

Rheological monitoring of *in situ* poly(acrylamide) gel preparation

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The sol-gel transition for a polyacrylamide gel during *in situ* preparation was investigated by dynamic rheology at constant frequency of 0.1 Hz and by means of temperature, pH and conductivity variation. The gels were prepared by polymerization of acrylamide crosslinked with N, N'-methylene-bis-acrylamide using a redox initiation (potassium persulfate / ascorbic acid) system

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1. Introduction

Hydrogels are polymers in three-dimensional network arrangement, which could absorb and retain large amounts of water. In the polymeric network hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure [1]. Polymer hydrogels have been proposed for many applications such as the controlled delivery of medicinal drugs, artificial muscles, sensors systems and contact lenses, and they have potential applications in structural materials. But their applications are limited due to their poor mechanical properties. To produce hydrogels with high mechanical strength, many approaches have been tried: (1) cross-linking by using special co-monomers or altering their composition [2,3], changing the type and concentration of cross-linking agent [4,5], and optimizing polymerization conditions [6,7]; (2) introducing interpenetrating polymer networks (IPN) into hydrogels [8–12]; (3) synthesizing organic/inorganic nanocomposite hydrogels [13–15]; (4) adopting the method of material enforcement [16,17].

The kinetic of cross-linking reactions is an attractive area for a large number of investigations to obtain better understanding of the cure behaviour and mechanism of macroscopic gelation, as well as for controlling the production process and final performance of systems. A variety of experimental techniques have been employed to study the kinetics of cross-linking reactions. The most popular techniques are Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance ¹³CNMR, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). Dynamic rheology is a powerful tool to monitor crosslinking and microstructural changes in a material, as it allows properties to be probed in at-rest conditions without disruption of the microstructure. The viscoelastic behaviour of polymer gels near the sol–gel transition have been studied experimentally and theoretically [18].

The main emphasis of these studies was to find the relationship between linear visco-elastic properties and the structure of gels at the gel point. The gel point is usually defined as the time or the degree of reaction at which the solution no longer remains liquid. Originally qualitative rheological considerations were used to define the gel point. The gel point often was determined visually when no flow of the system was observed upon tilting the reaction vessel. The experimental determination and predication of gelation is important for the processing of cross-linking polymers, whereas the criticality of the phenomenon and the universality of the properties at the gelation threshold make gelation interesting from a fundamental point of view. In a gelation process, the sol-gel transition [19–21] point, such as a particular temperature or a concentration is of primary importance in characterizing the network formation by either a chemical or a physical gelation process.

Thus, the formation of polymer gels can be monitored from the time evolution of viscoelastic material functions at the gel point, where the entire network process can be divided into two parts separated by the gel point.

The aim of this work is to monitor the gelation process in real time during the cross-linking copolymerization of acrylamide (AAm) with N,N'-methylene-bis-acrylamide (Bis), by dynamic and static procedures. *In situ* polymerization processes were carried out at two different onset initiator / accelerator ratios for a given Bis content.

2. Experimental

2.1. Materials

Acrylamide (Merck, Darmstadt, Germany) (AAm) as monomer, N,N'-methylene-bis-acrylamide (Sigma, St.

Louis, US) (Bis) as crosslinker, potassium peroxydisulphate (Merck, Darmstadt, Germany) (KPS) as initiator, ascorbic acid (Sigma, St. Louis, US)(AAsc) as activator, were analytical reagent grade and used as received.

2.2. Crosslinking copolymerization

The polyacrylamide gel was prepared by redox solution copolymerization of AAm and Bis at a concentration of monomers of 6 wt % in distilled water, for two onset weight ratios of initiator/accelerator, noted as 1(7/1) and 2 (1/7). The reaction was conducted at the temperature of 22 °C.

Typical method for the polymerization is described as follows: acrylamide (AAm) and N,N'-methylene-bis-acrylamide (Bis) were dissolved in distilled water. Potassium peroxydisulphate (KPS) and ascorbic acid (AAsc) solutions were added to the monomers solution mixture, respectively. The preparation of the mixture for the further gel was done just before the measurements and it took only 30 s. The feed composition of 10 mL stock solution in moles is shown in Table 1.

Table 1. Synthesis of polyacrylamide hydrogel.

Synthesis	Variant 1 7/1	Variant 2 1/7
Feed composition	KPS/AAsc	KPS/AAsc
AAm / Bis Feeding molar ratio	4.22/0.0065	4.22/0.0065
AAm, Mol $\times 10^{-3}$	8.4	8.4
Bis, Mol $\times 10^{-6}$	13	13
KPS, Mol	4×10^{-5}	5.7×10^{-6}
AAsc, Mol	5.7×10^{-6}	4×10^{-5}
Water, Mol	0.37	0.37

2.3. In situ dynamic and static gelation

Rheological experiments were carried out using a Bohlin CVO rheometer equipped with a Peltier device for temperature control. The measurements were performed by using parallel-plate geometry. Both plates are from stainless steel, the upper plate having the radius of 30 mm. The upper plate was set at the separation distance of 500 μm . 2 mL of stock solution of the reaction mixture was poured on the lower plate of rheometer for each determination.

