



Effect of Crosslinker Amount on Properties of Poly Phenylacrylamide Gels

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Abstract

The monomer phenyl acrylamide was synthesized by reacting acrylamide with chloro benzene in the presence of pyridine. Fourier transform infrared spectroscopy (FT-IR) was used to characterize the resulting monomer. High conversion poly phenyl acrylamide (PPAM) containing 0, 0.5, 1, 1.5 and 2 wt % (in conversion to mass of PPAA) of N,N'-methylenebisacrylamide (MBAA) as crosslinker have been successfully synthesized. The effect of MBAA percentage on swelling parameters, clarity, mechanical and thermal properties of the prepared xerogels and hydrogels were studied. 1.5 wt % of MBAA is required to obtain clear xerogels and hydrogels. The water content (EWC), volume fraction of polymer (ϕ_2) and weight loss during swelling decrease with increasing MBAA content. Young's and shear modulus (E and G) increase as MBAA content increases, the values of E and G are 0.661–3.878 MPa and 0.423–2.588 MPa, respectively. The hydrogels were characterized in terms of modulus crosslinking density (ν_e and ν_i) and polymer-solvent interaction parameters (χ). The results are 0.252–0.661 mol/dm³ for ν_e , 0.211–0.541 mol/dm³ for ν_i , and 0.813–0.987 for χ . Thermal properties of polymers enhance (T_g increase) by adding MBAA. These types of polymers and their hydrogels possess new properties with potential uses in different medical applications.

Keywords: Phenyl acrylamide; High conversion polymers; Mechanical properties; Swelling parameters; Crosslinking density.

1. Introduction

Hydrogels are hydrophilic polymeric networks that absorb water from 10% to hundreds times their dry weight and are insoluble in water because of the presence of a three-dimensional network [1]. Existing hydrogel materials, which are claimed to be useful in some important biomedical applications, are derived almost exclusively from hydrophilic monomers such as 2-hydroxyethyl methacrylate, glycerol methacrylate or N-vinyl pyrrolidone. These hydrogels, in general, have water contents ranging from 38 to 75%. The water content and modulus of hydrogels depend on the nature of monomers and crosslinking density [2, 3]. Although polymeric hydrogels have good biocompatibility, their mechanical strength on swelling is very poor. For getting materials combining biocompatibility with a

good mechanical strength, two methods are used: Copolymerization of hydrophobic monomers with hydrophilic monomers or using crosslinking agent [4].

Because of the high biocompatibility and low toxicity, the utilization of hydrogels as biomaterials has recently gained great importance. Today the major fields of hydrogels applications involve: injectable polymers, ophthalmic applications, topical applications as wound and burn dressings, dental applications, drug delivery systems [5], blood compatible materials [6], implants [7], and water saving systems [8]. Accordingly, it would be highly useful in a number of medical applications to provide a polymeric material having increased hydrophilicity,

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softness after hydration, mechanical strength and oxygen permeability.

Derivatives of poly acrylamide (PAM) are synthetic water-soluble polymers made from monomers of acrylamide (AM) [9]. In crosslinked form, they are highly water-absorbent, forming a soft gel used in such applications as electrophoresis and in manufacturing soft contact lenses [10]. They have used also as flocculants in waste water treatment applications as drug reduction agent and drilling fluid in enhanced oil recovery as additives in papermaking and as a drug-delivery agent [11]. In the straight-chain form, they are used as a thicker and as subdermal for aesthetic surgery. The gels of PAM derivatives were prepared by free radical polymerization using redox initiation (potassium persulfate / ascorbic acid) system [12].

The aim of this work is the preparation of phenylacrylamide monomer and its high conversion polymer. This work also studies the influence of crosslinking content (MBAA) on the properties of xerogels and hydrogels such as, optical homogeneity, swelling behavior, mechanical and thermal properties. No study has been reported on the study the properties of crosslinked poly phenylacrylamide hydrogels.

