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Preparation, Characterization of some new amino resin and Their copolymers as pH sensitive Hydrogel

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ABSTARACT

Four new Amino resins were prepared by condensation reaction between dimethylol acryl amide with diethylene triamine, 1,2-diamino propane, ethanol amine and ethylene diamine. The new resins were characterized by FTIR, UV and NMR spectroscopy techniques. Several copolymers were prepared from the new resins with Acryl amide via redox polymerization method which used (Ammonium per sulfate/ tetra methyl ethylene diamine) as initiator. The swelling ratio for all copolymers was measured as a function of pH and the obtained data reveals that the new copolymers are pH-sensitive hydrogels.

INRTODUCTION

pH sensitive polymer networks consist of a backbone polymer carrying weak acidic or basic groups. The backbone polymer provides a mechanical stability of the gel, whereas the ionizable group contributes to the pH sensitivity. As mentioned such synthesis can be performed as a cross linking polymerization, which is simultaneously synthesizing polymer chains and linking them concomitantly(1). On the other hand in a typical pH-sensitive polymer, protonation/deprotonation events occur and instruct the charge over the molecule (generally on carboxyl or amino groups), therefore it depends strongly on the pH. The pH induced phase transition of pH-sensitive polymer tends to be very sharp and usually switches within 0.2-0.3 units of pH (2).

For hydrogel containing acidic groups bound to their polymer chains, the H^+ comes off in basic solutions and combines with OH^-. Charge neutrality is maintained the increased cation concentration gives rise to an osmotic pressure that causes the gel to swell/deswell(3) . Hydrogels have been applied heavily as biocompatible material and used in a variety of applications, such application are contact lenses, drug delivery systems, medical grafts, skin replacements, and as pH sensor for monitoring the corrosion(4-6). Responsive hydrogel networks may be formed by various techniques; however the most common synthetic route is the free radical polymerization of vinyl monomers in the presence of di-functional crosslinking agents and swelling agents. The major disadvantage with hydrogels is their relatively low mechanical strength but this can be overcome by cross linking, by forming interpenetrating networks, or by crystallization that induces crystallite formation and drastic reinforcement of their structure(4).

The water content of synthetic hydrogels is controlled by the structure of the polymer, and with appropriate constituent monomers, can be made responsive to environmental factors such as pH, salt concentrations, temperature, and electric fields(7). If an ionic or hydrophobic monomer is incorporated into the hydrogel network, are responsive polymer is often created. This responsiveness takes the form of volume phase transition characterized by a sudden change in the degree of swelling upon small changes in the environmental conditions. In order to understand the swelling the swelling phenomenon in gels forces exerted on the gel must be examined. These forces include polymer-polymer affinity, hydrogen ion pressure, and rubber elasticity. The total pressure is the sum of all these forces and is called the osmotic pressure. The osmotic pressure determines whether the gel tends to take up fluid or expel it. Polymer-polymer affinity is a result of interactions between the polymer strands and the encompassing solvent and is a function of solvent concentration and the volume of the gel.

In the case of pH-sensitive hydrogels, the solvent is considered to be the water surrounding the hydrogel. These forces can either be attractive or repulsive depending on the electrical properties of the hydrogel molecule. In an attractive interaction, the polymer can reduce its overall energy by surrounding itself with more solvent molecules, whereas if the interaction is repulsive the solvent is expelled. This phenomenon explains how hydrogen ion concentration of the solvent (water) affects the tendency of the gel to absorb or discharge the surrounding solvent. Hydrogen ion pressure associated with the ionization of the polymer network, releases an abundance of positively charge hydrogen ions (H^+) into the gel fluid. If these ions are the only charge present they will strongly repel each other. However, the positive ions are immersed in a sea of negative charges attached to the polymer network and therefore the gels a whole maintains exact electrical neutrality.

The rubber elasticity of the hydrogel determines the ability of the hydrogel to expand and contract with the changing forces these material characteristics is affected by the degree of cross linking and temperature.

