

**SWELLING BEHAVIOR OF CHEMICALLY
CROSSLINKED PH-AND TEMPERATURE-SENSITIVE
(N-ISOPROPYLACRYLAMIDE-CO- 1-VINYL-2-
PYRROLIDONE) BASED ON NEW CROSSLINKER**

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ABSTRACT

In this contribution novel dual pH-and temperature- sensitive polymer matrices based on N-isopropylacrylamide have been developed. The hydrogels were prepared by bulk radical polymerization of N-isopropylacrylamide and 1-vinyl-2-pyrrolidinone in appropriate amounts of double distilled water. These copolymers were crosslinked using different mol % of traditional N,N-methylene bis acrylamide (MBA) and the new synthesized N,N,N- tri acrylamido melamine (MAAm) crosslinker. The resultant xerogels were characterized by extracting the soluble fractions and measuring the equilibrium water content. Lower critical solution transition temperatures (LCST) were measured by DSC. By altering the feed ratio, hydrogels were synthesized to have lower critical solution temperatures (LCST) around 40 °C. This ability to shift the phase transition temperature of the gels provides excellent flexibility in tailoring transitions for specific uses. The influence of environmental conditions such as temperature and pH on the swelling behavior of these polymeric gels was investigated. The swelling behaviors of the resulting gels show pH sensitivity. The prepared MAAm type NIPAAm/VP hydrogels exhibited a more rapid deswelling rate than MBA type NIPAAm/VP hydrogels in ultra pure water in response to abrupt changes from 20 °C to 50 °C.

Key words: Hydrogels, pH-and Temperature- sensitive gels, N-isopropylacrylamide, N,N,N- tri acrylamido melamine crosslinker.

INTRODUCTION

Hydrogels, by definition, are three-dimensional cross-linked polymeric networks that can imbibe large amounts of water [Hoffman (2002); Drury et al., (2003); DeRossi et al., (1991) & Dhara et al., (1999)]. These materials are generally classified into one of two categories based on their crosslinking chemistry [Hennink (2002)]. The first category entails physical gels which are defined as polymeric networks that are bound together via polymer chain entanglement and/or non-covalent interactions that exist between polymer chains [Hoffman (2002); DeRossi et al., (1991); Akiyoshi et al., (2000) & Collier et al., (2001)]. The attractive forces holding these networks together are typically based on hydrogen bonding, electrostatic or hydrophobic interactions and thus, the gels can be reversibly dissolved under certain conditions that would weaken these attractive forces. Many physical and chemical stimuli have been applied to induce various responses of the smart hydrogel systems. The physical stimuli include temperature, electric fields, solvent composition, light, pressure, sound and magnetic fields, while the chemical or biochemical stimuli include pH, ions and specific molecular recognition events [Hoffman (1997) & Bae (1997)]. Poly (N-isopropylacrylamide) (PNIPAAm) hydrogels are attracting more and more interest in biomedical applications because they undergo a sharp volume transition in water around 32–34°C, which is close to the body temperature [Tasdelen et al., (2005) & Zhang et al., (2004)]. Generally, in the case of temperature sensitive polymers, incorporation of a hydrophilic comonomer leads to an increase in LCST, whereas incorporation of a hydrophobic comonomer leads to a decrease of LCST [Eeckman et al., (2002) & Liu et al., (2004)]. Poly(1-vinyl-2-pyrrolidinone) (PVP) is one such hydrophilic hydrogel, which is also sensitive to changes in temperature, non-toxic in nature and is of particular interest to research for its affinity to water [Devine et al., (2003) & Devine et al., (2005)]. In the previous work [Atta et al., (2005)], a new method is proposed for introducing new crosslinkers to prepare pH- and temperature-sensitive hydrogels. The new crosslinkers are prepared by simple reaction of melamine with both methacryloyl- and acryloyl-chlorides to produce monomers with the same chemical structures as N-isopropyl acylamide (NIPAAm). In the present article, the prepared new crosslinker can be used to prepare novel dual temperature- and pH-sensitive poly(N- isopropylacrylamide-co- and 1-

vinyl-2-pyrrolidinone), NIPAAm/VP, hydrogels by chemical crosslinking with crosslinkers. Measurements of pH and temperature sensitivity of the prepared gels are another goal of the present study.