2. Experimental

2.1. Materials

The raw materials were all obtained from Aldrich-oma chemical Co. The initiator potassium persulfate (PPS) was purified by twice recrystallizations from water; it is filtered and dried under reduced pressure in the presence of calcium chloride. The crosslinker *N,N'*-methylenebisacrylamide, dichlorodimethylsilane (DMDCS), and all solvents were used as received.

2.2. Preparation of phenyl acrylamide

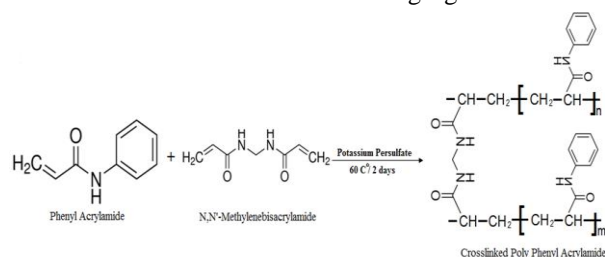
The monomer phenyl acrylamide was synthesized by reacting acrylamide with chloro benzene in the presence of pyridine, the mixture was stirred for (4 hr) at 40°C until appearance of white precipitate, the product was poured on watch glass, filtered and recrystallized using methanol then dried at 40°C.

2.3. Preparation of xerogels

Sample ampoules which have enough surface area and 13 mm diameter, were used to be suitable for the

isothermal condition during the polymerization. The ampoules were siliconized with a 2 % solution of (DMDCS) in chloroform and kept in an air oven for one day at 75 °C to allow the removal of polymer rods. Dissolved mixture in water consists of phenyl acrylamide, 0.5 wt % (PPS) as initiator and different amounts of (MBAA) as crosslinker (0, 0.5, 1, 1.5 and 2 wt %) was made up in a small stopper flask. The mixture was stirred for 15 minutes, and then transferred to the glass ampoules which have been siliconized previously. The contents of tubes were purged with nitrogen for (15 minutes) prior to the reaction in order to remove all oxygen. The glass ampoules were placed in a water bath at 60 °C, and allowed to polymerization for a specified time (2 days). The temperature is then raised and the tubes are placed in an oven at 70 °C for another one day. At the end of this time, polymerization is normally completed, after which the polymerized rods were removed from the tubes. The rods were then post cured for one day at 70 °C to complete the polymerization process and relieve any mechanical stresses present. The rods were cut as discs and dried exhaustively in an oven at 35 °C to constant weight.

The reaction is shown in the following figure 1.



Scheme 1. Schematic illustration of the process formation of crosslinked PPAA from PAA as monomer and MBAA as crosslinker.

2.4. Characterization

Perken Elmer-1650 spectrometer was used to record FTIR spectra of phenyl acrylamide on KBr Pellets in the range 200-4000 cm^{-1} .

2.5. Swelling Studies

The swelling of the discs was carried out at room temperature 25°C. The known weight and diameters of dried discs were put in sample vials (50 ml). The swelling time was counted from when the deionized water was added into the vial. At regular time intervals, the swollen discs were taken out using

tweezers, and the excess water on the surface of the discs was removed by wiping with the edge of Whitman No. 1 qualitative filter paper. They were weighted and returned to the vials immediately. The water content (EWC), reduction in the weight of the xerogels, extension ratio (ER) and volume fraction of polymer (ϕ_2) were calculated as [13]:

$$EWC \% = \frac{(W_s - W_d)}{W_s} \times 100 \quad (1)$$

$$WLS = \frac{(W_0 - W_d)}{W_0} \times 100 \quad (2)$$

$$ER = \frac{d}{d_0} \quad (3)$$

$$\phi_2 = \left(\frac{d_0}{d}\right)^3 \quad (4)$$

Where, d_0 and d are the diameters of dry and fully hydrated discs respectively. Thus, the volume fraction of water (ϕ_1) in the hydrogel at equilibrium is equal to $(1 - \phi_2)$.

