Supersorbent, Thermoresponsive P (NIPA-co-AA) Gels Preparation and Characterization--1

S. BASHIR, Z. IQBAL, B. AHMAD, M.NISAR, S. ZAKIR
Department of Pharmacy,
University of Peshawar, Peshawar, N.W.F.P. Pakistan

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Summary:We have been interested in the synthesis of hydrogels with fast swelling kinetics and supersorbent properties. So copolymer of NIPA and AA was prepared using bis as crosslinker and TEMED as activator. The copolymer was characterized by determining the swelling ratio in aqueous solution as function of time, ionic strength, temperature, concentration of monomer and crosslinker and best concentration for them is reported. The resultant chemically crosslinked networks show levels of swellability in water significantly higher than those previously reported for such copolymer using other crosslinkers. Also equilibrium swelling and deswelling was obtained after 8 hrs.

Introduction

Recently thermal sensitive N-isopropylacrylamide (NIPA) gels have attracted great scientific interest (as the stimulant – responsive behavior occurs in aqueous solutions, so becoming increasingly attractive for biotechnology and medicines) [1-5] for their technological potential in a variety of applications including drug delivery [6-7]. Some applications of thermosensitive gel require the incorporation of fixed ionizable groups in the polymer network (copolymerization). In the past NIPA was copolymerized with sodium acrylate, Vinyl pyrrolidone (VP), 2-Hydroxy ethylmethacrylate (HEMA) and many others [8-13]. Attainment of increased swellibility at ambient temperatures in these copolymer hydrogels is some times offset by either inconveniently high or completely absent values of lower critical swelling temperature Tc and did not provide optimum balance between swellability and Tc. Moreover hydrogels are not usually perfect biocompatible and cause undesirable body reactions. Further improvement in biocompatability, mechanical strength and durability will be critical in wider applications of hydrogel in biomedical and pharmaceutical areas. Enhancing these properties will make hydrogel acceptable for many applications to come. We prepared Poly (NIPA-co-AA) gels with N, N, methylene bisacrylamide (Bis), (frequently used due to its water

solubility coupled with the normal use of water as reaction medium) [14], characterize it and will use it for concentrating dilute solution of soluble macromolecules and for drug control release because strong gels with rapid swelling and deswelling response to temperature change can increase the transport rate of macromolecules

Results and Discussion

The conversion of monomers in to P(NIPA-co-AA) with 2.5 mol% Bis as crosslinker was more than 96 % in the present case. Recently [15] the same copolymer was prepared using Glyoxal bisdiallyl-acetal (GLY) as crosslinker with conversion factor of 90 %. The swelling and deswelling behavior of the polymer was first characterized using aqueous solution without model proteins. Figl, 2 shows the swelling and deswelling ratio trend with time in comparison to PVP (will be used as model protein latter) prepared using different crosslinkers [16]. The rate of water uptake is faster for P (NIPA-co-AA) than PVP in water (65 % is achieved within 45 minutes) and the process is practically completed after 120 minutes. This shows that P (NIPA-co-AA) can be used for concentrating dilute solution of PVP and thus proteins. In the past hydrogels of NIPA with other comonomers and crosslinkers have been proposed for concentrating/separating vaccines, yeast, bacteria and macromolecules [17-19]. The polymer absorbed more water due to its hydrophillicity while its structure will enable a complete exclusion of macromolecules (model proteins) due to size/shape effects. After 2 hours the hydrogel absorb water slowly and attained saturation after 8 hours. In case of GLY crosslinker for the same copolymer, the saturation time is more i.e. 26-hrs [15], which is attributed to the formation of skin layer on the xerogel surface restricting the creation of macroporous channels in the polymer network. Our results are in agreement with the theoretical equation of Tanaka and others [11,20].

Similarly in the 1st 30 minutes, 30% wt of water is lost by the hydrogel at 328K in the deswelling process, however as a whole it took the same time as swelling one i.e. 8 hrs. Heat transfer in water medium is homogenous initially and thus quick deswelling but at latter stage dense polymer skin layer formation at the surface leads to slow deswelling.