EXPERIMENTAL

Materials

Melamine and acryloyl chloride (AC) were supplied by (Aldrich, USA). Triethylamine (Aldrich, Germany), 1-methyl-2-pyrrolidone (NMP) (Aldrich, Germany), tetrahydrofuran THF, (Aldrich, Germany) and toluene (Aldrich, Germany), were used as received. 1-Vinyl -2-pyrrolidone (VP) and N-isopropyl acrylamide (NIPAAm) were supplied by Aldrich, USA. N,N-methylene bis acrylamide, MBA, (Aldrich, Germany) was used as crosslinker. The initiator, ammonium persulfate (APS), was supplied from Merck (Darmstadt, Germany). Double distilled water was used in hydrogel preparation and in swelling measurements. The experiments were carried out in a thermostatic water bath (Fryka, kaltechnik KB 300 Germany) equipped with both cooling and heating systems.

Synthesis and purification of N,N,N- tri acrylamido melamine crosslinker [Atta et al., (2005)].

Synthesis of crosslinked NIPAAm/VP copolymers

The crosslinked NIPAAm,VP copolymers were prepared by solution polymerization using water as solvent in the presence of APS (0.02 wt%) as initiator and the MAAm or MBA (1 wt%). The monomer ratios, ranging from 0.1 to 0.9 mol%, were used in the preparation of crosslinked NIPAAm/VP copolymers. The copolymerization reactions were performed in siliconized test tubes under N₂ atmosphere at 65 °C for 24 hr. The polymer rods were post-cured at 110 °C in air for 24 hr to ensure complete polymerization.

Characterization of crosslinked NIPAAm/VP copolymers

The sol fraction percentage (SF%) in the crosslinked xerogel discs was determined from the weight of the dried gel before and after water Soxhelt extraction. SF values are calculated according to the equation: $SF = (W_0 - W) 100 / W_0$; where W_0 and W are the weight of the discs before and after extraction, respectively. The dried discs were

subjected to swelling measurements at different pH and temperatures. The swelling lower critical transition temperatures (LCSTs), of the crosslinked NIPAAm/VP copolymers were measured using differential scanning calorimetry (DSC) (Du Pont 910 DSC).

For the swelling measurements, dried cylindrical discs with diameter 11mm and 5mm thickness were immersed in a solution of desired pH (2–12), ionic strength, I (0.1M) and temperature (10–50 °C).

Measurement of swelling parameters

The xerogel discs having dimensions (5mm)x(11mm) were swollen (after SF extraction) to equilibrium in different pH aqueous solutions at different temperatures (10–50 °C) on both heating and cooling. The swelling ratio (q) was obtained as: $q = W_h/W_x$; where W_h and W_x are the weights of hydrogel and xerogel, respectively. Equilibrium water content (EWC), volume fraction of polymer (ϕ_p) and volume fraction at crosslinking (ϕ_r) were calculated from swelling measurements as described in previous articles [Atta et al., (2005) & Atta et al., (2004)]. EWC values are calculated according to the equation: $EWC = (W_h - W_x) 100/W_h$. While ϕ_p and ϕ_r values are determined according to the equations: $\phi_p = (d/d_o)^3$, $\phi_r = q \phi_p$, where d_o and d are the diameters of xerogel and hydrogel discs, respectively.

Measurement of thermoreversibility

The dried gels were immersed in an excess of double distilled water at 25 °C for 24 hr. Each swollen gel was removed to fresh double distilled water at 50 °C, and the shrunken gel was weighed at various time intervals. Finally, the gel was reswelled in double distilled water at 25 °C and the swollen sample was weighed at various intervals. To measure the change in swelling ratio of the gel, this operation was repeated for three cycles.

Kinetics of swelling/deswelling

Thin discs (0.2mm)x(11mm) were used to measure the swelling/deswelling response rate. The water uptake capacity (W_u) is calculated from the equation: $W_u = (W_t - W_x) 100/W_e$, where W_x , W_t and W_e are the weight of xerogel, gel at time t and gel at equilibrium, respectively. The same equation was used to calculate deswelling kinetics at 50 °C.

Measurement of swelling ratios in various pH solutions and pH reversibility

The measurement of q values for the copolymeric gels under various pH solutions was the same as that in double distilled water. The pH values of various solutions adjusted by aqueous solution of HCl and NaOH were measured with a pH meter (Radiometer pH M 95) calibrated by standard buffer solution. The pH reversible experiments were carried out at pH 3 and pH 10 for 0.1M buffer solution at 25 °C.

