Title: Controlling the gelation temperature of biomimetic
polyisocyanides

Authors: Paul H.J. Kouwer, Paula de Almeida, Onno ven den
Boomen, Zaskia H. Eksteen-Akeroyd, Roel Hammink,
Maarten Jaspers, Stijn Kragt, Mathijs F.J. Mabesoone,
Roeland J.M. Nolte, Alan E. Rowan, Martin G.T.A. Rutten,
Vincent A.A. Le Sage, Daniël C. Schoenmakers, Chengfen
Xing, Jialiang Xu

PII: S1001-8417(17)30470-9
DOI: https://doi.org/10.1016/j.cclet.2017.11.002
Reference: CCLET 4317

To appear in: *Chinese Chemical Letters*

Received date: 21-8-2017
Revised date: 1-11-2017
Accepted date: 3-11-2017

Please cite this article as: Paul H.J.Kouwer, Paula de Almeida, Onno ven den Boomen, Zaskia H.Eksteen-Akeroyd, Roel Hammink, Maarten Jaspers, Stijn Kragt, Mathijs F.J.Mabesoone, Roeland J.M.Nolte, Alan E.Rowan, Martin G.T.A.Rutten, Vincent A.A.Le Sage, Daniël C.Schoenmakers, Chengfen Xing, Jialiang Xu, Controlling the gelation temperature of biomimetic polyisocyanides, Chinese Chemical Letters https://doi.org/10.1016/j.cclet.2017.11.002

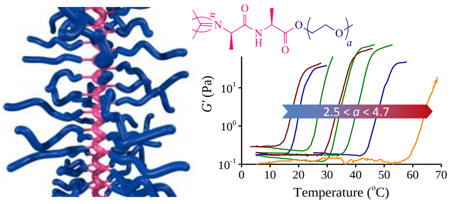
Communication

Controlling the gelation temperature of biomimetic polyisocyanides

Paul H. J. Kouwer*, Paula de Almeida, Onno van den Boomen, Zaskia H. Eksteen-Akeroyd, Roel Hammink, Maarten Jaspers, Stijn Kragt, Mathijs F. J. Mabesoone, Roeland J. M. Nolte*, Alan E. Rowan*, Martin G. T. A. Rutten, Vincent A. A. Le Sage, Daniël C. Schoenmakers[a], Chengfen Xing[a], Jialiang Xu[a]

Institute for Molecules and Materials, Radboud University, Nijmegen 6525 AJ, The Netherlands

Graphical Abstract



The gelation temperature and mechanical properties of aqueous ethylene glycol-decorated polyisocyanide solutions strongly depends on the length of the glycol tail. Copolymerisation of monomers with different tail lengths allows for precise engineering of the gel properties.

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords: Smart materials
Lower critical solution temperature
Polyisocyanides
Mechanical properties
Biomimetic polymers

ABSTRACT

Thermosensitive polymers show an entropy-driven transition from a well-solvated to a poorly solvated polymer chain, resulting in a more compact globular conformation. The transition at the lower critical solution temperature (LCST) is often sharp, which allows for a wide range of smart material applications. At the LCST, oligo(ethylene glycol)-substituted polyisocyanides (PICs) form soft hydrogels, composed of polymer bundles similar to biological gels, such as actin, fibrin and intermediate filaments. Here, we show that the LCST of PICs strongly depends linearly on the length of the ethylene glycol (EG) tails; every EG group increases the LCST and thus the gelation temperature by nearly 30 °C. Using a copolymerisation approach, we demonstrate that we can precisely tailor the gelation temperature between 10 °C and 60 °C and, consequently, tune the mechanical properties of the PIC gels.

Thermoresponsive polymer solutions show an abrupt transition from a dissolved to a precipitated state or gel. Many examples in the literature describe polymers with a lower critical solution temperature (LCST) when dissolved in water [1]. At low temperatures, such a polymer is hydrated by the solvent, often involving hydrogen-bonding interactions with the solvent, and forms a homogeneous solution. Beyond the LCST, however, intramolecular interactions are favoured and the polymer chain conformation changes from an extended coil to a collapsed globular conformation, which often leads to precipitation of the polymer from the solution. The potential applications of thermosensitive polymers are endless, ranging, for instance, from drug delivery and biomedical applications [2] (including polymers with transient thermal properties [3]) to smart functional surfaces [4].

A key parameter in LCST polymers is the transition temperature, which besides the molecular structure may depend on the polymer concentration, its molecular weight and the presence of salts or other solutes in the solution. The most studied material, poly(*N*-isopropylacrylamide) or pNiPAM shows an LCST of 32 °C, close to body temperature [5]. Over the years, many differently substituted poly(meth)acrylamides and other polymers have been characterised and transition temperatures virtually anywhere between 10 °C and 90 °C have been found [1]. This list also includes semi-biological materials, for instance elastin-like polypeptides [6] and cellulose derivatives [7]. A proficient approach to precisely tailor the LCST of a polymer solution is to prepare copolymers [8]. The

---

* Corresponding authors.
E-mail addresses: p.kouwer@science.ru.nl (P.H.J. Kouwer), r.nolte@science.ru.nl (R.J.M. Nolte), alan.rowan@uq.edu.au (A.E. Rowan).