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Temperature-induced formation of strong gels of acrylamide-based polyelectrolytes

Ranjith Krishna Pai [a], Jovice B.S. Ng [a], Saju Pillai [b], Lennart Bergström [a], Niklas Hedin [a,*]

[a] *Material Chemistry Research Group, Department of Physical Inorganic and Structural Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden*
[b] *Interdisciplinary Nanoscience Centre (iNANO), University of Aarhus, Ny Munkegade, 8000 Aarhus C, Denmark*

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ABSTRACT

Very strong physical gels have been formed by moderate temperature increases of concentrated aqueous dispersions of acrylamide-based copolymers. The results of rheometry, confocal laser scanning microscopy, and differential scanning calorimetric studies of acrylamide-based copolymers with acrylic acid (poly[AM-AA]) and the sodium salt of 2-acrylamido-2-methylpropane acid (poly[AM-NaAMPS]) suggest that the temperature-induced swelling of the polymer beads and dissolved chains creates strongly entangled polymer networks above the upper critical solution temperature. Analysis of the viscoelastic response showed that the time scale for the gelation process is about minutes to hours. The addition of high concentrations of Ca^{2+} resulted in a significant reduction in the modulus.

1. Introduction

Polyelectrolytes are used to control the colloidal stability and rheological responses of a wide range of industrially important products and processes, including in the food [1] and paper industries [2] and in enhanced oil recovery [3] and water purification [4]. The industrial significance of polyelectrolytes has prompted the rapid development of a synthetic technology to tailor their molecular architecture for specific applications [5,6]. Polyelectrolytes that respond to changes in pH, temperature, external field strength, or ionic strength, or that form strong gels are of particular interest for medical and pharmaceutical applications [6,7]. Solutions of polymers or polyelectrolytes are rheologically responsive to environmental parameters, and dispersions of polymer particles also display such responsive behavior. For example, poly-*N*-isopropylacrylamide (poly-NIPAM) polymer [8] particles have been shown to respond to changes in both temperature [9] and pH [10]. They respond rapidly to temperature changes and form gels at high temperatures. In addition to their technical applications and particular solution properties, polyelectrolytes modify the crystallization behavior of minerals formed from solutions [11–13]. Polyelectrolytes may affect crystal nucleation and growth patterns. Anionically charged oligopeptides have been shown to enhance calcite growth [14]. Temperature-dependent rheological responses could very well affect the calcium carbonate crystallization kinetics or the morphology of the particles formed. A particular interest of ours is the way in which such polyelectrolytes control calcium carbonate crystallization [15].

The gelation behavior and the strength of the gels formed relate to the phase behavior, crosslinking ability, and properties of the original solution/dispersion. Limiting the discussion to polymers that form physical gels, the stiffness of the polymer chains and the strength of each individual crosslink have significant effects on the strength and relaxation times of the gels formed [16]. Several mechanisms underlie the formation of crosslinks in a polymer gel: attraction between specific groups on the polymer chain, partial crystallization, and entanglement. The gelation process often proceeds with a concurrent phase separation. These phase-separated systems rarely form strong gels because the percolating dilute phase limits the connectivity. Hence, phase separation must be suppressed or eliminated when designing a strong gel.

The formation of very strong gels requires a high density of crosslinks, which typically means that the polymer concentration must be high. It is difficult to achieve a high polymer concentration because the high viscosity of solutions of high-molecular weight polymers limits the appropriate mixing conditions in concentrated solutions and therefore the concentration of crosslinks. Strong temperature-induced polymer gels have been prepared from highly concentrated solutions of polypropylene–polyethylene block copolymers (of relatively low molecular weight) [17]. Whereas dispersions of polymer particles can be prepared at high concentrations, gels of these particles typically have lower strength than gels of polymers. The gels of particles are also much more brittle than polymer gels [16]. The recent work on hydrogels has shown that it is possible to prepare highly concentrated solutions/dispersions of these weakly crosslinked particles. Changes

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* Corresponding author.
E-mail address: niklas.hedin@inorg.su.se (N. Hedin).

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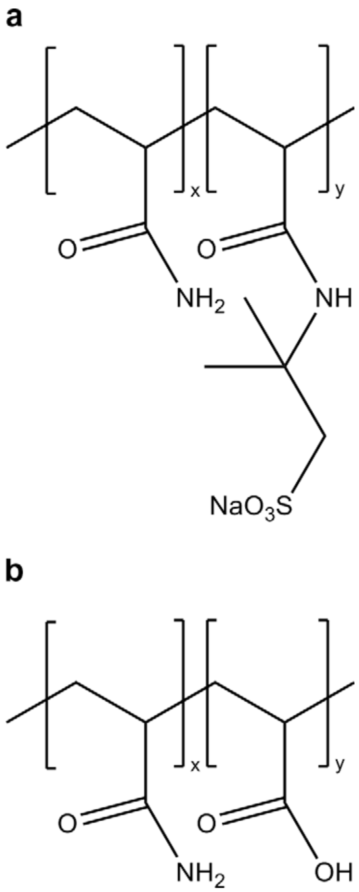
in environmental parameters, such as pH or temperature, transform them into strong gels [18].

