Influence of Gamma Radiation on physicochemical properties of Polyacrylamide in ethylene glycol at room temperatures

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Abstract

The aim of this work is to study the effect of gamma radiation on some rheological and optical properties of Polyacrylamide in ethylene glycol. The polymer irradiated with gamma rays to 127 and 254 (rad/min) for 10 minutes on a disk shape samples.

The rheological parameters (shear, Relative, specific, reduced, and Intrinsic viscosity), Average viscosity number molecular weight and Effective molecular radius, in addition, the optical parameters Absorbance, refractive index, Molar absorption coefficient, Reflectivity, Coefficient of finesse and Specific reflectance were studded.

The obtained results show decrease in (shear-relative-specific-reduced) viscosities, average viscosity molecular weight, original viscosity on other hand there is disparity in the values of effective molecular radius, absorption coefficient, refractive index, reflectivity coefficient of finesse, and specific reflectance as the dose increases.

The results show that radiation dose has effective influence on polymer chemical structure therefore its properties will be a function of radiation dose.

Introduction

Polyacrylamide is called PAAM for short, has several commercial applications in ethylene glycol. It was therefore worth-wile to obtain information about its behavior in ethylene glycol solutions [1,2]. It is a water-soluble high polymer and widely used in water treatment, petroleum, textile, paper-making, metallurgical, and other environment protection fields. There are totally three categories of PAAM: Anionic PAM, Cationic PAM and Non-ionic type. It is a synthetic, potassium-based, long-chain polymer, designed to attract either positively charged particles or negatively charged particles. It used to flocculate and coagulate suspended solids in water, wastewater, and soil. As described above, there are innumerable varieties of "PAAM", not just one. They were created to bring materials together to coagulate or flocculate suspended solids in order to extract them from water and wastewater or to reduce soil movement (erosion). They keep water cleaner, save soils, and keep certain

nutrients, pathogens, and pesticides from field and feed lot runoff. Polyacrylamide was first used during World War II by the US military for stabilization of newly built runways. PAAM was first used commercially in irrigated agriculture in the US in 1995. By 2001, over two million acres of farmland were being treated with PAAM. These products have very specific application methods and rates. They must be applied as recommended. In some instances, over application may actually decrease the performance of the product. When applied properly, PAAMs are extremely efficient and very cost-effective [7].

Polyacrylamide (PAAM), are polymer-based materials used to facilitate erosion control and decrease soil sealing by binding soil particles, especially clays, to hold them on site. In addition, these types of materials may also be used as a water treatment additive to remove suspended particles from runoff. PAAM increases the soil's available pore volume, thus increasing infiltration and reducing the quantity of storm water runoff that can cause erosion. Suspended sediments from PAAM treated soils exhibit increased flocculation over untreated soils. The increased flocculation aids in their deposition, thus reducing storm water runoff turbidity and improving water quality. PAAMs may be used as a water treatment additive to remove suspended particles from runoff. PAAMs may also be used to provide an appropriate medium for the growth of vegetation for further stabilization [3].

Usage of polyacrylamide make up dilute solution base on the trial first, usually 0.1%-0.5%. When make up dilute solution, try best to use water which is neutral. And the temperature is between 50-60^{o}C.

If used PAAM as flocculation agent it is necessary to select type and size of PAAM series products according to treated substance [6].

(1) Anionic PAM is suitable for higher density, inorganic suspension substance with positive charge.
(2) Cationic PAM is suitable for suspension substance with negative charge and containing organic substance.
(3) Non-ionic PAM is suitable for separating mixed organic and inorganic suspension; the solution is neutral or acid. [6]

All polymers increase the viscosity of the solvent in which they are dissolved. This increase allows for a convenient method of determining the molecular weight of polymers. Since the viscosity method is not based on rigorous physical laws, it must be calibrated by standards of known molecular weight with narrow molecular weight distributions. Several important viscosity functions are used in viscosity studies [3].

Extrapolation to zero polymer concentration is intended to eliminate polymer intermolecular interactions. As shown in Figure 1, the curves of both plots should be linear and have a common intercept that is the intrinsic viscosity.

The intrinsic viscosity (also termed the limiting viscosity number) should be independent of the fluid shear rate. In other words, the solution viscosities measured and used to find the intrinsic viscosity in the Huggins or Kraemer plots must be the "zero" shear viscosities determined in the low shear or first Newtonian regions of flow curves. A flow curve is a plot of apparent fluid viscosities versus shear rate. Each flow curve is experimentally determined using a fixed polymer concentration. If the polymer solution concentrations are low and the polymer molecular weights are also low, then the solution viscosities measured for the flow curve are constant or independent of the shear rate.

The solution viscosities measured under these conditions are first Newtonian viscosities or the "zero" shear viscosities. However, as the polymer concentration increases and/or the polymer molecular weigh increases, the flow curves become shear dependent or non-Newtonian. Usually, for non-Newtonian polymer solutions the apparent solution viscosity decreases as the shear rate increases. This type fluid is usually referred to as shear thinning or pseudo plastic fluid flow behavior. To minimize the unwanted shear thinning effect, it is desirable to operate a viscometer at low shear rates.

