



Research Article

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## *Preparation and Characterization of Macroporous Hydrogels from Copolymers Networks*

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### ABSTRACT

*New hydrogels based on (MAA) and (NVP) copolymers crosslinked with (BAA), were prepared by free radical cross-linking copolymerization, with a NVP percent molar composition of 10, 47.5 and 85. These hydrogels have been characterized by (FTIR), (SEM), (TGA /DSC) coupling. The results show four steps of degradation. The degradation rate is inversely proportional to the mole percent of NVP, and SEM shows that the hydrogels have a pore size between 7.14 to 13.33  $\mu\text{m}$ .*

**Key words:** *Hydrogels, Thermal Stability, Carboxylic Acid, FTIR, Scanning Electronic Microscopy.*

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### INTRODUCTION

Hydrogels are three-dimensional networks which can be obtained by polymerization of monomers having functional groups or by chemical modification of precursor polymers [1, 2]. These hydrogels are generally crosslinked materials containing hydrophilic functional groups, such as carboxylic acids, amines and hydroxyls which are capable of absorbing large quantities of water [3, 4]. Among the many methods of hydrogel characterization which have been implemented by researchers, we used FTIR spectroscopy, SEM (scanning electronic microscopy), and DSC (differential scanning calorimetry). Huma et al synthesized Poly (N-vinyl pyrrolidone-co-n-butyl methacrylate) crosslinked with Diethylene glycol dimethacrylate (DEGDMA) and trimethylol propane tri-methacrylate (TMPTMA) [5]. The morphology of the crosslinked copolymers were investigated by SEM, these micrographs show that the porosity of hydrogels was responsible for a higher degree of solvent swelling. The micrographs of copolymers crosslinked by DEGDMA decrease with increasing cross-linker concentration. Chen prepared the trimethylchlorosilane/hydrogel with the average pore size (10.7 nm) [6]. TGA, DTA and DTG of these polymers, show an initial loss of 8.7% weight up to 100°C corresponding to evaporated water. For the thermal decomposition of the crosslinked polymer matrix at 168 °C and 593 °C, this produces loss of 85.3% weight. DSC curves of TG and TG-cl-(PVP-co-PAMPSA) have peaks at 200 °C of polymer matrix. Angar studied the rheological behavior of poly (acrylamide-co-itaconic acid) hydrogels [7].

### MATERIALS AND METHODS

The materials used include Methacrylic acid (MAA), N-vinylpyrrolidone (NVP), Bisacrylamide (BAA) (Sigma–Aldrich, USA), initiator Potassium persulfate (KPS) (Sigma–Aldrich, USA), and solvent Methanol (Shanghai Chemical Group, China).

The samples were analyzed using FTIR spectroscope IFS66 in the region of 4000–400 $\text{cm}^{-1}$ . Prior to the measurement, the samples were dried under vacuum until reaching a constant weight. The dried samples were

pressed into the powder, mixed with 10 times as much KBr powder, and then compressed to make a pellet for FTIR characterization.

SEM was used to investigate the morphology of the prepared hydrogel. Measurements were taken on a ZeissDSM982G with acceleration of 20 kV.

For thermal properties "aniabsis 204 Phoenix" thermal apparatus was used with nitrogen flow (12 mL/min). In thermogravimetric analysis, polymer samples were heated from room temperature to 800°C at a rate of 5 K/min.

## Methods

### Synthesis of poly [(MAA-co-NVP)-cross-BAA]

Poly (MAA-co-NVP) hydrogels were synthesized by copolymerization in solution of methacrylic acid and N-vinylpyrrolidone monomers crosslinked with bisacrylamide were dissolved in water (5ml), by using potassium persulfate (PPS) as an initiator and nitrogen atmosphere then the reaction system was kept at 60°C, between (2h-3h20min). Three different copolymers were obtained with NVP percent molar composition of 10, 47.5 and 85, shown in Table1.