The gelation kinetic determination was realized at 22 °C, a frequency (ν) of 0.1 Hz and shear stress (σ) of 0.1 Pa to ensure a linear regime of oscillatory deformation. The macrostructure of the obtained gel was not damaged after the different rheological tests.

Monitoring the gelation process *in situ* allows to minimize the sources of error, the elastic and viscous properties of the prepared gels being determined during the measurements [22-23]. To obtain reproducible rheological data for hydrogels below the standard 10%

error, each experiment was three times repeated for the final conclusions.

In situ static gelation was followed by measuring temperature, pH and conductivity on pH/Conductivity/TDS/°C/°F Meter 510 Series Oakton Instruments. The determination was performed during gelation process onto 10 mL solution (with mentioned composition given in Table 1), at 22 °C, the electrodes being totally immersed in solution.

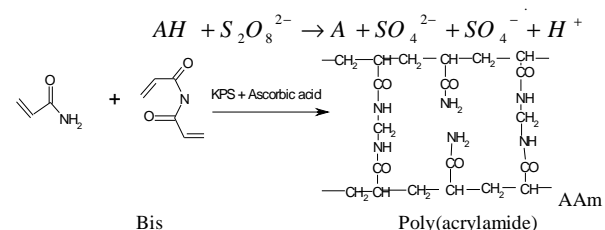
For all experiments average and standard deviations were calculated from a minimum of three different measurements.

3. Results and discussion

Cross-linked polyacrylamide gels are formed from the polymerization of acrylamide monomer in the presence of smaller amounts of N,N'-methylene-bis-acrylamide. N,N'-methylene-bis-acrylamide is essentially two acrylamide molecules linked by a methylene group and is used as a cross-linking agent. Acrylamide monomer is polymerized in a head-to-tail fashion into long chains, and occasionally a bis-acrylamide molecule is built into the growing chain, thus introducing a second site for chain extension. In this way, long chains of acrylamide are built up, being cross-linked by the introduction of the occasional bis-acrylamide molecule into the growing chain.

The polymerization of acrylamide is an example of free-radical catalysis, and is initiated by the addition of potassium peroxydisulphate and ascorbic acid. The reduction of peroxydisulphate by ascorbic acid follows a chain mechanism in which ascorbic acid is oxidized to dehydroascorbic acid. It was established already that the ascorbate ion (mono) in aqueous solution is responsible for the high reducing action [24]. The proposed mechanism by Mushran [25] of the reduction of peroxydisulphate by ascorbic acid involves the formation of ascorbate radicals

(AH^-) in the aqueous polymerization initiated by the redox system $\text{K}_2\text{S}_2\text{O}_8$ / ascorbic acid, the starting reaction step between $\text{S}_2\text{O}_8^{2-}$ and the monomer forms a complex, which breaks down liberating the initiating radical. Under such conditions, ascorbate (AH^-) and sulphate ion radicals ($\text{SO}_4^{\cdot -}$) are the active species which initiate the polymerization. The presence of molecular oxygen in the reaction system, instead of inhibiting, autocatalyses the polymerization rate.



The elastic (G') and viscous (G'') modules, were monitored during the *in situ* polymerization of acrylamide

with *N, N'*-methylene-bisacrylamide in the presence of the redox initiation system potassium persulfate/ascorbic acid.

In order to appreciate the sol – gel transitions, the system was previously evaluated in our studies [26-28], according to the Winter – Chambon criterion [29-30] that identifies the gel point as being the instant in time when the moduli scale are an identical fashion with frequency. The above relationship implies that the loss tangent, $\tan \delta = G''/G'$, is independent of frequency at the gel point. The gelation point was estimated as the point at which the slope approaches zero [31].

The gelation process evolution at 22 °C as a function of the weight ratio of initiator/activator (variants 1,2 in Table 1) is illustrated in Figs. 1 and 2.

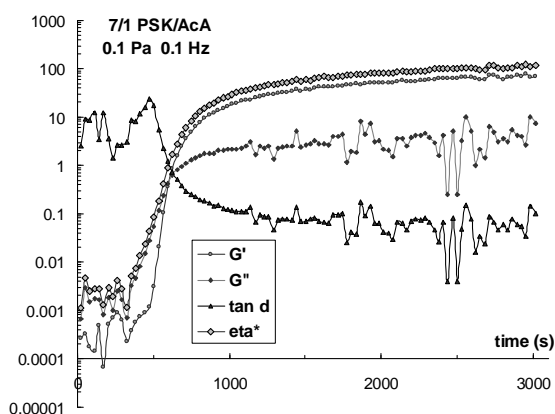


Fig. 1. Variation of elastic module G' , viscous module G'' , loss tangent $\tan \delta$, viscosity (η^*) in time, for KPS/Aasc weight ratio = 7/1, $\nu = 0.1$ Hz, $\sigma = 0.1$ Pa and 22 °C onset temperature.