RESULTS AND DISCUSSION

The numbers of polymeric gels capable of a thermotropic collapse were strongly limited. These polymers are reported as poly(N-alkylacrylamides) [Saito et al., (1993)], poly(N-vinyl caprolactam) [Makhaeva et al., (1996)], and poly(vinyl methyl ether) crosslinked by γ -radiation [Ichijo et al., (1994) & Moerkerke et al., (1998)]. These gels were synthesized by several methods, which include: forming a heterogeneous networks through a phase separation method [Kabra et al., (1991)] introducing free ends grafts through polymeric chains [Kaneko et al., (1998)] ; use of silane crosslinking agents [Zhang et al., (2001)] cold polymerization methods [Zhang et al., (1999)] using of polyethylene glycol as a pore-forming agent during the polymerization reaction [Zhang et al (2001)] two-step polymerization methods [Xue et al., (2002)]. In addition, it was reported that a thermosensitive gel could also be prepared as a result of binding of the cationic surfactant, tetraphenyl-phosphonium chloride, to a negatively charged polyelectrolyte gel [Isogai et al., (1996)]. It was demonstrated previously that novel crosslinkers based on N,N,N- tri acrylamido melamine (MAAm), which have either methacrylate or acrylate groups, can be used as crosslinkers to synthesize thermo responsive gels [Atta et al., (2005) and Atta et al., (2004)]. The properties of polymeric hydrogels are highly influenced by crosslink density and also, in the majority of cases, on the functionality of crosslinkers [Asoh et al., (2006) & Kishi et al., (2003)]. Wide varieties of acrylate crosslinkers have been used to form crosslinked networks. In bulk or solution polymerization the choice of crosslinkers is quite broad. However, the solubility of many crosslinkers in water-phase polymerization becomes marginal. Much effort has been expended on attaining high levels of purity in the monomers, but the literature indicates otherwise with regard to the crosslinking agents. In

this respect, a simple method was used to synthesize two crosslinkers based on polyfunctional acrylate and methacrylate. The ability to use these new crosslinkers to synthesize novel series of temperature and pH sensitive hydrogels is the main goal of the present investigation. In the present investigation, MAAm and MBA crosslinkers were used to synthesize thermo sensitive hydrogels based on NIPAAm and VP monomers in their network structures. In this respect, APS at 0.1 (wt%) was used as initiator to polymerize NIPAAm and VP monomers. Different mol percentages of crosslinkers were used to investigate the variation of crosslinker types and concentrations on polymerization.

Crosslinked NIPAAm/VP Copolymers:

Crosslinked NIPAAm/VP copolymers were prepared via solution polymerization using water as solvent and different weight percentage of MAAm and MBA crosslinkers ranging from 0.5 to 4%. The monomer ratios of NIPAAm/VP 0.9:0.1, 0.7:0.3, 0.5:0.5, 0.3:0.7 and 0.1:0.9 (mol/mol%) were used in all cases. NIPAAm/VP copolymers could be crosslinked due to the presence of $-C=C-$ groups of MBA and MAAm grafts that can react with another monomers or with crosslinkers in presence of initiators. The crosslinking mechanism of these copolymers is based on radical polymerization of double bonds of NIPAAm/VP with a tetra functional and hexafunctional MBA and MAAm crosslinkers, respectively.

The SF values of the prepared NIPAAm/VP copolymers crosslinked with 1% of both MAAm and MBA crosslinkers were measured. using Soxhlet extraction with water after 48 hr, and the results are listed in **Table 1**. The effect of weight percentage of both MAAm and MBA crosslinkers on NIPAAm/VP (with 0.5 mol ratio of VP) on SF values were determined and listed in **Table 2**. The data listed in **Tables 1 and 2**, show that SF values decrease inversely with increasing amounts of crosslinker concentrations. It was found that all the NIPAAm/VP xerogels form gel in hot water, indicating that MAAm and MBA are effective crosslinkers for NIPAAm/VP. It was also noted that all prepared xerogels were transparent but became opaque in hot water. Careful inspection of the SF data for crosslinked NIPAAm/VP copolymers indicates lower SF values for the MAAm crosslinked copolymers than for those crosslinked with MBA. On the other hand, it was observed that, SF values were increased with increment of NIPAAm contents. This can be explained on the basis of different reactivity ratios

between MAAm or MBA with PNIPAAm, PVP and NIPAAm/VP copolymers, which can be arranged in order PVP > NIPAAm/VP > PNIPAAm. The SF (%) data indicate that MAAm is more efficient for crosslinking NIPAAm/VP than MBA. Accordingly, MAAm is appropriate to use as a crosslinker for NIPAAm/VP copolymers due to its capability to copolymerize well with VP.

Table (1): Swelling Parameters at 20 °C of Crosslinked NIPAAm/VP Copolymer Hydrogels.