From polymer dilute solution viscosity experiments, many macromolecular characteristics of a polymer can be determined such as molecular weight and certain polymer hydrodynamic dimensions. These experiments are not time consuming and do not require expensive equipment.

The intrinsic viscosity measured in a specific solvent is related to the molecular weight, M, by the Mark-Houwink equation.

$[\eta] = K M^{a}$.

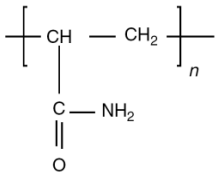
The fact that the intrinsic viscosity of a given polymer sample is different in different solvents gives one insight into the general shape of polymer molecules in solution. A long-chain polymer molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly curled mass (coil) and a rigid linear configuration. All possible degrees of curling may be displayed by any one molecule, but there will be an average configuration which will depend on the solvent. In a "good" solvent, one that shows a zero or negative heat of mixing with the polymer, the molecule is fairly loosely extended, and the intrinsic viscosity is high [3].

The measurement of the viscosity of polymer solutions is called viscometry and the apparatus used is called the viscometer [3].

A capillary viscometer is used to get a measure of the viscosity of very dilute polymer solutions. The solution is allowed to flow through a capillary of known diameter under the action of a pressure drop as a fully developed laminar flow and the time taken to flow through a given length is measured [4].

Experimental

1. Material:



polyacrylamide is [PAAm; 2-propenamide homopolymer [9003-05-08]; Cyanamer (American Cyanamid)] a Vinyl polymers class . Its major applications flocculants in water treatment, paper manufacture, mining, and oil recovery; absorbents; gels for electrophoresis[7].

polyacrylamide used in this work has a molecular weight region 5×10^5 to 6×10^6 g/mol by using osmosis pressure[5] ,it is dissolved Water, ethylene glycol, formamide, hydrazine, Nonsolvents Methanol, hydrocarbons, and other common organic liquids[5].

2. **Samples preparation:**

Using ethylene glycol, 10 different concentrations of each sample at room temperatures were prepared; the solutions were prepared by adding a known weight of the polymer to fixed volume of ethylene glycol.

3. **Density measurements:**

The densities of the solutions were determined using the density bottle 25 ml & electrical sensitive balance.

4. **Flow time:**

The values of flow times for all samples were measured by using Ostwld viscometer at room temperature with water bath.

5. **Absorbance**:

Using U-2000 spectrophtometer after scan the solvent peak value and fixing this wave length the absorbance of samples were measured for different concentration at room temperature as shown in Fig. (6).

6. **Refractive index (n):**

Using a digital refractmeter the values of all samples measured as shown in Fig (7).

7. **Irradiation method :**

The main source of (GAMMA) radiation with low dose rate irradiation ^{60}Co, about 127-254 (rad/min) 10 minutes on a disk shape samples, where used in order to obtain dose uniformly during the irradiation. The distance between the source and the sample was 80 cm.

Theoretical calculation

1- **Shear viscosity (η_s):**

These values were calculated for all samples, using the following relation (17):

$$\frac{\eta_s}{\rho_s t_s} = \frac{\eta_e}{\rho_e t_e} \quad (1)$$

Where; η_s and t_s are shear viscosity & flow time for the samples& (η_e, t_e) are the same parameters for ethylene glycol.(ρ_s,ρ_e) are the densities of each sample &ethylene glycol.
These values are shown in fig (1) for different concentration.

2- **Relative, specific & reduced viscosity (η_{rel}, η_{sp}, η_{red}):**

The above viscosities were calculated by using the following relations [17]:

$$\eta_{relative} = \frac{\eta_s}{\eta_e} = \frac{t_s}{t_e} \quad (2)$$

$$\eta_{specific} = \eta_{relative} - 1 \quad (3)$$

$$\eta_{reduced} = \frac{\eta_{specific}}{C} \quad (4)$$

Where: C is the sample's concentration.

3- **Intrinsic viscosity |η|:**

Plotting a graph for $\eta_{relative}$ against concentration of all samples had been drawn; the intercept with Y - axis of this graph is |η|.
The calculated values of |η| were tabulated in table (1).

4-Average viscosity number molecular weight (M_v):

An empirical equation is used to describe the intrinsic viscosity/molecular weight relationship, the Mark-Houwink equation,

$$|\eta| = KM_v^{\ a} \quad (5)$$

Where a and K g/cm^3 are constants for specific polymer/solvent/temperature.
The values of |η| had been taken from table (1), and the constants (K, a) are depended on polymer type. The value of the M_v of this polymer was calculated from following relation (5). $|\eta| = 13.6XM_v^{\ 0.54}$ the calculated values are shown in table (2).

5. **Effective molecular radius (r_{eff}):**

Using the equation from ref (11), the effective molecular radius of all samples was calculated.

$$r_{eff} = \sqrt{\frac{slope}{6.3 \times 10^{24}}} \quad (6)$$

Where the slop is for a graph plotted between $\eta_{reduced}$ and molar concentration of all samples as shown in table(3).