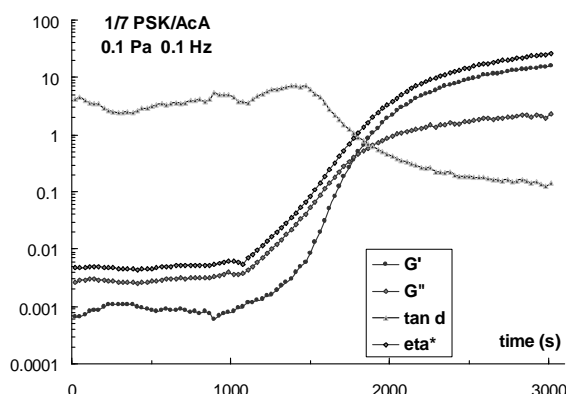


Fig. 2. Variation of elastic module G' , viscous module G'' , loss tangent $\tan \delta$, viscosity (η^*) in time, for KPS/Aasc weight ratio = 1/7, $\nu = 0.1$ Hz, $\sigma = 0.1$ Pa and 22 °C onset temperature.

It is underlined the influence of the weight ratio between initiator and accelerator on the gelation process. Thus, 7/1 KPS/Aasc weight ratio (variant 1 in Table 1)

favors the gel point appearance at smaller time (860 seconds approximately) while the reverse KPS/AAsc weight ratio (variant 2 in Table 1) has a negative effect on the gel point appearance, lead to the greater time (about 1900 seconds); these data are agreed with the literature information [32], on the delay of reaction determined by the increase of ascorbic acid concentration in the redox pair initiation system. Thus, at high concentration of ascorbic acid, the rate of free radicals-forming and their concentration in the reaction medium decrease, because of the increase of hydrogen ions concentration. At small concentration of ascorbic acid, hydrogen ions concentration doesn't considerably vary, but the free radicals' formation takes place with a constant rate.

Taking into account the ratio G''/G' , it is found that 7/1 KPS/Aasc weight ratio lead to a hydrogel with higher elastic properties ($G''/G' = 3.797$) agreed with the subsequent application demands, while the other variant of the initiation components lead to a ratio $G''/G' = 13.75$, for a hydrogel with lower elasticity.

The monitoring of temperature as well as pH and conductivity variation during *in situ* static gelation of AAm with Bis is illustrated in Fig. 3. It is observed that the temperature as well as the conductivity increase during gelation process whereas pH passes to acidic values owing to dehydroascorbic acid presence. Temperature increase is explained by the exothermic reaction during polymerization process. The initiation system offers the needed carriers in order to obtain a system where conductance occurs, the charged particles acting as current carriers. As it is well known the conductivity has a substantial dependence on temperature, in case of polymers with increasing temperature the conductivity increases according to an exponential law [33]. Normally, the system fulfills at gelation owing to increase of the temperature, and the conductivity is growing too.

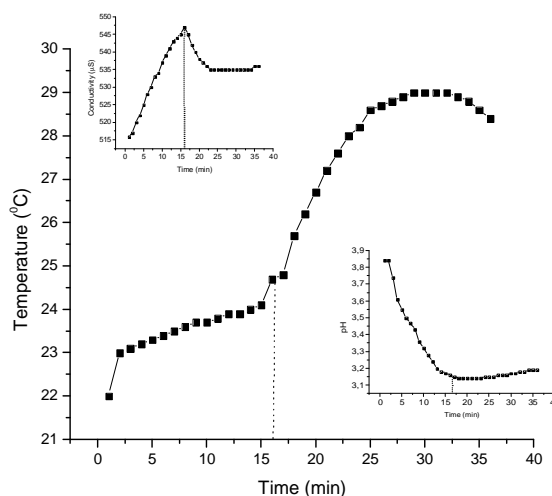


Fig. 3. Monitoring of temperature, pH and conductivity in the static gelation process of AAm with Bis for 7/1 KPS/AAsc weight ratio, at 22 °C onset initial temperature.

The maximum of the conductivity as well of temperature during gelation process was registered around of 960 seconds polymerization time, which determined us to ascribe this value as being the *gelation point* for the studied system.

4. Conclusions

Hydrogels based on acrylamide were prepared by simultaneous crosslinking polymerization with a bifunctional cross-linker N,N'-methylene-bis-acrylamide and a KPS/Aasc redox initiating system at two onset weight ratio. In real-time the gelation process is monitored by following the viscoelastic parameters throughout the in situ cross-linking (in the rheometer) and by temperature, pH and conductivity determination.

It was found the optimal weight ratio of the redox initiators pair from the viewpoint of elastic properties of the obtained hydrogel is 7/1 potassium persulfate /ascorbic acid.

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