Copolymers NIPAAm/ VP (mol%/mol%)	Swelling Parameters (crosslinked with 1% MBA)				Swelling Parameters (crosslinked with 1 %MAAm)			
	EWC (%)	Q (g/g)	φ_p	φ_r	EWC (%)	Q (g/g)	φ_p	φ_r
90/10	89.1	8.2	0.0902	0.74	92.7	12.7	0.0661	0.84
70/30	91.4	10.7	0.0766	0.82	95.3	20.3	0.0433	0.88
50/50	92.5	12.3	0.0691	0.85	96.8	30.5	0.0295	0.90
30/70	93.9	15.4	0.0610	0.94	97.5	40.2	0.0241	0.97
10/90	94.5	20.5	0.0478	0.98	97.8	45.4	0.0218	0.99

Table (2): Swelling Parameters at 20 °C of Crosslinked NIPAAm/VP (50 mol % / 50 mol%) Copolymer Hydrogels.

Crosslinker contents (Wt %)	Swelling Parameters (crosslinked with 1% MBA)				Swelling Parameters (crosslinked with 1% MAAm)			
	EWC (%)	Q (g/g)	φ_p	φ_r	EWC (%)	Q (g/g)	φ_p	φ_r
0.5	94.5	17.4	0.0505	0.88	97.5	40.4	0.0211	0.85
1	92.5	12.3	0.0691	0.85	96.8	30.5	0.0295	0.90
2	91.03	10.1	0.0811	0.82	96.1	25	0.0352	0.88
4	89.2	8.3	0.0904	0.75	93.8	15.18	0.0534	0.81

Swelling Behavior:

From the earlier discussion it is believed that the crosslinked NIPAAm/VP copolymers with MAAm crosslinker consists of very heterogeneous networks having dangling chains formed (especially) at the end of crosslinking. The inhomogeneous network structures of NIPAAm/VP copolymers originated by the incorporation of MAAm crosslinker that can affect the behaviors of the network in aqueous media. The effect of both pH and temperature of aqueous media on the swelling and deswelling behaviors of crosslinked NIPAAm/VP copolymers is discussed in the coming section. Swelling of ionic gel is a consequence of the balance between ionization of ionic group of the polymer network and constraint imposed by the polymer chains. In the present system, the swelling parameters EWC, q , Φ_p and Φ_r values of NIPAAm/VP gels in double distilled water at 20 °C were determined and listed in **Tables (1,2)**. It was found that, the water content of crosslinked gels in presence of MBA was less than that crosslinked with MAAm. It was also noted that, NIPAAm/VP crosslinked with MBA have higher Φ_p than that crosslinked with MAAm. This can be referred to formation of high crosslink density network due to high reactivity of NIPAAm/VP copolymer with MBA crosslinker. Panayiotou and Freitag [Panayiotou et al., (2005)] carried out work to study of crosslinking degree on the swelling behavior of PNIPAAm hydrogels and concluded that a lower degree of crosslinking leads to a higher swelling ratio. As the crosslinking agent incorporated in this study was 1 wt% of the total monomer content in all instances, the number of crosslinking chains per mass of liquid decreases as the molecular weight of the crosslinking agent increases. This led to high swelling values, which increased with increasing molecular weight of the crosslinking agent. The samples containing higher molecular weight crosslinking agents swelled to a higher extent by virtue of their longer crosslinked chain lengths. Swelling in all cases was found to change the size of the original hydrogel, while the original shape was maintained. If a xerogel imbibes at least 20 times its own weight of aqueous fluid while retaining its original shape, it is called a superabsorbent hydrogel [Schild (1992)]. The samples synthesized with the higher molecular weight crosslinking agent (MAAm) absorbed over 12.7-45.4 times their weight in water, while maintaining good gel integrity and can be characterized as superabsorbent.

Swelling and deswelling kinetics:

In this section the influence of copolymer composition and crosslinker concentrations on swelling and deswelling behaviors of NIPAAm/VP copolymer in double distilled water are studied. The swelling and deswelling kinetic curves of crosslinked NIPAAm/VP copolymers having different compositions at 20°C were determined and represented in **Figure 1**. The deswelling kinetics of these copolymers at 50°C were measured and plotted in **Figure 2**. From **Figure 1**, it was noted that dependence of water uptake on molecular weight and type of the crosslinking agent. Careful inspection of hydration curve in **Figure 1a**, of NIPAAm/VP/MAAm system, it was observed that at the first stage of the curve, the swelling rate is very high, and the water can penetrate easily into the polymer network. This is highlighted by the fact that after 2 hr, water uptake is over 60% of the total water absorption of the fully hydrated hydrogels. As the test samples approached complete hydration, the rate of water absorption began to level off. This is due to the retractive force of the crosslinked structure counterbalancing the thermodynamically driven swelling [Peppas et al., (2000)]. **Figure 2b** shows that, hydrogels containing lower molecular weight crosslinking agent, MBA, yielded a slow rate of water uptake during 2hr. However, it should be taken into consideration that this value is representative of the overall water uptake. The deswelling kinetics of NIPAAm/VP at 50 °C is shown in **Figure 2**. Comparing the swelling time and deswelling times, it was found that the deswelling times are lower than the swelling times. This means that NIPAAm/VP deswells much faster than swelling especially for copolymers having high VP and crosslinker contents. The results can be attributed to the fact that the more heterogeneous network allows for faster shrinking upon water desorption [Norisuye et al., (2002)]. This also can be explained on the basis that copolymers shrink from the swollen state at which the diffusion resistance of water is considered to be small [Gotoh et al., (1998)].