The changing balance of the free opposing forces results in the observed phase transition. The concept that whenever possible the gels will adjust its volume so that the total osmotic pressure is zero, gives phase transition hydrogels the properties essential for pH sensing applications. If the osmotic pressure is initially positive, the gel takes up fluids. If the pressure is negative, the gel expels fluid and shrinks. This course continues until the total of all three forces reach equilibrium. Time to reach equilibrium and mechanisms of dynamic swelling are affected by migration of residual ionic initiators and the difference between the inside and the outside of the gel(4).

2. MATERIALS AND EXPERIMENTAL

2.1 Materials

Ethanolamine, ethylenediamine, 1,2-diaminoprapane, diethylenetriamine, dimethyl formamide were supplied by Fluka Co. , Absolute ethanol, N, N, N', N'-tetra methylenethylenediammine were supplied by GCC Co. , phosphoric acid, sodium bicarbonate were supplied by H&W Co. and Acryl amide, ammonium persulfate ,methylene bis acrylamide were supplied by BDH Co.

2.2 Preparation of amino resins (A and B)

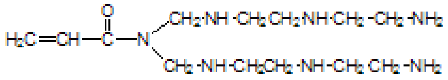
The reaction was carried out in 100ml three neck flasks fitted with stirrer, dropping funnel and condenser. The reaction vessel was charged with 2.06g (0.02mole) of diethylene triamine in (50±5°C), and then dimethylol acryl amide1.31g (0.01 mole) was added drop wise over a period of one hour ((Dimethylol acryl amide was prepared via the reaction between acryl amide and formaldehyde in alkaline medium(8))). After end of addition, the temperature was raised to (100±5°C) maintained at this temperature for three hours, at the end of reaction the product was dissolved by (DMF) and dried at (70±5ºC) under vacuum 0.1mmHg, the purification process repeated for three times, and the product kept away from atmosphere (hygroscopic) . The resins B and D were prepared as same as (A). To prepared the new resin (B) was used dimethylol acrylamide with 1,2-diamino propane and to prepared the new resin (D) was used dimethylol acryl amide with ethylene diamine.

2.2 Preparation of amino resins (C)

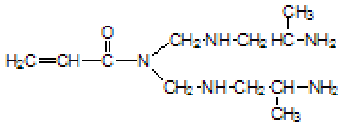
The reaction was carried out in 100 ml three neck flasks fitted with stirrer, dropping funnel and condenser. The reaction vessel was charged with 1.22g (0.02mole) of ethanol amine with 1ml concentrate phosphoric acid, and then dimethylol acryl amide1.31g (0.01mole) was added drop wise over a period of half hour at (50±5ºC). After end of addition, the temperature was raised to (135±5ºC), and maintained at this temperature for five hours, at the end of reaction, the excess of ethanol amine was distilled under vacuum, the product was cooled, and neutralized by 10% sodium bicarbonate, then dissolved by ethanol absolute, filtered from salts, then dried, the purification was repeated for three times, then dried under vacuum of 0.1mmHg at (80±5ºC) for 24 hours. The structures of the new amino resins are shown in Table (1):

Table (1): The chemical structures for the new amino resins

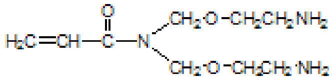
A



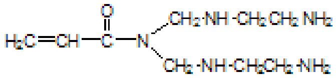
B



C



D



2.3 Characterization of the new resins

The new amino resins were characterized by FTIR as a viscous solution by using sodium chloride disc, FTIR spectrum is shown in figures (1), the select stretching vibration band of the representative groups of each resins are shown in table (2**).**

Table (2): The important characteristics FTIR stretching and bending vibration band for the new compounds