2.6. Compression Measurements

An Instron 3366 machine analyzer was used for compression strain–stress testing. The crosshead speed was set at a fixed rate of 2 mm/min, and the load was run until the sample was broken. For testing, the hydrogels were cut into strips with dimensions of \sim (25 mm in length, 5 mm in width and 2 mm in thickness). Young's modulus (E) for the hydrogels was obtained as the slopes in plots of the stress (τ) versus strain ($\lambda - 1$), as follows:

$$\tau = E(\lambda - 1) \quad (5)$$

Where τ is the applied force per unit area of hydrogel and λ is the ratio of deformed length (l) of hydrogel to its undeformed (l_0). The effective crosslinking density (ν_e) of hydrogels can be obtained from the compression-strain measurements via the kinetic theory of rubbery elasticity [14].

$$\tau = G(\lambda - \lambda^{-2}) \quad (6)$$

$$G = RT \nu_e \phi_2^{1/3} \quad (7)$$

G can be obtained from the slope of the stress, τ , versus $(\lambda - \lambda^{-2})$. In Equation (7), ϕ_2 is the volume polymer fraction, R is the gas constant (8.314 J K⁻¹ mol⁻¹) and T is the absolute temperature. The polymer/solvent interaction parameter, χ , which

represents the specific interaction between water and polymers, can be calculated from the Flory-Rehner equation [15].

$$\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2 + \nu_e V_1 (\phi_2^{1/3} - 2 \phi_2 f^{-1}) = 0 \quad (8)$$

In which V_1 is the molar volume of water (18.05 × 10⁻³ dm³ / mol at 298° K) [16] and f is the functionality of the cross-linker agent. The molecular mass between cross-links, M_c can be calculated via Equation (10), in which ρ is the density of the xerogel.

$$M_c = \rho / \nu_e \quad (9)$$

The theoretical cross-linking density ν_t was calculated from the following relationship:

$$\nu_t = C f / 2 \quad (10)$$

Where, C is the concentration of cross-linking agent with functionality f . Because $f = 4$ for EGDMA [16], equation (10) is reduced to:

$$\nu_t = 2C \quad (11)$$

The values of C were calculated from the weight concentration of EGDMA by using (198.22 gm mol⁻¹) as the molar mass of EGDMA and by taking the densities of the xerogels.

2.7. Thermal Properties

Thermal degradability of the polymer was studied by TGA using Perkin Elmer in a nitrogen atmosphere at a heating rate of 10 °C /min from 0 to 800 °C and glass transition temperature (T_g) was determined using a DSC-Mettler calorimetric system.

3. Results and Discussion

3.1. Characterization of Phenyl acrylamide

As shown in Figure 2, the strongest band at 1673 cm⁻¹ is attributed to the C=O stretching vibration. The second strongest band at 1597 cm⁻¹ is attributed to C-C ring-stretching vibration of benzene. A broad band at 3400 cm⁻¹ corresponded to the N-H asymmetrical stretching vibration of the second amide. A band at 1330 cm⁻¹ corresponded to C-N and N-H stretching vibration. The sharp band at 1430 cm⁻¹ is attributed to the C-N stretch vibration. A peak at 3210 cm⁻¹ is attributed to the C-H stretching vibration on the benzene ring. The weak peak at 2930 cm⁻¹ is

attributed to C-H symmetrical stretching on CH_2 group. A band at 745 cm^{-1} is ascribed to C-H out-of-plane wagging vibration from the substituted benzene ring and a band at 598 cm^{-1} is attributed to C-C twisting vibration of the phenyl ring. All above absorption bands appeared in the FTIR spectrum of poly phenyl acrylamide unless absence of the absorption band at about 1640 cm^{-1} which belongs to olefinic double bond $\text{C}=\text{C}$ as supporting the formation of polymer.