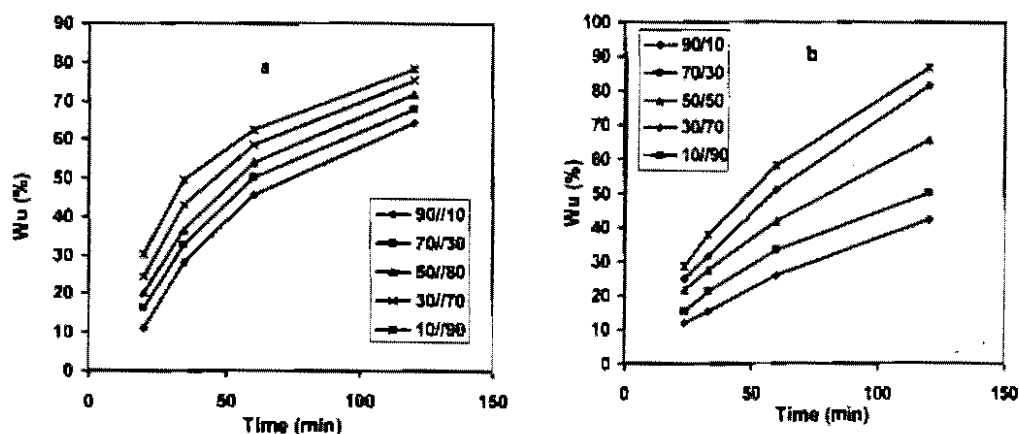


Fig. (1): Swelling kinetics of crosslinked NIPAAm/VP copolymers at 20 °C crosslinked with a) MAAm and b)MBA crosslinkers.

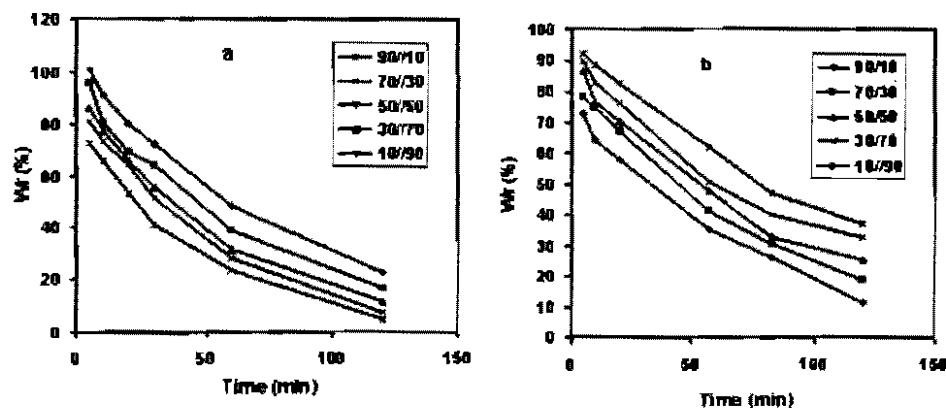


Fig. (2): Deswelling kinetics of crosslinked NIPAAm/VP copolymers at 50 °C crosslinked with a) MAAm and b)MBA crosslinkers.