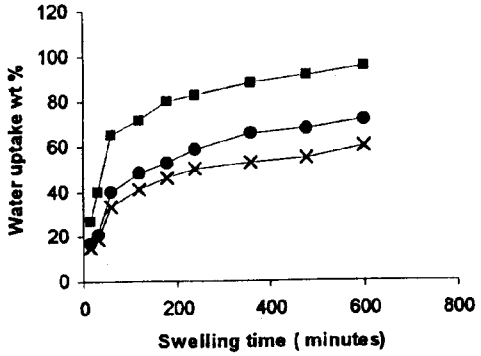

Fig. 1: Swelling behaviour variation with time of P(NIPA-co-AA) gel (■), PVP-HEMA(●), PVP-DVB(X) in water.

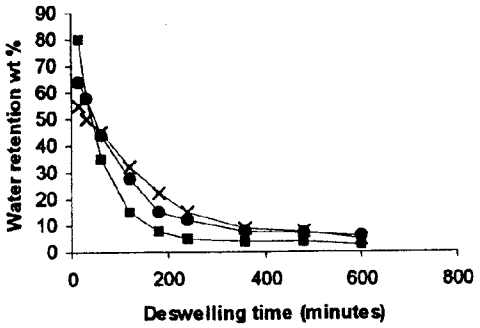

Fig. 2: Deswelling behavior variation with time of P(NIPA-co-AA) gel (■), PVP-HEMA (●), PVP-DVB (x) in water.

The effect of ionic strength and temperature on the swelling ratio of copolymer was also investigated. The swelling of super absorbent polymer is enhanced due to electrostatic repulsion if the three-dimensional polymeric network contains ionizable groups. However by the addition of electrolyte solution, these electrostatic forces are checked and the swelling is reduced [21]. With the addition of 0.2 M NaCl salt, no substantial decrease in swelling ratio was observed. This finding is further supported by the effect of temperature on the swelling ratio with 0.2-M salt solution (fig.3). The mass of the polymer in the gel preparation was 0.4 % of M_1 so the mass of water absorbed per unit mass of dry polymer was 12 times larger than the swelling ratio. Gels containing even 5 % ionizable monomer did not collapse at 50 °C. Here the polymer is collapsed at around 32°C and small decrease in the

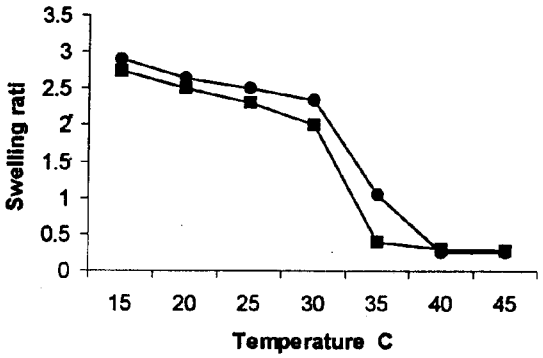

Fig. 3: Effect of temperature on swelling ratio in water (●) and 0.2 % NaCl (■) Process time 45 minutes.

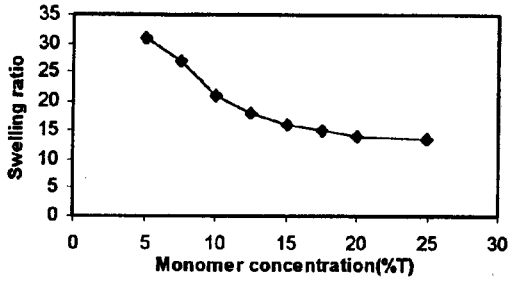

Fig. 4: Swelling ratio variation of P(NIPA-co-AA) gel with monomer concentration at 20°C.