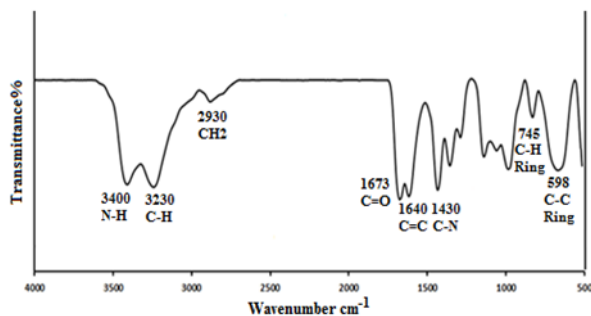


Fig. 2. FT-IR spectrum of phenyl acrylamide monomer

3.2. Optical homogeneity

When the preparation process of xerogels was completed, a visual assessment of homogeneity and optical clarity was made. Figure 3 shows photograph of some prepared xerogels with different degree of optical clarity. The xerogel without MBAA is opaque and requires only 1.5% MBAA for transparency. The results clearly reveal that; the increased in compatibility with concentration of MBAA enhanced transparency for xerogels; this may be explained by the fact that, MBAA increases compatibility in addition to functioning as a crosslinking agent, yielding enhanced transparency for xerogels. In addition, the improvement of optical homogeneity may be expected from the fact the introduction of MBAA as a crosslinking agent increases the cross-link density, and hence restricts the mobility of the polymer chain. Light transmission of UV visible spectra confirms these results; an increase in the transmission is expected as the MBAA increased. A maximum transmission of more than 90% has been achieved through xerogel disks (1 mm thickness). Incorporation of a crosslinking agent as an ultimate means of forcing compatibility between existing polymer chains, is well established [17, 18].

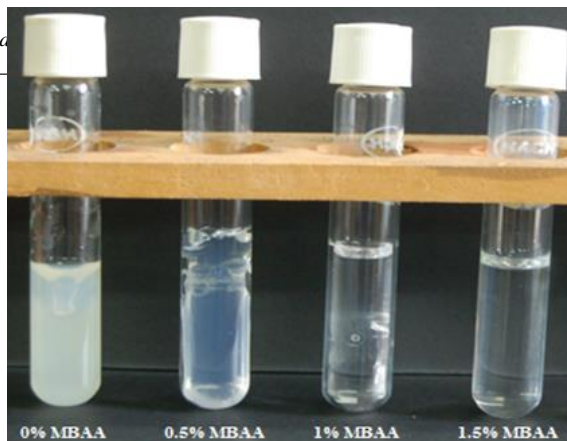


Fig. 3. Photograph of some prepared xerogels with different optical clarity

3.3. Swelling behavior

Table 1 summarizes the swelling properties of five PPAA with different amounts of MBAA within the range 0–2 wt %. All swelling parameters decrease with increasing amount of MBAA present in the gel formation system. The EWC values are in the range 69.11–55.96 %. The results clearly reveal that with increasing crosslinker content in the hydrogel, the swelling capacity significantly decreases. The observed results are quite common and may be explained by the fact that the increasing number of crosslinks in the hydrogel lowers the molecular weights between the crosslinks [19] and thereby reduces the free volumes between the macromolecular chains, which then become accessible to penetrant water. Another explanation for the observed finding may be that molecules the greater number of crosslinks in the hydrogel results in a restrained mobility of the macromolecular chains that does not permit water penetration and brings about a depression in the swelling ratio [20]. It was found from Table 1 that the weight loss in the hydrogels (18 %) decreases to its half value (9 %) by the increasing of crosslinker to 2 wt %. The decreasing in ER with increasing MBAA amount is attributed to the increase of the crosslinking density. This finding has been frequently reported in many other investigations [21].