6. Molar absorption coefficient (a_e):

To calculate (a_e) of the samples, the following equation was used :

$$\frac{\log I_o}{I} = A = \frac{a_e}{C} \quad (7)$$

Where: I_o is the intensity beam of light special wave length.
I is the absorbed intensity of the same beam
A is absorbanc of the same absorbed beam.
L is the pathlength of the same absorbed beam.
C is molar concentration of the sample.

If we plot, A against C and if we substituted L=1 cm in the above equation which represent the thickness of the test tube or the distance of the electromagnetic waves which transmitted through the thickness of the test tube or distance of electromagnetic waves which transmitted through the solution.

$$\frac{A}{C} = a_e \qquad (8)$$

7- Reflectance (Re)

The reflectance can be calculated for all samples by using the following empirical equation [12]:

$$\mathrm{Re} = \left(\frac{n-1}{n+1}\right)^2 \qquad (9)$$

Where n is the reflective index.

8- Coefficient of finesse (F)

The coefficient of finesse**.** It is a measure of the interference fringe sharpness and contrast. These values were calculated for all samples, using the following relation[13]:

$$F = \frac{4\,\mathrm{Re}}{(1-\mathrm{Re})^2} \qquad (10)$$

Where Re is the reflectivity.

9- Specific reflectance (Rs)

The following equation can be calculated the specific reflectance[13].

$$Rs = \frac{1}{\rho}\frac{(n^2-1)}{(n^2+2)} \qquad (11)$$

Where ρ is the density and n is the reflective index.

Results & Discussion

All measured & calculated properties for all samples at different concentrations were shown in figures (1, 2, 3, 4, 5, 6, 6, 8, & 9) and tables (1, 2, 3, 4).

The results show that Gamma irradiation decreased the viscosity (figs.1-4) due to the cleavage of the polypeptide chains [16], and this decrease in the flocculation activity is attributed to a weakening of the inter particle bridging by a change from a strong adsorption of the bridging polymer to two particles to a strong adsorption of the bridging polymer to one particle but weak adsorption of the bridging polymer to the other particle.[15].

The color of polymer will be changed to light yellow with fission on the sample surface this because of production H_2, CO_2, NH_3 & other components[10].

The dependence of Optical properties (figs. 5-8 &Tabs.3,4)on absorbed dose showed two distinct regions which were associated with intramolecular cross-linking and chain scission (decrease), intermolecular cross-linking (increase). For a given polymer system, storage modulus showed a linear increase with absorbed dose (after a small induction dose), indicating the formation of additional cross links. The efficiency of cross-link formation could be correlated in terms of the critical concentration. The logarithmic decrement showed a sudden drop at low doses (the induction dose) and then leveled off with further irradiation indi-eating a rapid elimination of loose chain ends. [14]

After irradiation the value of specific reflectance (fig.9) increased with radiation; this because of penetration of ionizing radiation in the polymer & cross linking the chains caused by absorption of high energy radiation. The directly effect of ionizing radiation on Vinyl molecule in solid state lead to produce hydroxyl root, hydrogen peroxide hydrated electrons (10).

Conclusion

1- The effect of ^{60}Co source on Polyacrylamide yield decreasing in its molecular weight as reported.
2- Radiation Dose is important factor in polymer radiation, therefore it's properties will be a function of it .
3- The decreasing in molecular weight of this polymer after radiation may be useful to using this polymer in some low molecular weight polymers technology.

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Table (1)

Values of original viscosity before and after irradiation	
PAAM	$\|\eta\|$
Before irradiation	74.6173
127 rad/min	51.33
254 rad/min	41.17

Table 2

values of average viscosity molecular weight for PAAM before and after irradiation	
PAAM	M_v average molecular weight
Before	119074.8937
127(rad/min.)	59144.14667
254(rad/min.)	39311.72903

Table 3 effective molecular radius for before and after radiation

PAAM	Slope $\frac{\eta_{sp}}{C}$	effective molecular radius
Before irradiation	647.8	1.01403*10-11
127(rad/min.)	482.8	8.75414*10-12
254(rad/min.)	611.5	9.85208*10-12

Table 4: Molar absorption Coefficient for Polyacrylamide in ethylene glycol

Solvent	**Molar absorption Coefficient**
before irradiation	2.67
127 rad /min	0.979
254 rad /min	2.066