Comp.	**Asy N-H**	**Sym N-H**	**C-H**	**C=O**	**C=C**	**C-N**	**C-H bend**	**N-H bend**	**C-O**
A	**3450**	**3350**	**2948-2835**	**1675**	**1550**	**1309**	**1450**	**1675**	**1049**
B	**3450**	**3400**	**2970-2950**	**1666**	**1577**	**1217**	**1413**	**1666**	**1050**
C	**3450**	**3350**	**2950-2900**	**1575**	**1550**	**1300**	**1384**	**1650**	**1050**
D	**3400**	**3280**	**2952-2887**	**1650**	**1546**	**1234**	**1407**	**1650**	**1047**

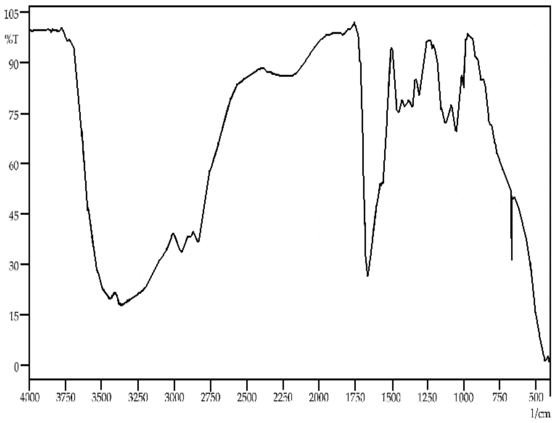
The UV measurements were carried out for the solutions of the additives in distilled water. The assigned UV spectra were analyzed and the max wavelength **λ_{max}** were obtained. Figure (2) illustrate the distinguishing UV absorbance peaks for the prepared compounds.

NMR spectroscopy can be explained the structure of organic compounds by giving the good information about the functional groups which that contains hydrogen, and carbon atoms. Figures: (3) to (5) represent NMR spectra for some of new amino resins and the important position can be explained in Table (3).

Table (3): reprehensive the important NMR position.

Sample	**δ_{CH2} ppm**	**$\delta_{=CH}$ ppm**	**$\delta_{=CH2}$ ppm**	**δ_{N-H} ppm**
A	2.40* 2.70 2.90	4.00	3.80	1.60
C	2.30§ 2.50 2.90**	3.80	3.70	2.70
D	2.80 1.50***	3.8	3.0	1.70

(*) This value belongs to (–CH_2-) group that attached with acryl amide group in A compound.
(§) This value belongs to (–CH_2-) group that attached with acryl amide group in C compound.
(**) This value belongs to (–CH_2-) group that attached with oxygen atom for C compound.
(***) This value belongs to (–CH_2-) group that attached with acryl amide group in D compound.



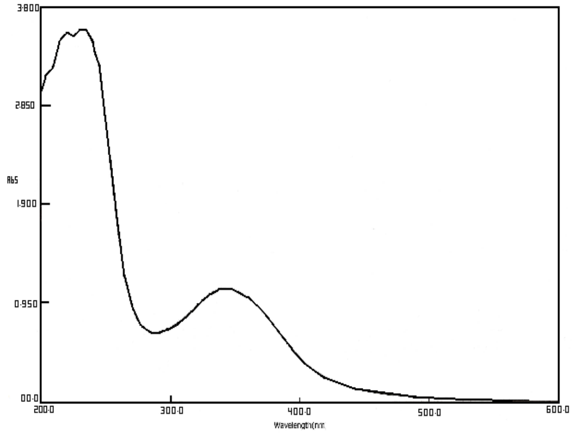


Fig.(1): The IR spectrum for the resin A **Fig. (2)** : The UV spectrum for the resin A