**Table 1.** Experimental conditions of radical copolymerization MAA and NVP with BAA (solvent: water, temperature 60°C and initiator PPS)

Hydrogels	MAA (mol%)	NVP (mol%)	BAA (mol%)	PPS (mol%)	Eau (ml)	T °C	time
Poly[(MAA-co-NVP)-cross-BAA]	47,5	47,5	5	4	4	60	2h
	85	10	5	4	4	60	3h20min
	10	85	5	4	4	60	1h30min

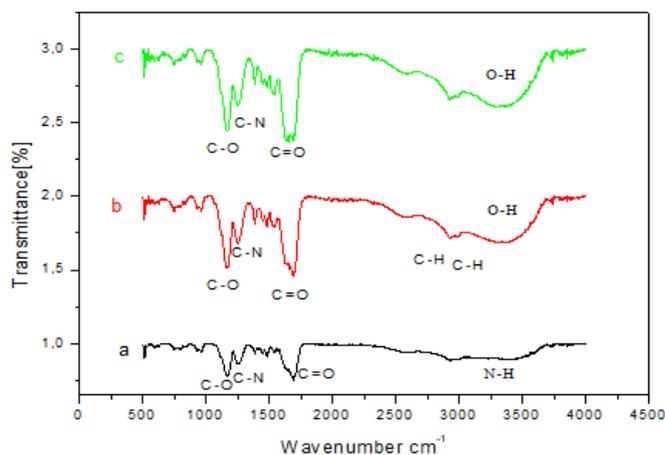
### Purification of the Poly ((MAA-co-NVP)/cross BAA) hydrogels

The poly ((MAA-co-NVP)/cross BAA) hydrogel was immersed in water to remove the extractables for 5 days, then removal of water by methanol for 6 days. The purified hydrogels were first dried at room temperature for 1 day at 60°C under vacuum for another 3 days.

## RESULTS AND DISCUSSION

### FTIR analyses

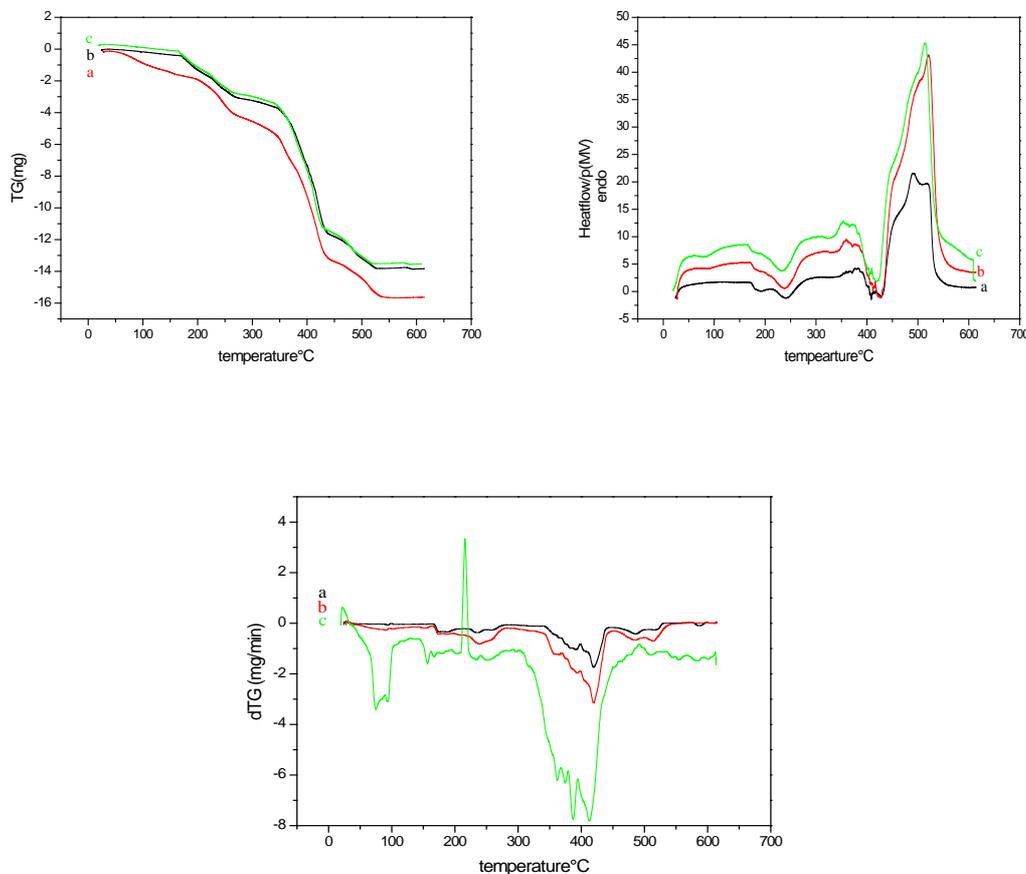
The structure of poly (MAA-co-NVP/cross-BAA) was characterized by FTIR as shown in Fig.1: exhibiting the characteristic band at 3410  $\text{cm}^{-1}$  which was attributed to water (O-H), a band at 3286  $\text{cm}^{-1}$  corresponding to the N-H of bisacrylamide or O-H of methacrylic acid, a band at 2932  $\text{cm}^{-1}$  corresponding to the C-H of the  $\text{CH}_3$  groups, a band at 1686  $\text{cm}^{-1}$  corresponding to the C=O bond of NVP, a band at 1636  $\text{cm}^{-1}$  corresponding to the C=O of methacrylic acid, a band at 1254  $\text{cm}^{-1}$  corresponding to the C-N bond of bisacrylamide, and a band at 1166  $\text{cm}^{-1}$  corresponding to the C-O bond of methacrylic acid.