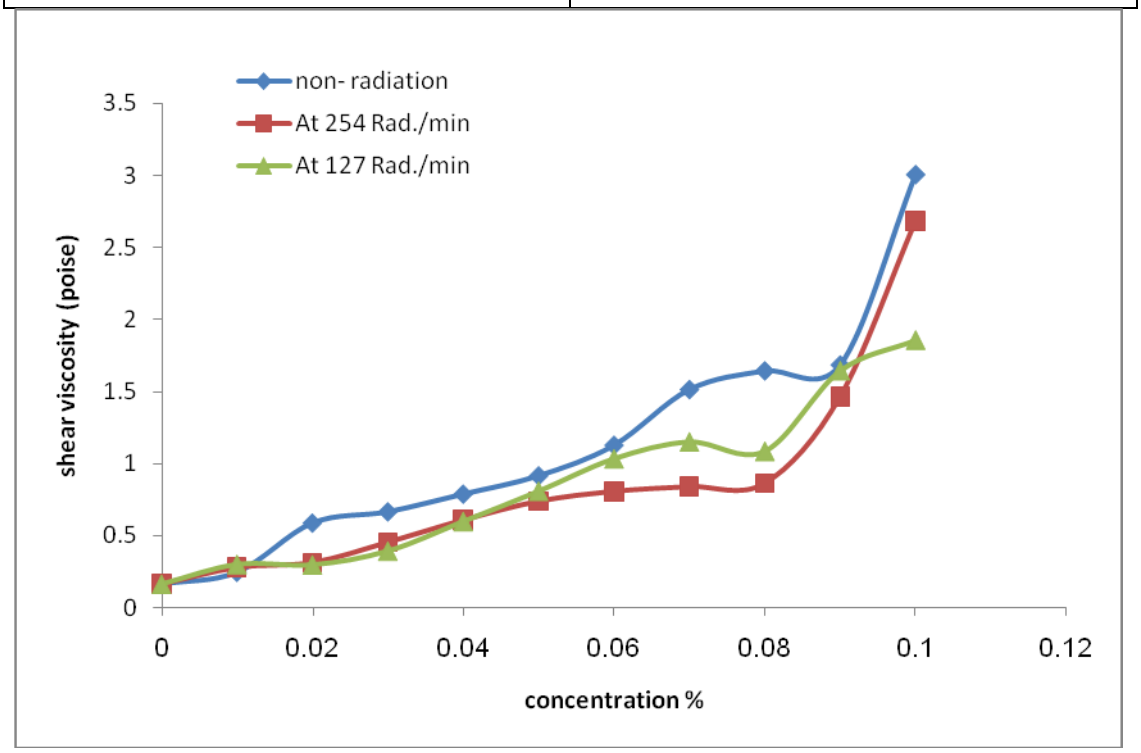

Figure 1: shear viscosity changed with concentration for PAAM in Ethylene glycol.

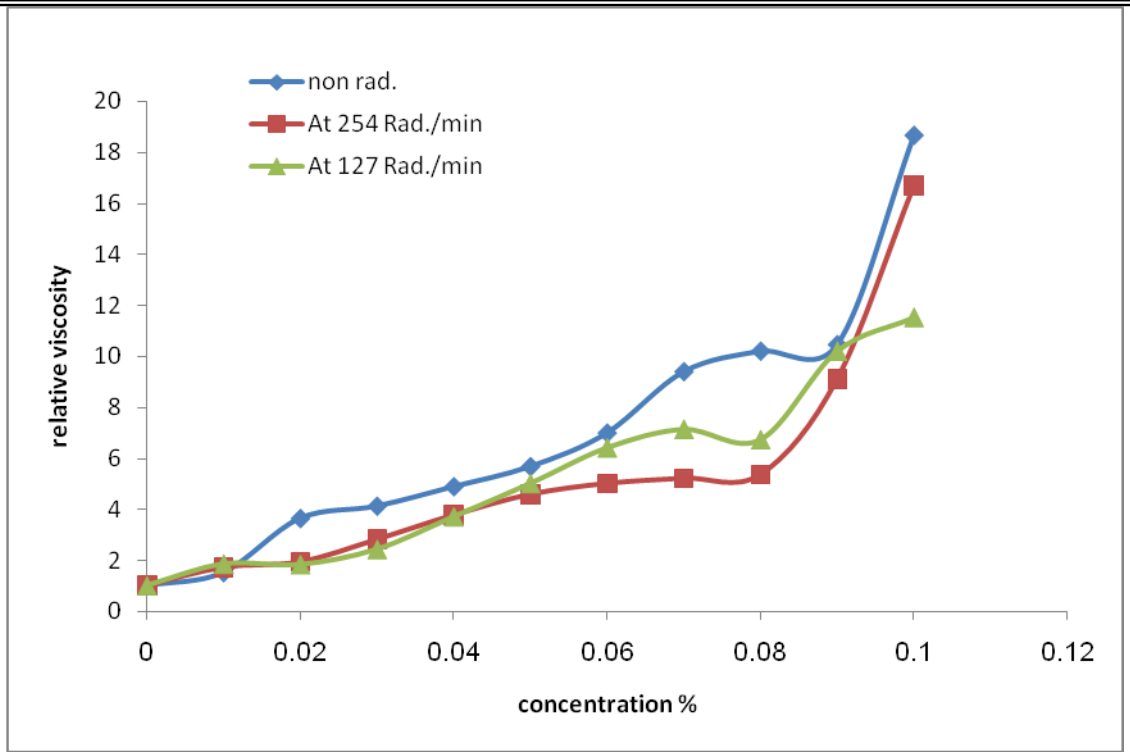

Figure 2: Relative viscosity changed with concentration for PAAM in Ethyleneglycol.

