Z, Xu X D, Chen C, Wang G, Wang B, Zhang X, Zhuo R: Study on novel hydrogels based on

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
<http://www.appliedrheology.org>

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
<http://www.appliedrheology.org>

- thermosensitive PNIPAAm with pH sensitive PDMAEMA grafts, *Coll. Surf. B* 67 (2008) 245–252.
- [33] Tanford C: *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley, New York (1980).
- [34] Saeki S, Kuwahara N, Nakata M, Kaneko M: Upper and lower critical solution temperatures in poly(ethylene glycol) solutions, *Polymer* 17 (1976) 685–689.
- [35] Zhou X, Li J, Wo C, Zheng B: Constructing the Phase Diagram of an Aqueous Solution of Poly(N-isopropyl acrylamide) by Controlled Microevaporation in a Nanoliter Microchamber, *Macromol. Rapid Commun.* 29 (2008) 1363–1367.
- [36] Heskins M, Guillet J E: Solution Properties of Poly(N-isopropylacrylamide), *J. Macromol. Sci. A* 2 (1969) 1441–1455.
- [37] Williams C, Brochard F, Frisch H L: Polymer Collapse, *Annu. Rev. Phys. Chem.* 32 (1981) 433–451.
- [38] Hiemenz P, Timothy L: *Polymer Chemistry*, Marcel Dekker Inc, New York (2007).
- [39] Brandup J, Immergut E H: *Polymer Handbook*, John Wiley & Sons, New York (1993).
- [40] Coppola L, Gianferri R, Oliviero C, Nicotera I, Ranieri G: Structural changes in CTAB/H₂O mixtures using a rheological approach, *Phys. Chem. Chem. Phys.* 6 (2004) 2364–2372.
- [41] Gabriele D, Cindio B, Antona P: A weak gel model for foods, *Rheol. Acta* 40 (2001) 120–127.
- [42] Boris D C, Colby R H: Rheology of Sulfonated Polystyrene Solutions, *Macromol.* 31 (1998) 5746–5755.
- [43] Mours M, Winter H: Mechanical spectroscopy. In *Experimental methods in Polymer Science*, Tanaka, T., Ed. Academic Press, San Diego (2000).
- [44] Simon B, Ross-Murphy: Structure-property relationships in food biopolymer gels and solutions, *J. Rheo* 39 (1995) 1451–1463.
- [45] Rao M: *Rheology of Fluid and Semisolid Foods: Principles and Applications*, Aspen Publishers, Springer, Gaithersburg, (1999).



This is an extract of the complete reprint-pdf, available at the Applied Rheology website
<http://www.appliedrheology.org>