Effect of temperature on swelling parameters:

The swelling degree of the hydrogels depends on the balance between the repulsive and attractive specific intermolecular interactions i.e. van der Waals forces, hydrophobic interaction, hydrogen bonding and electrostatic interactions. Temperature is another parameter that affects the balance of interactions in some specific gels. The volume change of these gels may be referred to a thermodynamic characteristic of their

linear polymers [Alupej et al., (2002)]. Hydrogels containing NIPAAm are among the most widely studied materials [Costa et al., (2002)]. The coil- to – globule transition of aqueous solutions of poly (NIPAAm) and their gels are referred to various types of interactions [Snowden et al., (1993)]. In this respect, NIPAAm/VP copolymers forming relatively strong hydrogen bonds formed between water molecules and N–H or C=O groups in dilute solutions, become weaker and break as temperature is raised, resulting in the endothermic heat of phase separation. While hydrophobic interaction may be arises from interaction between isopropyl groups of NIPAAm and hydrophobic sites of MAAM crosslinker. All NIPAAm/VP xerogel discs were swollen in water at room temperature and all gels swelled uniformly, and had smooth edges and definite shape. LCST values of the swelled gels were measured by DSC as described in the experimental section. LCST values for NIPAAm/VP having different composition of crosslinks with 1% of MAAM and MBA crosslinkers were determined and listed in **Table 1**. The LCST values of crosslinked NIPAAm/VP gels (having VP mol ratio 0.5) with different weight ratios of MAAM and MBA were measured and listed in **Table 2**. It was observed that LCST values decrease with increase crosslinker contents. This can be attributed to the increase in hydrophobicity of the copolymers. Consequently, the network becomes more inhomogeneous due to the high possibilities of formation of end free chains by increment of crosslinker contents. It was also observed that NIPAAm/VP copolymers crosslinked with MBA have higher LCST values when compared with those crosslinked with MAAM crosslinker. This can be attributed to the formation of high crosslink density networks. This reflects on the low possibilities of NIPAAm/VP crosslinked with MBA to form less heterogeneous networks than those crosslinked with MAAM. The effect of temperature on q values of crosslinked NIPAAm/VP with 1% of MAAM and MBA was measured and represented in **Figure 3**. The relation between q and temperature of swelling media for crosslinked NIPAAm/VP with different weight ratios of MAAM and MBA were plotted in **Figure 4** which obtained that the extent of crosslinking increases and consequently the swelling decreased [Abdelaal et al., (2007)]. In this respect, the gels were swelled to equilibrium at 25 °C for 24h and the swelling capacity will be measured at equilibrium. The gels were transferred to measure their swelling capacities at different temperatures. The gel swelling capacity was measured every hour until the gel reaches the equilibrium at definite

temperature of swelling. The time of swelling at different temperature was changed according to gel composition and type of crosslinker. It was noted that, the q values were changed at the same temperatures which were determined from DSC measurements. The increase in the swelling ratio above 20 °C indicates that the hydration rate of NIPAAm/VP copolymers having high VP contents increases than the rate of dehydration which arises from hydrophobic interaction of dangling chains and incorporation of VP above 20 °C. The other curves of copolymers having high VP content show a fall in swelling capacities with increasing temperature, which becomes sharper. The reversible nature of swelling and deswelling was confirmed from the repeated swelling measurements of crosslinked NIPAAm/VP copolymers, which indicates that the same q values were recorded at the same temperatures.

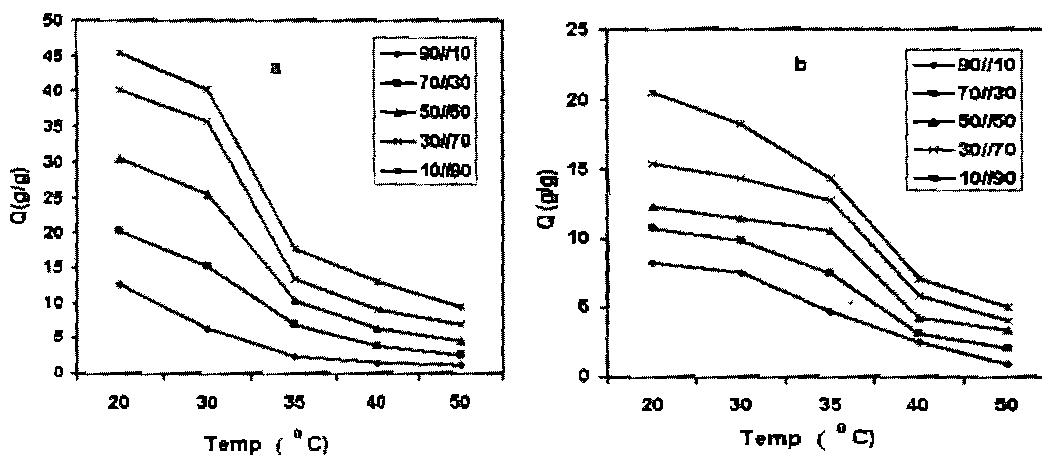


Fig. (3): Effect of Temperature on the Swelling Capacities of the crosslinked NIPAAm/VP copolymers with 1 % of a) MAAm and b) MBA crosslinkers.