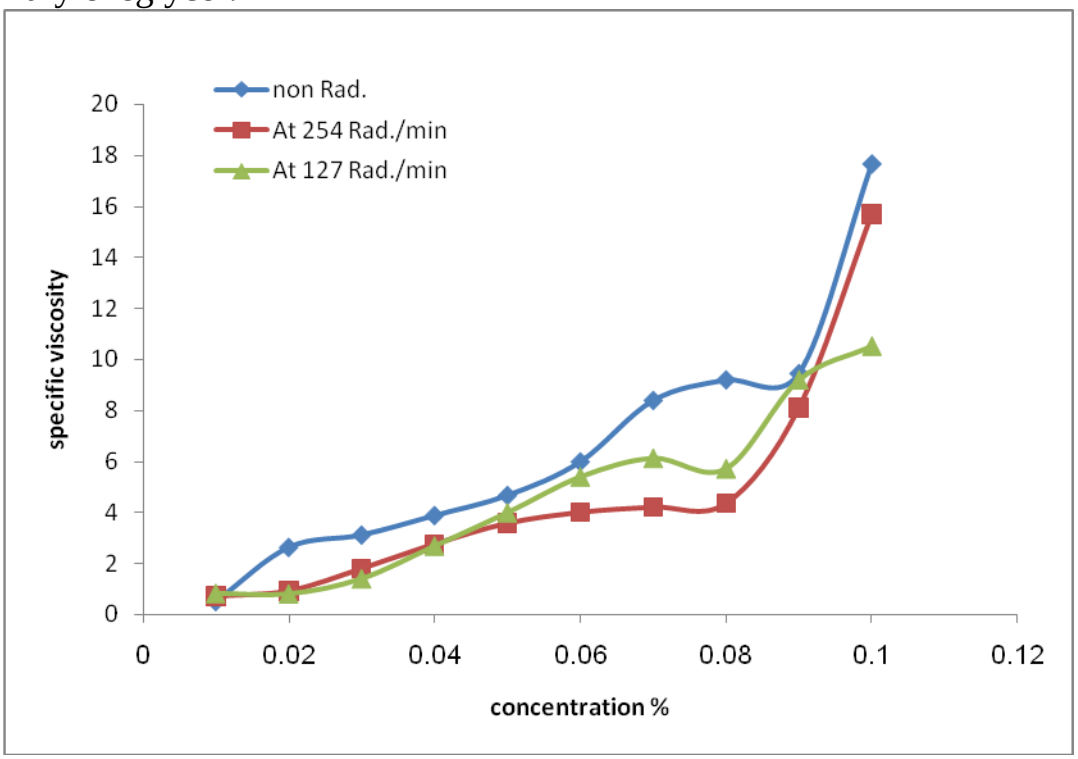

Figure 3: Specific viscosity changed with concentration for PAAM in Ethylene glycol.

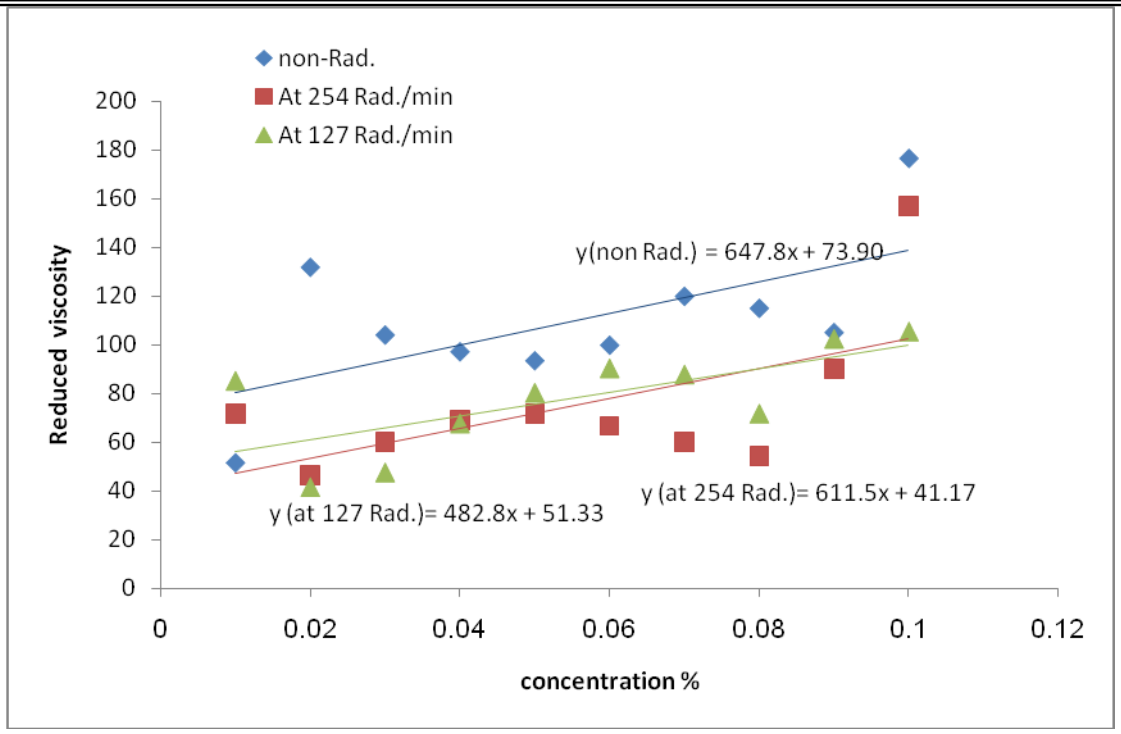

Figure 4: Reduced viscosity changed with concentration for PAAM in Ethylene glycol.