**Figure 1.** FTIR spectra: (a)-Poly [(MAA-co-10%NVP)-cross-BAA], (b)- Poly (MAA-co-47.5 % NVP)-cross-BAA], (c)- Poly (MAA-co-85 % NVP)-cross-BAA]

### Thermal analyses

Fig.2. gives the thermograms (TGA /DSC). In the first step, mass is lost due to regions with a low degree of crosslinking within hydrogel which is converted to the oligomers according to Table2. In the first step, we have a total degradation of hydrogel in the form oligomers (Table 3).



**Figure 2.** Thermograms (TGA-DTG/DSC) coupling of (a)-Poly [(MAA-co-10%NVP)-cross-BAA], (b)- Poly[(MAA-co-47,5 % NVP)-cross-BAA], (c)- Poly[ (MAA-co-85 % NVP) -cross-BAA].

**Table 2.** Degradation rate, Melting temperature and DTG of hydrogels in the first step

Hydrogels	Degradation rate %	Temperature Interval C°	Melting temperature C°	DTG (mg/min)
10%NVP	21.41	175 à 281	192	-0.30
47.5%NVP	12.50	178 à 290	244	-0.45
85%NVP	10	101 à 320	318	-0.10

**Table 3.** Degradation rate, Melting temperature and DTG of hydrogels in the second step

Hydrogels	Degradation rate %	Temperature Interval C°	Melting temperature C°	DTG (mg/min)
10%NVP	64.28	368 à 444	247	-0.38
47.5%NVP	58	345 à 441	330	-0.78
85%NVP	54	325 à 480	-	-

Table 2 and 3 show that the degradation rate is inversely proportional to the mole percent NVP, which confirms the allow degree of crosslinking within hydrogel variants to the function NVP. We also note that temperature interval is proportional to mole percent NVP, the latter gives a thermal stabilization important for hydrogels. DSC thermograms of this hydrogel show that the melting temperature values are proportional to the mole percent NVP. These results suggest that the increase of the melting temperature of hydrogels is related to the content of NVP.

In the last step, degradation of the oligomers in the form of small gas molecules takes place. The positive sign of the melting kinetic (DTG) confirms that the degradation of oligomers reacts with the nitrogen gas of the