Swelling of Hydrogels.

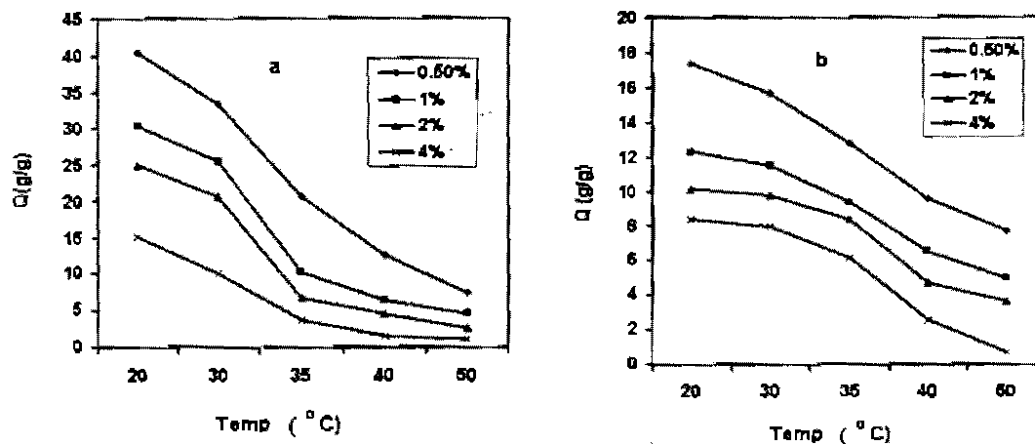


Fig. (4): Effect of Temperature on the Swelling Capacities of the crosslinked NIPAAm/VP copolymers with different concentrations of a) MAAM and b) MBA crosslinkers.

On the other hand, it was observed that the swelling ratios for all NIPAAm/VP gels were decreased with increasing temperature near their LCSTs. However, NIPAAm/VP gels show different swelling ratios depending on VP contents. The phase transition temperature of the crosslinked copolymers was shifted to higher temperature with increasing VP content. At the same time, the phase transition of NIPAAm/VP was shifted to lower value when the crosslinking was completed with MAAM crosslinker. This can be referred to formation of dangling chain in presence of MAAM crosslinker. Consequently, the hydrophilicity of gels decreases and the phase transition temperature was shifted to lower temperatures. It was also observed that, the swelling ratio increases with increasing the temperature up to LCST. This can be referred to the formation strong hydrogen bonds formed between water molecules and N-H or C=O groups.

Effect of pH on Swelling Parameters:

Measurements of the degree of swelling were carried out at different pH of PB solutions, having total ionic strength of 0.1. The relationship between swelling degree of NIPAAm/VP hydrogels, having different compositions, and pH of swelling solution at 25 °C is plotted in Figure 5. The effect of pH on the swelling degree of NIPAAm (0.5 mol ratio)/ VP (0.5mol ratio) crosslinked with various percentages of both

MAAm and MBA is presented in Figure 6 The swelling degrees in PB solutions turned out to be larger than those measured in water and appear to be affected by the pH of the swelling medium. The behavior of the hydrogels was unexpected as they did not contain ionizable groups. It was noted that the swelling of the hydrogel increased with increasing pH of the PB solutions Figure 6.

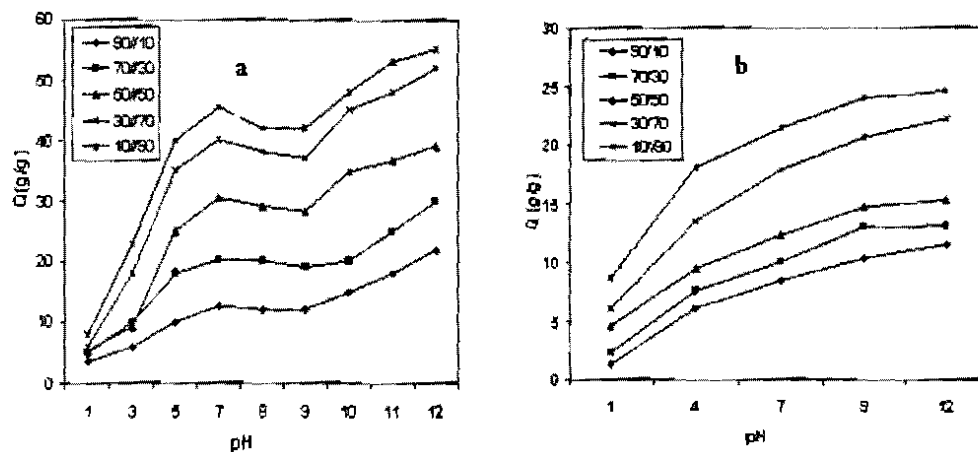


Fig. (5): Swelling and pH relations of the crosslinked NIPAAm/VP copolymers with 1 % of a) MAAm and b) MBA crosslinkers in aqueous solution and 0.1 M KCl at temperature 20 °C.