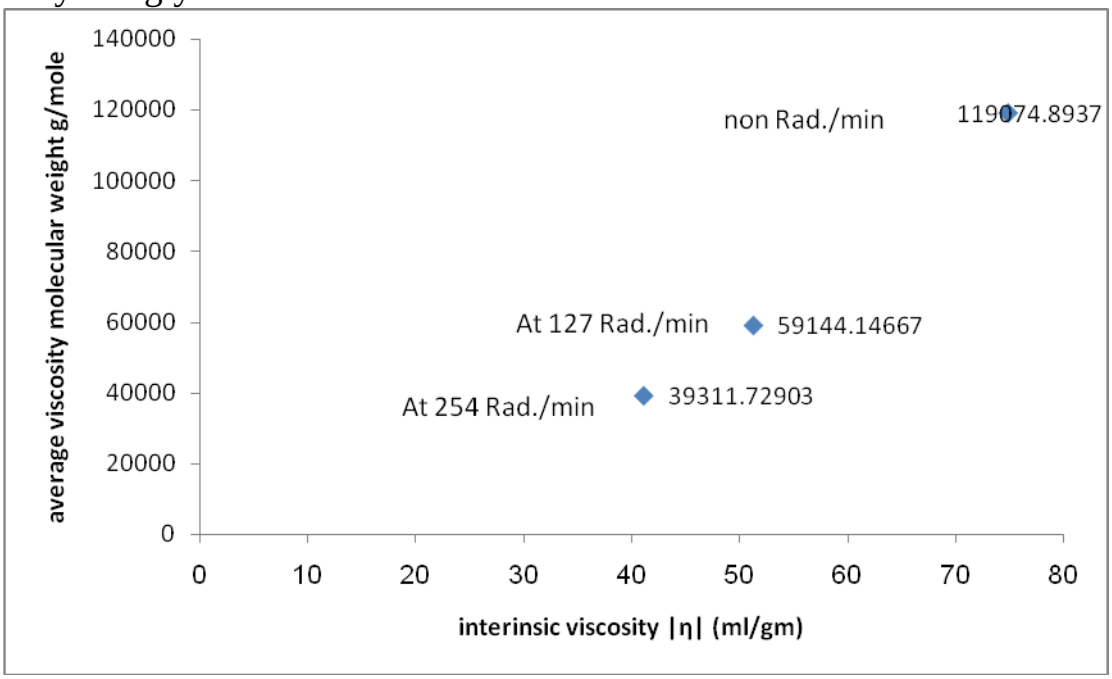

Figure 5: Average viscosity molecular weight of polyacrylamide before and after Radiation.