Table 1

Swelling parameters of PPAA hydrogels with different amount of MBAA

MBAA%	EWC%	ER	Φ_2	Φ_1	Weight loss%
0.0	69.11	1.44	0.322	0.678	18.02
0.5	66.28	1.38	0.451	0.549	15.72
1.0	62.78	1.23	0.500	0.500	12.59
1.5	59.05	1.11	0.569	0.431	10.94
2.0	55.96	0.92	0.612	0.388	9.51

3.4. Tensile Testing

The initial crosslinking concentration also plays an important role in determining mechanical properties of hydrogels. A higher MBAA concentration generally leads to a stronger and harder gel with lower water content. Results derived from stress-strain measurements as depicted in Table 2 shows that an increase in the concentration of MBAA results in a concentration increase Young's and shear modulus. Young's moduli are significantly smaller for hydrogels, which exhibit more swelling. Thus, when MBAA content decreases; the final material is very soft with poor mechanical properties (lower modulus). This indicates that the degree of crosslinking in the network played a major role in the mechanical properties of the hydrogel. For an elastic hydrogel, the ratio of **E** to **G** should be equal to 3.0 for a small strain. From the set of data in Table 2, the values of **E/G** do not deviate significantly from the average value of 1.5.

Table 2

Table 3

Theoretical network parameters of xerogels containing different concentrations of MBAA with effective network densities of the swollen gel

MBAA %	\bar{P} (kg dm ⁻³)	Moles (g mol ⁻¹)	V (xerogel) (dm ³)	$C \times 10^{-2}$ (mol dm ⁻³)	ν_e (mol dm ⁻³)	ν_c (mol dm ⁻³)
0.0	0.811	-	0.0981	-	-	0.201
0.5	0.994	0.0040	0.0964	6.544	0.211	0.252
1.0	1.027	0.0090	0.0944	11.621	0.377	0.415
1.5	1.055	0.0142	0.0925	17.222	0.463	0.524
2.0	1.078	0.0196	0.0917	24.009	0.541	0.611

In general ν_e varies with ν_c according to the following equation [23]:

$$\nu_e = \alpha + \beta \nu_c \quad (13)$$

Where α is the value of effective cross-linking induced even in the absence of any included chemical crosslinker. It may arise from physical cross-linking, chain transfer, defects in the network and presence of dimethacrylates as an impurity in methacrylates [24]. The parameter β is a measure of cross-linking efficiency ($\beta = \nu_e/\nu_c$ when $\alpha = 0$). The linear dependence of ν_e on ν_c according to equation (13) is indicated in Figure 4, and by applying a linear least-square fit of the data, the following interrelationship was found:

$$\nu_e = 0.081 + 1.52 \nu_c$$

Tensile properties of PPAA hydrogels containing different concentration of MBAA

MBAA content %	Young's moduli (E) (Mm ⁻²)	Shear moduli (G) (MN m ⁻²)	E/G
0.0	0.661	0.423	1.569
0.5	1.234	0.857	1.448
1.0	1.955	1.433	1.367
1.5	2.993	2.011	1.486
2.0	3.878	2.588	1.520

3.5. Network Structures

Determination of share modulus (G) allowed the effective crosslinking density (ν_e) to be evaluated; thereby yielding the molar mass between crosslinks (M_c). Table 3 contains the effective crosslinking density in the swollen state. Increase crosslinking agent content enhanced hydrophobic bonding [22] and, consequently, the effective crosslink density increased. Table 3 shows also the values of densities, concentration and theoretical crosslinking densities.

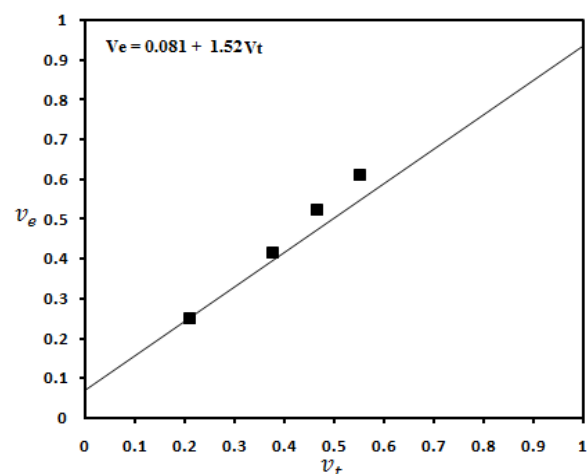


Fig. 4. Dependence of measured effective crosslink density (ν_e) on theoretical crosslink density (ν_f) for the gels at different amounts of MBAA