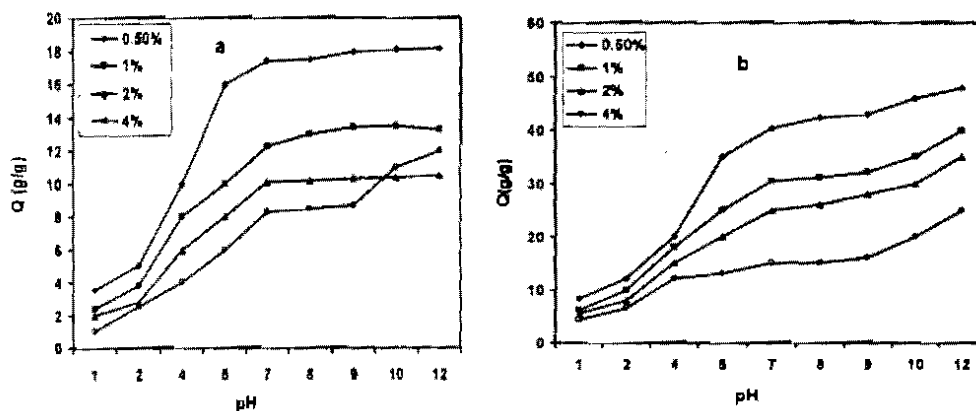


Fig. (6): Swelling and pH relations of the crosslinked NIPAAm/VP copolymers with with different concentrations of a) MAAm and b) MBA crosslinkers in aqueous solution and 0.1 M KCl at temperature 20 °C.

This can be attributed to the fact that some of dangling chains can be hydrolyzed to ionic carboxylic group. It was also observed that there are two double-steps of swelling at different pH solutions, indicating the presence of two ionic groups having different dissociation constants. In addition it was noted that swelling increases with increasing pH from 2 up to 7, but stabilizes at pH 9. It was also noted that the swelling degrees of NIPAAm/VP gels increased with increasing NIPAAm content at pH from 4 to 7. This is attributed to the complete dissociation of acid groups of MAAm above its dissociation constant pK_a and pH values, after which the degree of swelling increased with increasing pH from 9.5 to 12. This can be associated with the hydrolysis of amide groups of VP or MAAm, and MAAm crosslinkers in alkaline solutions [Lee et al., (1999)]. This trend was verified by the increasing swelling ratios with increasing crosslinker contents, as indicated in **Figure 6**, at pH 9.5 to 12. The results shown in this figure indicate that the swelling ratios of gels at pH 10.4 are larger than those in the solution with pH 4. This evidence shows that the amide groups on the copolymeric gels are easily hydrolyzed to form carboxylate groups under alkaline conditions. This phenomenon was confirmed by Park and Hoffman [Park et al., (1994)]. On the other hand, the higher swelling ratios of the gels at pH 10.4 than those determined at pH 4 can be attributed to ionic repulsion between carboxylate ions at pH 10.4.

CONCLUSIONS

The following conclusions can be withdrawn from the previous results:

- 1- New crosslinker was used to form NIPAAm/VP hydrogels which have higher water uptake than conventional crosslinked NIPAAm/VP hydrogels.
- 2- The prepared hydrogels show pH- and temperature- sensitivity and can be referred to formation of dangling chains and hydrolysis of these chains to carboxylic groups at different pH values.

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دراسة سلوك الزيادة الحجمية للبوليمرات كيميائية التصلب والحساسية لكل من درجة الحموضة ودرجة الحرارة بواسطة - أيزوبروباييل مع 1 - فينايل-2- بيروليدون باستخدام عامل تصالبي جديد.

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الهدف من البحث تخليق عامل تصالبي جديد لخلق بوليمرات حساسة لدرجة الحرارة ودرجة الحموضة معا، ولها ايضا نفس التركيب الكيميائي لأكثر المونومرات حساسية لدرجة الحرارة وهو - ايزوبروباييل اكريلاميد ومن ثم استخدام هذا العامل في خلق جيل ايوني يعتمد على 1- فينايل-2- بيروليدون مع - ايزوبروباييل اكريلاميد وقياس التمدد العكسي والانكماش نتيجة للتغير في درجة الحموضة ودرجة الحرارة.