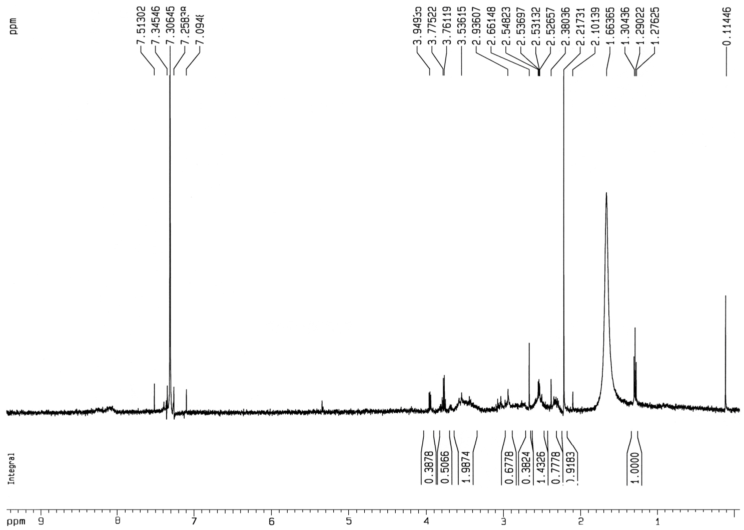


Fig. : (3) : The NMR spectrum for the resin A

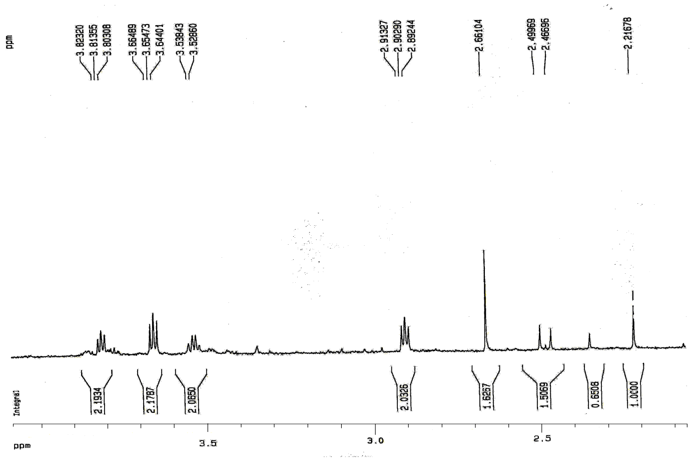


Figure (4): NMR spectra for compound C for region (0-4) ppm

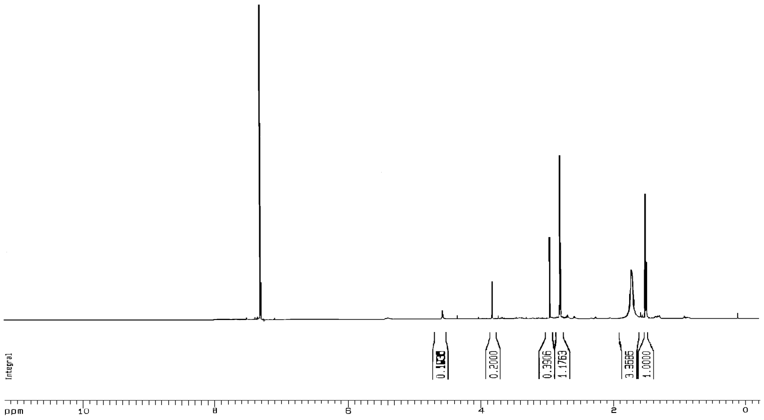


Figure (5): NMR spectra for compound D

The obtained analysis data were in good agreement with the FTIR, UV and NMR confirming the expect structures of the new amino resins.

2.3 Preparation of copolymers (A1-A6):

1g acryl amide, 1g from the new resin (A) and 0.1g methylene bis acryl amide as cross linking agent were dissolved in 100ml distilled water then 1% Ammonium persulfate (10%w/v in distilled water) was added and mixed followed by addition (0.5%) N, N, N', N'-Tetra methyl ethylene diamines as accelerator to the initiation step of polymerization process with stirring for several few minutes to complete the polymerization reaction. The other copolymers for other new amino resins [such as (B), (C), and (D)] were prepared as same as amino resin (A). Table (4) shows the quantities that used in the preparation of the polymer gels:

Table (4): The composition of the prepared copolymer

Sample No.	ACAm (g)	A (g)	MBAcAm (g)	H_2O(g)
A1	1.0	1.0	0.1	100.0
A2	2.0	1.0	0.2	100.0
A3	3.0	1.0	0.3	100.0
A4	1.0	1.0	0.2	100.0
A5	2.0	1.0	0.3	100.0
A6	3.0	1.0	0.4	100.0