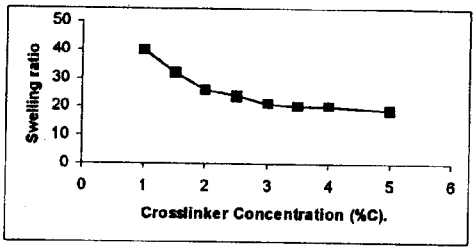

Fig. 5: Swelling variation of P(NIPA-co-AA) gel with crosslinker Concentration at 20°C.

swelling ratio showing less than 5 % ionizable monomers. It was reported [22] that gels having 4.7% ionizable monomer did not collapse at 42 °C and with 18.8% even at 80 °C [2]. On the other hand at 60 °C for spherical NIPA gels having 18.8% ionizable monomer, discontinuous volume phase transition was observed [23] however this discrepancy was solved by our recent study (paper submitted) by taking into consideration the effect of pH.

The effect of monomer concentration and crosslinker

The structure of the gel is determined by the chemical properties of its components, concentration and polymerization conditions. Gels are swollen networks, which allow small molecules to move freely and exclude large molecules due to pore size, and the pore size is decided by the concentration of the monomer or crosslinker. The experimental results and their effect on swelling are summarized in fig 4,5. The extent of swelling decreased with increasing monomer concentration and amount of crosslinker and approached an asymptote at 4 %C and 15 %T, thus showing structural properties of network. Different scientists [24-26] concluded different concentrations of monomer and crosslinker. However our results are reproducible and closer to that of Tanaka et.al. [27]. At low concentration, ring formation (cyclization) is favored and turbidity was observed for copolymer gel of P (NIPA-co-AA) at monomer concentration above 15 %T or percentage crosslinker above 4 %C.

Experimental

Material

The monomers N-isopropylacrylamide (NIPA) from Eastman Kodak Company, NY, was recrystalized in n-hexane before use to remove an initiator, P-methoxy phenol and Acrylic acid (AA) from Sigma Chemical Co was purified described elsewhere [14]. N, N methylene bisacrylamide (BIS), the crosslinker from Fluka Chemical Co was recrystalized from chloroform-petroleum ether mixture and dried in vacuum oven for 24 hours. Ammonium persulphate (APS) the initiator, N, N, N, N-tetramethylenediamine (TEMED), the activator, both from Aldrich Chemical Co. were used as received and deionized water from Millipore water purification system.

Copolymerization

3.0 g of NIPA, 12.5 mol % of AA corresponding to NIPA, 2.5 mol % bis crosslinker, 0.0512 g of initiator and 20 ml of deionized water were mixed, stirred well and degassed with N_2 for 20 minutes in ice cold water. During this 3 mol % TEMED with respect to NIPA + AA, was added as an activator to the mixture and then medium size Pyrex test tubes were filled, tightly sealed and copolymerized at 253K for 28 hours. The copolymer was cut in to disc of 3 mm each and put in to deionized water for 72 hours to remove unreacted

monomers if any. The samples were dried in vacuum oven and conversion ratio was calculated using

$$C.R = Mo/M$$

Mo is the weight of the monomer + crosslinker + initiator and M the xerogel and the swelling and deswelling was measured gravimetrically using the formula:

$$W = 100(m_1-m_2)/m_1$$

W is water uptake capability, m_1 weight of hydrogel at equilibrium and m_2 weight of xerogel

$$w_1 = 100(m_t-m_2)/m_1$$

here w_1 is water retention, m_t is weight of hydrogel at certain time, m_2 that of xerogel and m_1 the hydrogel at equilibrium condition.

%T = mass of all monomers in gm/volume of solution in cm^3

%C = 100(mass of crosslinker/mass of all monomers).

Conclusions

N, N methylene bis acrylamide give high conversion rate (96 %) and thus a better crosslinker so for reported in the literature for the preparation of P(NIPA-co-AA) copolymer. Desired pore size gel can be prepared by changing the concentration of the monomer and crosslinker. Monomer concentration above 15 %T and crosslinker above 4 %C are not advisable due to turbidity for the preparation of P(NIPA-co-AA) and finally gels whose swelling are sensitive to temperature or concentration of the surrounding medium can be exploited to concentrate dilute aqueous solutions of macromolecular solute in gel extraction process.

Acknowledgements

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