Synthesis of Thermosensitive Poly(N-isopropylacrylamide) Hydrogel and its Copolymer by Gamma Irradiation

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Abstract

The linear polymer of N-isopropylacrylamide (NIPA) formed by irradiating dilute aqueous solution is found to be a thermosensitive polymer with lower critical solution temperature (LCST) of ~ 33 °C. Gamma radiation induced polymerization studies showed that the reaction of $^1$H / $^1$OH / eaq radicals with NIPA result in nearly equal yield of gel fraction and the hydrogel is observed to have very little swelling below pH 3 and above pH 10. NIPA has also been copolymerized by chemical crosslinking method with ethylene glycol methacrylate acid phosphate (EGMP) for extraction of lanthanide ions from aqueous solution utilizing the difference in binding characteristic of the metal ions with the copolymer below and above LCST.

Introduction

The gel synthesized from NIPA monomer is a well known thermosensitive gel which shows a discontinuous volume phase transition in response to temperature changes (Panda et al., 2000). The crosslinked gel of NIPA undergoes a reversible volume transition at ~ 34 °C. Below this temperature the polymer dissolves in water and chains exist in an extended state. Above 34 °C, it acquires a dehydrated coiled state expelling bonded water and polymer precipitates out from solution. When extractant molecules are copolymerized in a polymer network, the mobility of extractant molecules is limited and the complex formation between metal ion and extractant molecules may be affected by the conformation of polymer network (Kenji and Yoshio, 2000).

Experimental

The linear polymer of NIPA was synthesized by irradiating aqueous solution of NIPA (4 wt%) in a gamma chamber to a total gamma dose of 8 kGy. The crosslinked polymer of NIPA was synthesized by irradiating aqueous solution of NIPA (10 wt %) for different times in a gamma chamber (dose = 0.48 kGy/hr) under experimental conditions such that only $^1$H/ OH / eaq radicals react with the monomer. The % gel formed was estimated from the weight ratio of water insoluble fraction to the feed monomer. The copolymer of NIPA and EGMP
were prepared by free radical polymerization in dimethyl formamide (DMF). N,N'-methylene bis(acrylamide) was used as a cross linker. The polymerization was carried out at 60 °C for 24 hours.

**Results and Discussion**

Gamma radiolysis of 4 wt% aqueous solution of NIPA was found to give very good yield of linear polymer after irradiating with 8 kGy dose (dose rate = 8 kGy/hr). The aqueous solution of linear polymer of NIPA (10.25 mg/ml) was observed to be a temperature sensitive material. The LCST of linear polymer was determined by laser light scattering method. The diameter of polymer molecules decreased from 290 nm (25 °C) to 20 nm (35 °C) having a transition temperature of ~33 °C (Fig 1).

At 25 °C, strong hydrogen bonding hydrophilic groups on the polymer chains with surrounding water molecules makes it water-soluble. However at higher temperature the hydrogen bonding weakens hydrophobic interactions result in the folding of the polymer chains and the polymer precipitates out from the solution. 10 wt% aqueous solution of NIPA was gamma irradiated (dose rate = 0.48 kGy/hr) for different periods of time, under conditions such that only one of the radiolytic species (‘H/ ‘OH/e\textsubscript{aq} \-) react with NIPA. The gel % was observed to increase with gamma dose (Fig 2), although the yield of the gel formed on reaction with e\textsubscript{aq} \- was low, but the yields have not followed the G values of primary radiolytic species of water radiolysis. tert-Butyl alcohol radical contribution may explain the high yield of gel formed on reaction with e\textsubscript{aq} \- and H \- atoms. The swelling ratio of NIPA hydrogel was determined in aqueous solution of different pH. It is clear from Fig 3 that swelling ratio remained same in the pH range of 3 - 10. Both at lower and higher pH,
An appreciable decrease in swelling ratio was observed. This may be due to hydrolysis of amide group of the polymer in highly alkaline and acidic solutions. Copolymer of monomer such as NIPA and EGMP were prepared by free radical polymerization in DMF by both chemical and radiation means. N,N'-methylene bis (acrylamide) was used as a crosslinker. For chemical polymerization, benzoyl peroxide was used as an initiator. The gel synthesized by gamma irradiation (10 kGy, dose rate = 0.48 kGy/hr) was found to be thermo insensitive and its swelling ratio was independent of temperature. The gel synthesized by chemical polymerization shows thermosensitivity in water and have been used to extract lanthanide elements into the gels from an aqueous solution containing 500 mg of metals/dm³. The initial pH of aqueous solution were adjusted over the range of 0.5 to 3.5 by adding HNO₃.

In preliminary experiments, extraction of Europium, Eu(III) was 81% and 17% at 50 °C and 28 °C respectively. 0.05g of dry gel was used for the experiment. Further experiments are in progress to optimize experimental conditions wherein radiation polymerize gel retain their thermosensitivity.

**Conclusions**

The % of PNIPA gel formed increased with gamma dose and reached a saturation of ~ 90% at a gamma dose of 0.22 kGy. The yield and the nature of the polymer depend on total gamma dose, dose rate and monomer concentration, but independent of initiating radical. The NIPA and EGMP copolymer gel obtained by conventional method can be beneficially used for the extraction of the lanthanide elements from an aqueous solution.

**References**


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**Fig. 3 Swelling ratio of NIPA hydrogel kept in aqueous solution of different pH.**
About the authors …

**Dr Anjali Acharya** obtained her M.Sc. and Ph.D. in Chemistry from Utkal University. She joined as a Research Associate in Radiochemistry Division, under CSIR-scheme in 1997. She was awarded Dr K.S. Krishnan Research Associateship in 2000 and worked on synthesis, characterization and applications of stimuli sensitive hydrogels in RTDS. She has 25 publications to her credit.

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