AcAm= Acryl amide MBAcAm = N, N, N', N'-Tetra methyl ethylene diamines

6.8.2-Swelling studied as a function of pH:

The dried new hydrogels were equilibrated in the buffer solution pH (1-10) for 24 hours then they were removed from the buffer solution, tapped with filter paper to remove excess water, and weighted. The swelling ratio (Q) is defined as:

$$Q= (W_s-W_d)/W_d$$

Where: W_s is the weight of swollen hydrogel and W_d is the weight of the dried hydrogel. Figures (6) to (9) shows that the swelling ratio (Q) as a function of pH.

3. RESULTS AND DISCUSSION :

Several rate processes should be taken into account when investigating the swelling mechanism in pH-sensitive hydrogels. Ion diffusion, diffusion limited chemical reactions, ion migration, and consequently electrical and mechanical readjustments of the polymer network are some of the mechanisms that affect the swelling of the hydrogel(4) . These factors can be applied to study the swelling ratio (Q) as a function of pH for many hydrogels which were prepared from the new amino resins. The plots which that draw as a function of pH gives insight into the swelling response of these gels that mentioned in Figures (6) to (9). There were not any quantity of waters can be absorbed whereas the gels tends to be stable. The study of swelling ratio as a function of pH for example for gel (A1) illustrates a sudden decrease in water absorption between pH=2 and pH=8 because the reaction of this gel was very sensitive to swelling. This experimental data can be used to verify performance of coating candidates that responsive to pH and compatible with the long period grating sensor element. In other words the gel (A1) swelling in acidic medium and shrinking in basic medium therefore any acidic environment or basic environment can be sensed by gel (A1) as sensor for pH in both media (acid and base). Also the pH of the environment for gels (A1), (A2), and (A3) have not affected on the time of immersion, it was shown that increasing the acryl amide ratio leads to give the reverse behavior i.e. increasing the swelling ratio in basic medium and decreasing in acidic medium because the migration of the ions(4) due to hydrolysis of amide groups in basic medium to carboxylate groups (anions) that leads to decreasing in the positive charged on hydrogel then the hydrogel swell in limit period, after these manner repulsion force between water and hydrogel increase.

In same way other hydrogel can be studied, the increasing of crosslinking agent concentrations can be considered as important factor which has an effect on swelling ratio for the gels. For example the comparison between gel (A1) and (A4) shows high swelling ratio for gel (A1) than (A4) whereas as the cross linking concentration in A1 is 1% of acryl amide while in case A4 is 1% of (acryl amide + amino resin A) as shown in Table (4). Therefore although (A1) and (A4) have the same behavior in swelling and shrinking but the swelling value for (A1) was higher than its value for (A4) and the decreasing range for (A1) gel was higher than that for (A4) due to increasing in the crosslinking agent concentration, and that may be leads to decrease the pore size which absorbed water, also cause a less diffusion chemical reaction for the group that ready to form positive charge (protonation), more of that it was presses less polymer interaction forces**(4)**. According to the results these gels can be using as pH-sensitive hydrogel for monitoring the corrosion in alloys like carbon steel and brass as well as in metals. The swelling ratio (Q) was studied as a function of time at constant pH by using three pH values that include 2, 7, and 9 respectively, at constant pH=2, QB4 has higher swelling ratio (Q=24) than other hydrogels, but at constant pH=7, QD5 has higher swelling ratio other than hydrogels that formed (QD5=13) , while at pH=9 (QC3=9.25) has higher swelling ratio values, from all these higher value QB4 has higher swelling ratio after of 25 hours of immersion for all hydrogels. The crosslinking agent concentration has affect on swelling ratio, where, for the case of QB4 the concentration of crosslinking agent is (2%) for (acryl amide + resin B), while in case of QB1 the concentration of cross linking agent is (1%) for only acryl amide, but B1 hydrogel is formed from equal quantity of (acryl amide + resin B), at pH=2 QB4>QB1, where QB1=6, the increasing in crosslinking agent concentration leads to increase the protonated center that increased the swell position for both amino groups in resin B and the positive carbon atom in the amide groups that formed by protonation process for the carbonyl groups in amide groups which attract more water molecules in acidic medium(pH=2) this effect in case of B4 higher than in B1. the effect of pH changing on swelling ratio(Q) reveals that QC5 has higher value compared with other hydrogels (QC5=55) at pH=10, where in case of C5 hydrogel consist of (2 acryl amide + 1 resin C+ 3% of both acryl amide and resin C as concentration for crosslinking agent) , in case of QC5 hydrolysis of amide groups in basic medium (pH=10) to carboxylate anions that attract the water molecules as ammonium cations that formed from solvated ammonia which hydrolyzed in basic medium from amide groups in aqueous solutions. At pH=1 the higher swelling ratio is (QD6=17). These values can be interpreted also depending on the ratio of acryl amide and crosslinking agent as in above.

