11.6 Radiation Polymerization and Crosslinking of \(N\)-isopropylacrylamide in Aqueous Solution and in Solid State

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Abstract: Poly(N-isopropylacrylamide) hydrogels were synthesized by radiation induced simultaneous polymerization and crosslinking. Aqueous monomer solutions and pure monomer, without crosslinker, were irradiated in nitrogen atmosphere at a \(^{60}\)Co gamma source. The conversion from monomer to polymer and crosslinked gel was investigated as a function of temperature and monomer concentration. The swelling behavior of the gels showed clear dependence on the synthesis conditions.

INTRODUCTION

Poly(N-isopropylacrylamide) (PNIPAAm) shows a typical thermal reversibility of phase transition in aqueous solutions. That is, it precipitates from solution above a critical temperature called the lower critical solution temperature (LCST) and dissolves below this temperature. When it is crosslinked, the obtained hydrogel collapses above LCST, while it swells and expands below LCST (Hirokawa and Tanaka, 1984). The poly(NIPAAm) hydrogel was used as a model system for thermally induced volume phase transition of gels (Otake \textit{et al.}, 1989) and was proposed for various biomedical applications (Hoffman, 1987).

Crosslinking of linear polymers or polymerization and crosslinking of monomers either by chemical means or gamma radiation has been used to produce these gels. Gehrke (1993) reviewed the study of the variables which can influence the properties of the chemically crosslinked poly(NIPAAm) gels. Monomer purity, reaction temperature, initiator type and concentration and total reaction time all had significant effects on the swelling properties of the gels.

We are interested in the synthesis of PNIPAAm hydrogels by radiation polymerization and crosslinking (Nagaoka \textit{et al.}, 1993). Here we describe the synthesis of this hydrogel by radiation polymerization and crosslinking in aqueous monomer solution and in pure monomer. Since there is no crosslinker in these systems, we refer to such gels as "self-bridged" gels. The mechanism of the gel formation is different in the aqueous solution from the crosslinking in the pure monomer. In the case of the aqueous solution, the monomer radicals are mainly formed by the indirect effect of radiation based on the reaction of the products of water radiolysis with the monomer. When bulk monomer is irradiated, the radicals are formed by the direct radiation effect. The difference in the radical formation and the mechanism of polymerization and crosslinking in these different systems, depending also on irradiation temperature and dose, are responsible for the different microstructures of the gels that results in different swelling behavior.

The results described here are part of a systematic study of the mechanism of crosslinking and swelling behavior of self-bridged poly(NIPAAm) gels, that started recently in our laboratory.
EXPERIMENTAL

In the work reported here, the synthesis was done by irradiating a 10 % w/w aqueous solution of NIPAAm (Eastman Kodak), in a glass tube with 3 mm inner diameter. All irradiations were carried out under nitrogen atmosphere at 25 °C with a $^{60}$Co gamma source with doses up to 1000 kGy at dose rate of 10 kGy/h. The pure monomer was also irradiated under the above mentioned conditions, at several different temperatures in the range from 0 to 80 °C (The melting point of N-isopropylacrylamide is 65 °C).

After the polymerization the gels were removed from the tubes and washed in distilled-deionized water for three weeks. The gel fraction was measured after Soxhlet-type extraction in ethanol for 24 h and drying the extracted gel in vacuum to constant weight. The swelling is determined gravimetrically after 24 h equilibration of gels in water at fixed temperature, then calculated as a weight ratio of the swollen sample to the dry one.

RESULTS AND DISCUSSION

When the monomer is irradiated in aqueous solution, monomer radicals are mostly generated by the indirect effect based on the reactions of the products of water radiolysis with the monomer [Chapiro, 1962]. Some of these intermediates will form monomer radicals, while others undergo recombination or other reactions. Radicals are also generated by the direct radiation effect, but to a much lesser extent. After these initial processes, monomer radicals combine and propagate to form a linear or slightly branched, but soluble polymer (sol fraction) until the dose reaches the gel point. Once the polymer is formed, it is itself radiolyzed, since the primary $H^+$ and $OH^-$ radicals are very efficient for abstracting hydrogen from the polymer molecule. These polymer free radicals also contribute to chain initiation and cross-link formation. Once the gel point is reached, the amount of the gel grows rapidly (Fig. 1).