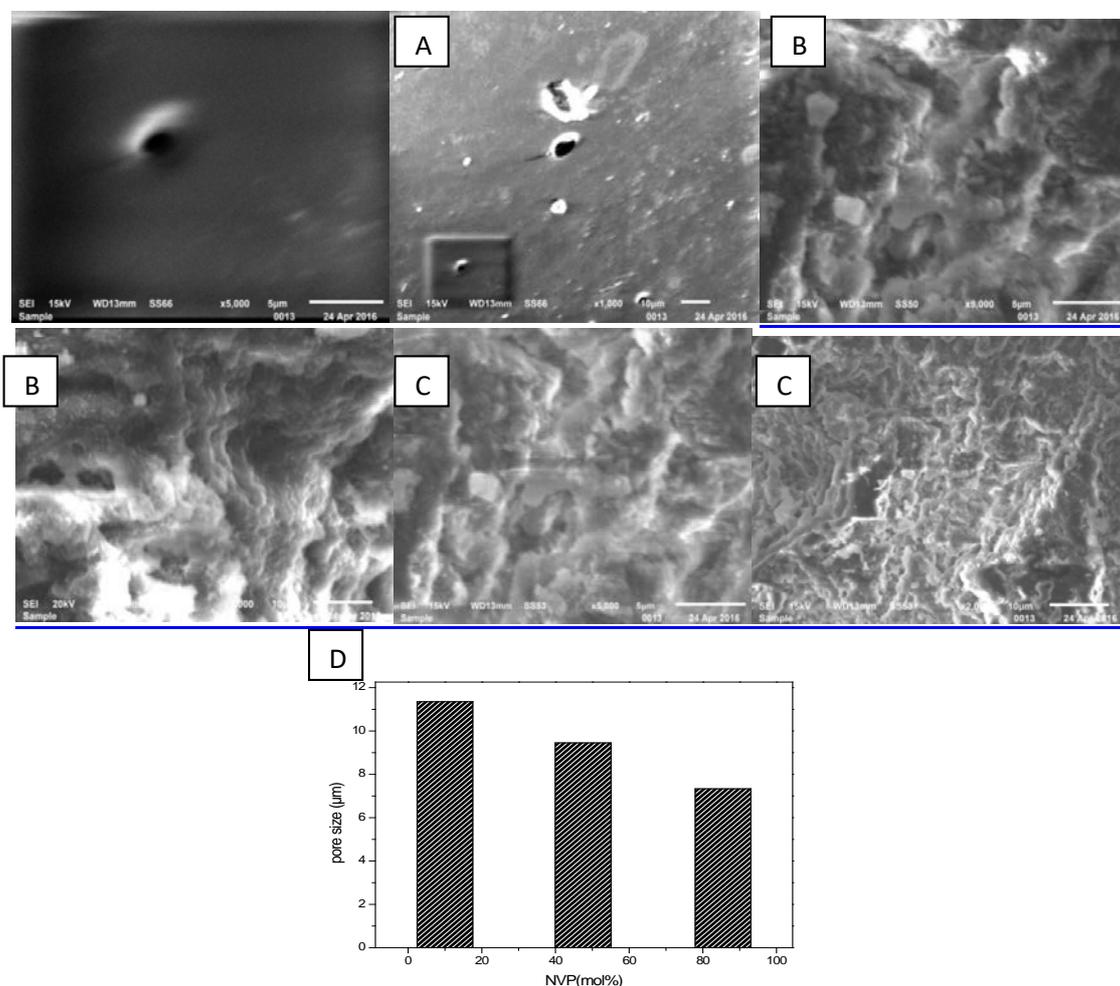
apparatus. We found that the degradation rate (small gas molecules) is proportional to the mole percent NVP according to Table 4.

**Table 4.** Degradation rate, Melting temperature and DTG of hydrogels in third step

Hydrogels	Degradation rate %	Temperature Interval C°	Melting temperatureC°	DTG(mg/min)
10%NVP	14.30	460 à 525	-	-
47.5%NVP	21.50	450 à 535	-	-
85%NVP	25.18	500 à 595	508	+0.20

**Morphological analyses by SEM**

The SEM images of poly (MAA-co-NVP)-cross-BAA] polymers in Fig.3, showed that the surfaces of the poly [(MAA-co-NVP) cross-BAA] hydrogels (47.5; 85 mole% NVP) show irregular surfaces with a rough and compact appearance. The hydrogels have macroporous structures. The morphology of the hydrogel surface poly (MAA-co-10%NVP)-cross-BAA] is shown in photo (A) which has a homogeneous porous surface, with an average pore diameter 13.33µm. The average pore diameter of poly [(MAA-co-47.5%NVP-cross-BAA] hydrogels is around 10 µmin photo (B). The average pore diameter of poly [(MAA-co-85%NVP)-cross-BAA] hydrogels is approximately 7,14µm in photo (C). After the results were obtained from the pore diameters, the latter is inversely proportional to the molar ratio of NVP [8] in photo (D), which confirms the previous results obtaining the swelling ratio [9, 10].



**Figure 3.** Scanning electron microscopy (SEM) of (A)-Poly (MAA-co-10%NVP/cross 5% BAA), (B)- Poly (MAA-co-47,5 % NVP/cross 5% BAA), (C)- Poly (MAA-co-85 % NVP/cross 5% BAA), (D) pore size values As a function of molar ratio of NVP

**CONCLUSION**

Novel and super-swelling hydrogels of poly [(MAA-co-NVP)-cross-BAA], underwent thermal analyses. Four steps of degradation were obtained, the degradation rate is inversely proportional to the mole percent NVP. The SEM images showed that the hydrogels have macroporous structures averaging pore diameters between 7.14 to 13.33 $\mu\text{m}$ .

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