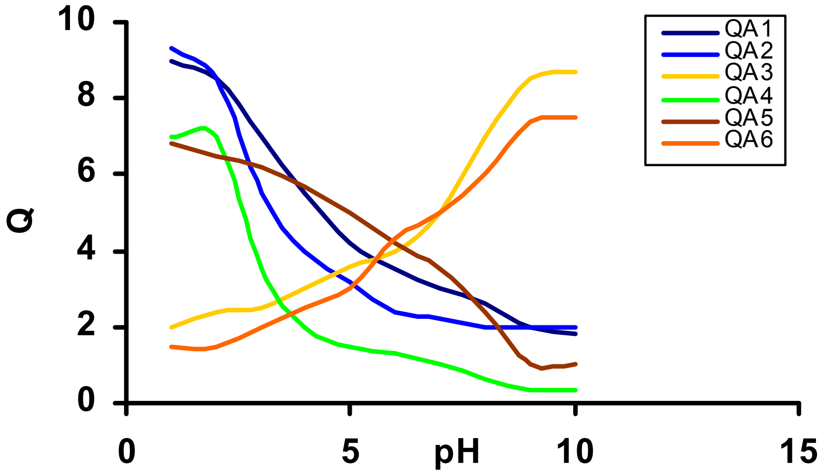


Figure (6): swelling ratio (Q) as a function of pH at time constant for (A) hydrogels.

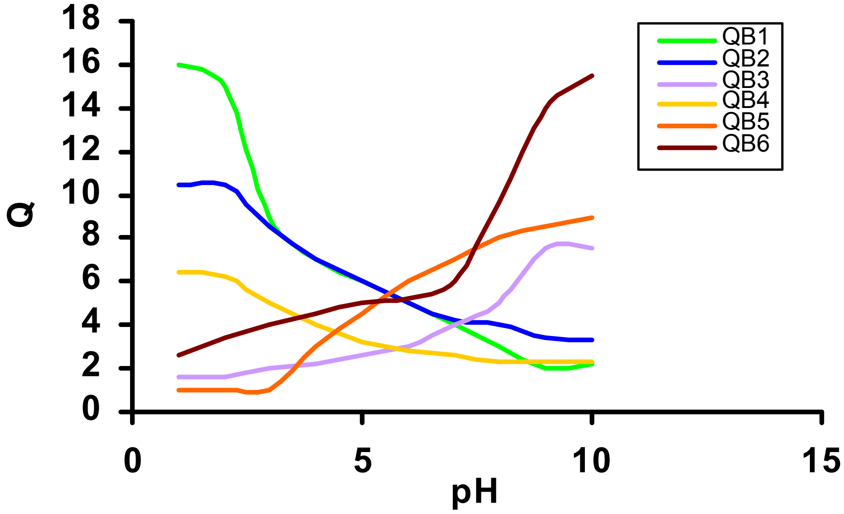


Figure (7): swelling ratio (Q) as a function of pH at time constant for (B) hydrogels.