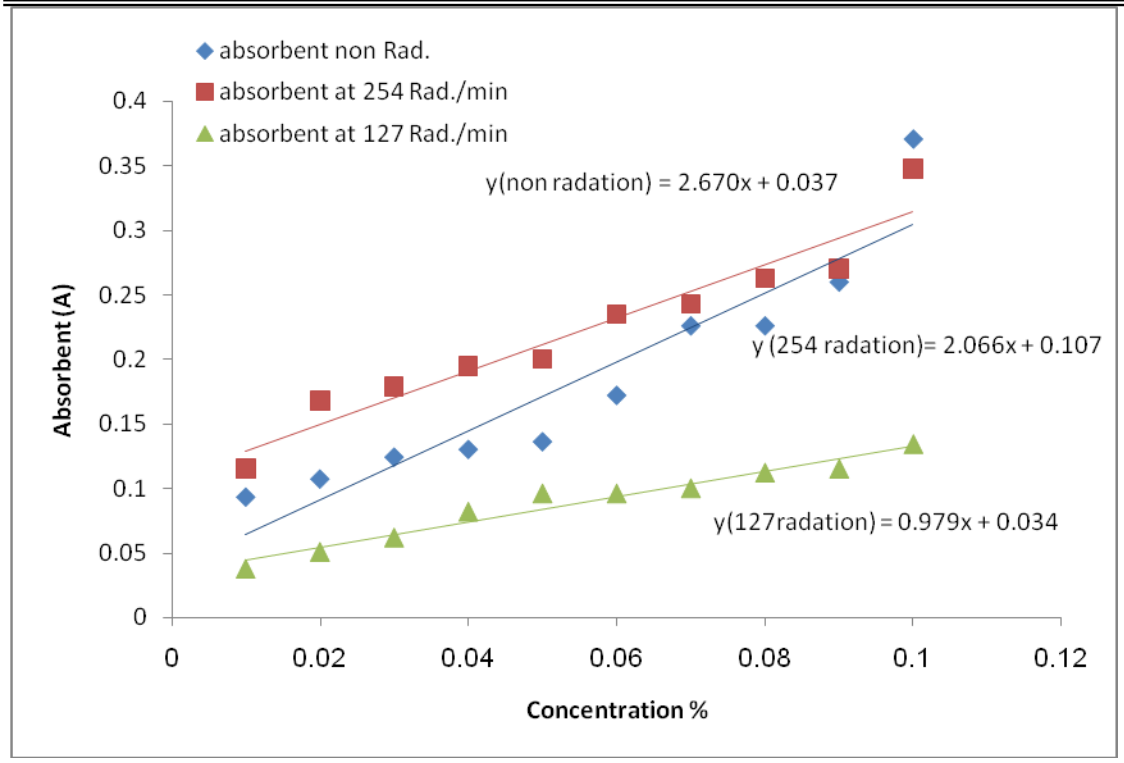

Figure 6: absorbent of polyacrylamide in ethylene glycol at different concentration before and after radiation.

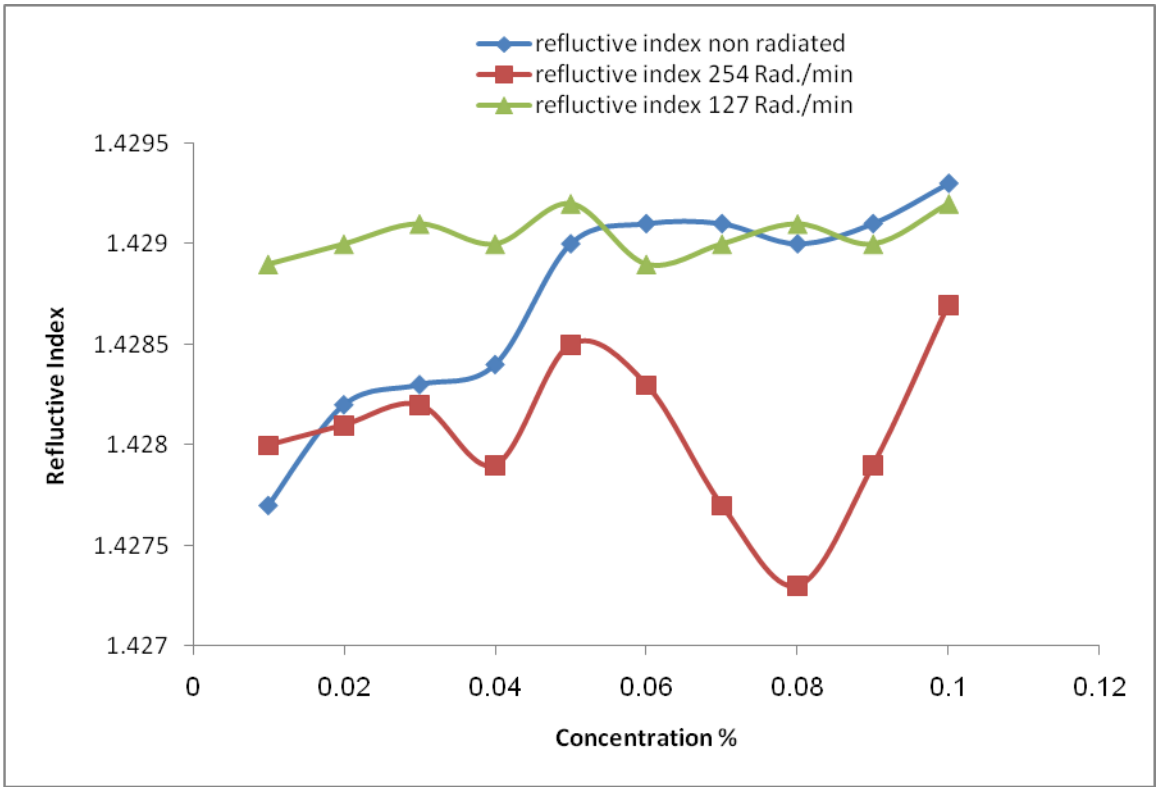

Figure 7: Reflective index of polyacrylamide in ethylene glycol at different concentration before and after radiation.