For the present system obtained by thermal polymerization, the values ν_f being smaller than ν_e . The average molecular weight between consecutive crosslinks (M_c) is another structural parameter characterizing the three-dimensional network structure. It is directly related to the crosslink density. The M_c values determined for every gel system are given in Table 4. The results obtained show that the average molecular weight between the crosslinks is affected by the concentration of MBAA and scientifically decreased with increasing the crosslinking concentration.

The polymer-solvent interaction parameter χ at swelling equilibrium represents the specific interaction between water and polymers. Values of $\chi > 0.50$ suggest that the solvent employed is thermodynamically poor. Table 4 reports the values of the polymer-solvent interaction parameter; an increase in MBAA content led to decrease in χ . This behavior can be explained by the relative hydrophilicity of the MBAA. All calculated χ values exceeded 0.50, thus an increase in the MBAA content leads to a reduction in the polymer/water interaction.

Table 4

Network parameters of PPAA hydrogels containing different concentrations of MBAA

MBAA%	ϕ_2	$M_c \times 10^{-3}$ (g mol ⁻¹)	χ
0.0	0.322	7.442	0.987
0.5	0.451	5.998	0.939
1.0	0.500	3.771	0.889
1.5	0.569	2.685	0.860
2.0	0.612	1.981	0.813

3.6. Thermal Analysis

The glass transition temperatures (T_g) were measured for poly phenylacrylamide xerogels with different concentration of MBAA (0, 0.5, 1, 1.5 and 2%). The T_g 's were (193, 198, 205, 216 and 221), respectively. As expected, the data revealed that with an increase in MBAA content, the value of T_g increased as a result of increasing the rigidity of the polymer. The thermal stabilities of the xerogels were determined by (TGA) and are presented in Figure 5. It is observed that the weight loss percentage decreased against the temperature by increasing amount of MBAA in xerogels. The larger amount of

a crosslinking agent restricts the segmental mobility of the macromolecular chains, thereby the T_g increased and weight loss decreased, this is a common effect of crosslinker on thermal properties of a polymer [24].

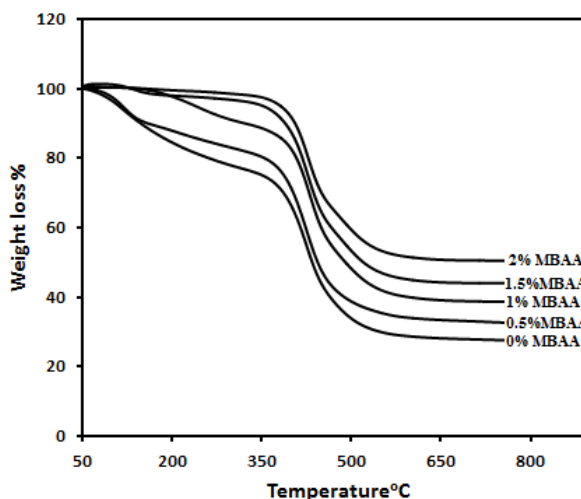


Fig. 5. TGA thermogram of PPAA xerogels with different amount of MBAA

4. Conclusion

The monomer PAA was successfully synthesized. High conversion polymer was prepared by polymerization mixture of PAA and MBAA via free radical polymerization using potassium persulfate as initiator. Optical clarity enhances with increasing MBAA. Swelling properties have been determined in deionized water and found that they decrease with addition of MBAA. Stress-strain measurements yielded the Young's module, the effective crosslinking density and the polymer-water interaction parameters. The restriction of chain

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