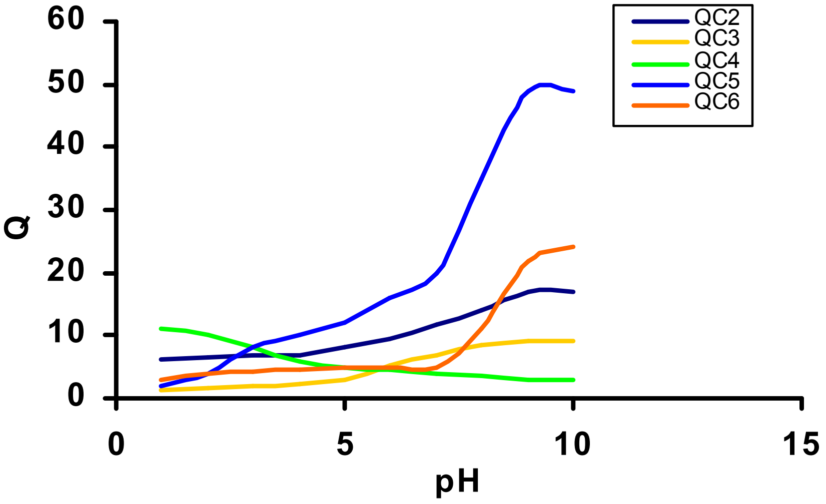


Figure (8): swelling ratio (Q) as a function of pH at time constant for (C) hydrogels.

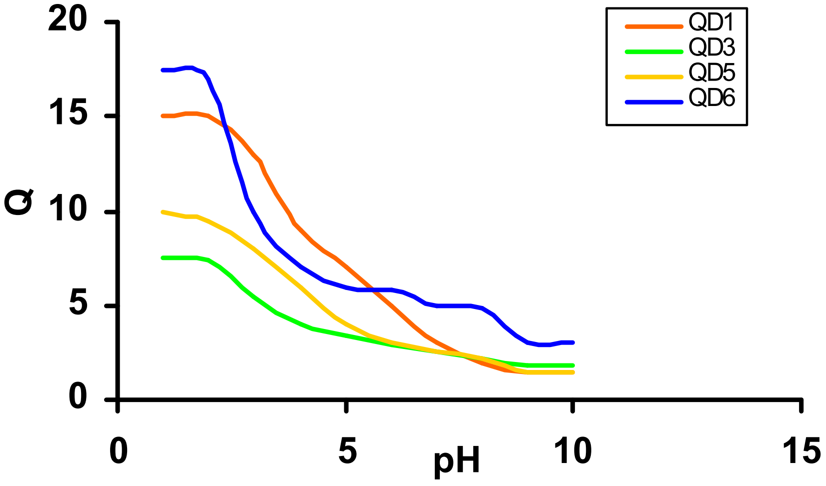


Figure (9): swelling ratio (Q) as a function of pH at time constant for (D) hydrogels.

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الخلاصة

حضرت أربع راتنجات امينية جديدة بالتفاعل التكثيفي بين ثنائي مثيلول اكريل امايد مع أربع أمينات مختلفة. شخصت الراتنجات الجديدة بمطيافيات الأشعة تحت الحمراء وفوق البنفسجية والرنين النووي المغناطيسي وأثبتت النتائج صحت التراكيب المتوقعة. حضرت بعد ذلك العديد من الكوبوليمرات باستخدام هذه الراتنجات الجديدة مع الاكريل امايد بطريقة بلمرة الأكسدة-الاختزال باستخدام البادئ المكون من الامونيوم بير سلفيت مع رباعي مثيل اثيلين ثنائي الأمين .قيست نسب انتفاخ الكوبوليمرات الجديدة كدالة للزمن والدالة الحامضية وبينت النتائج ان هذه الكوبوليمرات هي من نوع البوليمرات الهلامية الحساسة للدالة الحامضية .