![Graph showing gel formation during irradiation of different concentrations of NIPAAm](image)

Fig. 1. Gel formation during irradiation of: (O) 5 w/w %; (□) 10 w/w %; and (▲) 20 w/w % aqueous solutions of NIPAAm.
PNIPAAm gels can also be obtained by radiation polymerization and cross-linking of the pure monomer. In this case, the radicals are formed only by the direct radiation effect, and they mobility is low, thus the gel doses are much higher than in the case of polymerization in aqueous solutions (Fig. 2). For example, the gel dose for pure monomer is about 13 kGy at 25 °C, as compared to 71 Gy in 10 w/w% aqueous solution, at the same temperature. The radiolysis of the polymer also occurs, and these polymer radicals will to some extent contribute to the further polymerization and crosslinking. With the increase in temperature the mobility of the molecules increase and the gel dose becomes as low as 1.5 kGy near the melting temperature at 60 °C, and only about 8 Gy when the monomer is irradiated in the molten state at 70 °C.

![Figure 2](image-url)

**Fig. 2.** Gel formation in the irradiated pure monomer at the following temperatures: (O) 0; (□) 25; (△) 60; (●) 70, and (■) 80 °C.

The most important property of PNIPAAm hydrogels is their temperature-induced inverse volume phase transition in aqueous solutions. The volume phase transition of the gels is similar to the coil-globule transition of the polymer chains [Dusek and Patterson, 1968], and the thermoshrinking behavior is caused by a critical balance of hydrophobic and hydrophilic groups at the polymer chain [Taylor and Cerankowski, 1975; Otake et al, 1984]. At low temperatures a strong hydrogen bonding between these hydrophilic groups and the surrounding water will cause the formation of a highly organized water layer around the polymer chains [Shild and Tirrell, 1990]. This enables the good solubility of the polymer chains, as well as the swelling of the gels. With increasing temperature the hydrogen bonding weakens, leading to a reduction in the structuring of water around the hydrophobic groups. As this structured water is released, the interactions between hydrophobic side groups of the polymer increase. Above the LCST, which is around 32 °C for PNIPAAm, these hydrophobic interactions become dominant, and the refolding of the polymer chains will cause the shrinking of the gel.

The swelling behavior of the self-bridged PNIPAAm gels is illustrated on Figs 3 and 4. Figure 3 shows the swelling of the gels synthesized from aqueous solutions, while on Fig. 4, the swelling of gels obtained by irradiation of the pure monomer, can be seen. All gels show high swelling at temperatures below 32 °C, and shrinking above this temperature. Besides this expected temperature dependent swelling of PNIPAAm gels, Fig. 3 shows an interesting effect of absorbed dose on the swelling of the gels that shows a difference between PNIPAAm gels synthesized by chemical crosslinking method and by radiation of a pure monomeric system. When gels are crosslinked chemically, usually the lower the crosslinking percentage, the higher the swelling ability of the gels. Above the critical temperature, however, all gels shrink to a similar volume, independently from the crosslinking percentage. In our case, when aqueous solutions of the
monomer are irradiated, the gels synthesized at high doses (high crosslinking percentage), collapse to a much smaller volume than the gels synthesized at low doses. Besides, the change in the swelling with the increase in temperature becomes continuous. This effect reflects the microscopical structure of the gel network, that changes with dose [Nagaoka et al, 1993].

![Fig. 3](image1.png)

**Fig. 3.** Swelling characteristics of PNIPAAm gels crosslinked during the radiation induced polymerization of a 10 w/w % aqueous solution of NIPAAm. The solutions were irradiated at the following doses: (O) 20; (▲) 50; ( ■ ) 160; and ( ● ) 320 kGy.

![Fig. 4](image2.png)

**Fig. 4.** Swelling characteristics of PNIPAAm gels synthesized by radiation polymerization and crosslinking of a pure monomer at 80 °C and at the following doses: (O) 10; (□) 30; (△) 50, and (●) 200 kGy.
At the start of the polymerization, the network consists only of polymer chains forming giant molecules with branches and entanglements and with very few real crosslinks. We call this structure "tree" structure. When the gel swells below LCST, the polymer chains tend to distance from each other. The swollen coils will exclude one another from the volume defined by their radius of gyration. With increasing dose, the fraction of real network ("ladder" structure) would increase. The chains are then forced together by their crosslink points and will overlap somewhat. The higher the fraction of the ladder over the tree structure, the lower the flexibility of the chains, and the gel swells less. At still higher doses, a radiation-induced degradation of the previously formed ladder structure will take place. This degradation will lead to a network structure which we call "broken ladder". This change affects only the shrinking of the gel, because this increased flexibility of chains near the braking point would facilitate the hydrophobic interactions between the polymer chains above the volume phase transition temperature. Besides, in the broken ladder, the pores of the gel became bigger. As a result, more water could be expelled from the network, and the gel collapses to a smaller volume.

On the other hand, when the gels are obtained by irradiating a pure monomeric system above the melting temperature, all gels synthesized with doses between 30 and 200 kGy, have similar swelling behavior (Fig. 4). This fact indicates, that no major changes in the microstructure of these gels occurs under these irradiation conditions. The changes in the crystallinity and the microstructure of these gels is presently under investigation.

REFERENCES