The combination of low cost and versatility makes polyacrylamide and acrylamide (AM)-based polyelectrolytes attractive candidates for a wide range of applications [19,20]. Many AM-based polymers and polyelectrolytes form gels under certain conditions. Chemically crosslinked aqueous poly-AM gels collapse when the temperature is lowered, which is related to the increased aqueous solubility of the uncharged acrylamide moieties at high temperatures [21]. AM-based copolymers that contain charged groups display temperature-induced gelation in that the temperature for gelation decreases with increasing charge density along the backbone of the polymer [22].

We have prepared anionic AM-based polyelectrolytes that contain carboxylic acid groups using acrylic acid (AA) as the comonomer. Sodium salts of 2-acrylamido-2-methylpropane sulfonic acid (NaAMPS) were used to modify the poly-AM to a more water-soluble polyelectrolyte, poly(acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate) (poly[AM-NaAMPS]) [23]. These linear polymers were prepared using a suspension–polymerization method, which results in the formation of relatively large polymer beads consisting of highly entangled polyelectrolytes [24]. Here, we studied the temperature-induced gelation of concentrated dispersions of acrylamide-based AA (weak acid) and acrylamide-based NaAMPS (weak base salt) polyelectrolytes using viscoelastic measurements. The use of the suspension–polymerization route, which yielded a product that contained highly entangled polymer beads, allowed us to prepare highly concentrated dispersions/solutions of these noncrosslinked polymers. We observed a dramatic increase in the storage modulus over a relatively narrow temperature range. Gelation was related to the temperature-induced swelling and the formation of a strongly entangled polymer network. The effect of the addition of Ca^{2+} ions on gelation behavior was studied in detail and related to the phase behavior of the polyelectrolyte beads in the dispersions.



Scheme 1. Chemical structures of copolymers. (a) poly(AM-co-NaAMPS) and (b) poly(AM-co-AA), where $x/y = 5.7$.

2. Experimental

2.1. Materials

The AM (B.D.H., UK) monomer (Caution: acrylamide is a neurotoxin. Do not try to repeat this synthesis without proper care) was crystallized from chloroform (B.D.H., UK; HPLC grade), filtered, and subsequently dried under vacuum at temperatures below 30 °C. AMPS (Aldrich Chemicals) and AA (Aldrich Chemicals) were used without further purification. The sodium salt of AMPS was prepared by dissolving 50 g of AMPS in 145 mL of milli-Q™ water, with the subsequent addition of 27.8 g of NaOH, with cooling and constant stirring. The solution was titrated with $NaOH_{aq}$ (1000 mol/m^3) to pH 7. The total solid content of the NaAMPS/water precursor material was 58.5 wt%. The polymer initiator, ammonium persulfate (APS; Merck), and toluene (Merck) were used as received. The chemical formulae for the acrylamide-based polyelectrolytes synthesized and studied are presented in Scheme 1.

2.2. Synthesis of poly(acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate)

Random copolymers of poly(acrylamide-co-sodium 2-acrylamido-2-methylpropanesulfonate), poly(AM-NaAMPS), were synthesized with free-radical suspension–polymerization using a redox initiator. The monomers AM (6.37 g) and NaAMPS (3.63 g) and the initiator APS (0.0061 g) were dissolved in 15 mL of milli-Q™ water. After the solution had been purged with nitrogen gas for 30 min, the mixture was transferred to a funnel. A surfactant, sorbitan monooleate (SMO; 2.25 g) was added to toluene (46.2 mL) in a round-bottomed flask with three necks. The SMO solution in toluene was kept at a temperature of 50 °C and the aqueous solution of the monomers was added dropwise with stirring. The polymerization reaction was allowed to proceed for 4 h, after which the reaction vessel was cooled to room temperature and the polymer material was retrieved by filtration and precipitation with acetone. The polymeric material was washed in milli-Q™ water and precipitated twice with acetone, and then dried under vacuum at a temperature of 50 °C. The fraction containing the NaAMPS moieties in the copolymer was identified by ^{13}C nuclear magnetic resonance (NMR) spectroscopy and was in good agreement with that of the added monomers (i.e., molar ratio for AM/NaAMPS = 85/15).

2.3. Synthesis of poly(acrylamide-co-acrylic acid)

Random copolymers of poly(acrylamide-co-acrylic acid), poly(AM-AA), were synthesized with a suspension–polymerization reaction, similar to that described above. The monomers AM (8.29 g) and AA (1.45 g) and the initiator APS (0.0061 g) were dissolved in 15 mL of milli-Q™ water. The mixture was purged with nitrogen for 30 min. The surfactant (2.46 g SMO) was added to 46.2 mL of toluene, and the polymer was synthesized, purified, and characterized in a similar way to the poly(AM-NaAMPS) polyelectrolyte (as described in detail above).

2.4. Differential scanning calorimetry (DSC)

Thermal analysis of the copolymers was performed with DSC on 10 wt% samples using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter. The temperature was swept from 25 °C to 90 °C at a