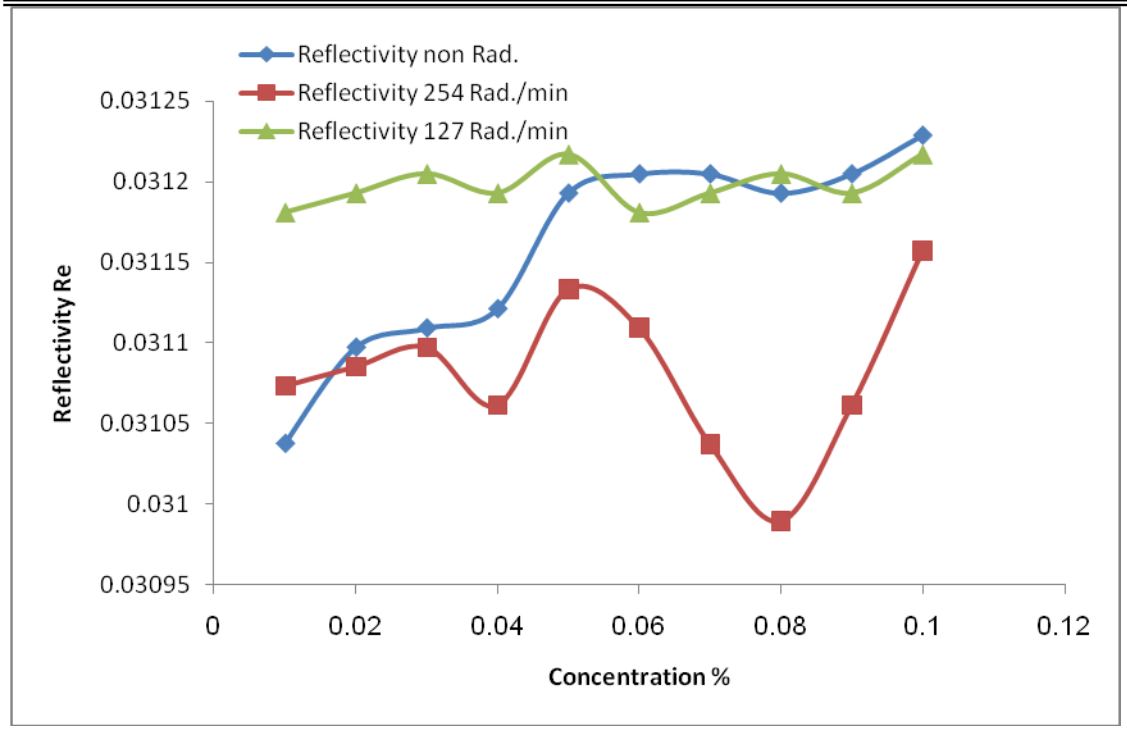

Figure 8: Reflectivity of polyacrylamide in ethylene glycol at different concentration before and after radiation.

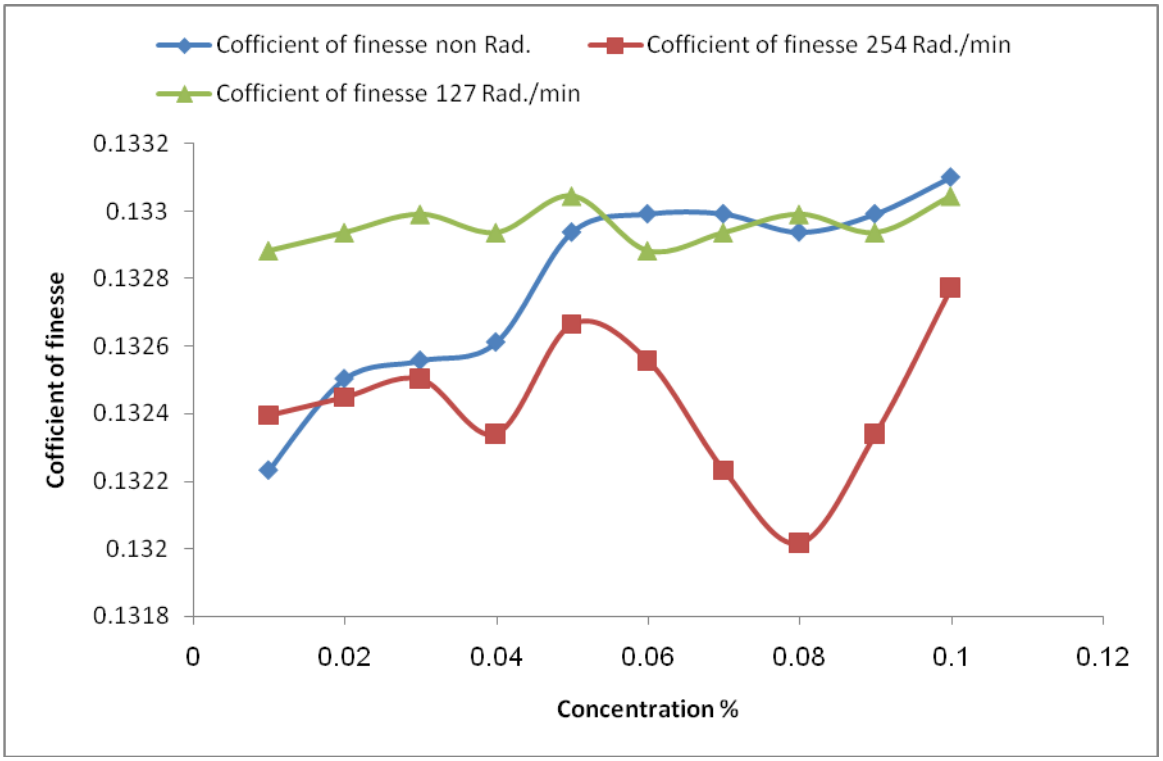

Figure 9: Coefficient of finesse of polyacrylamide in ethylene glycol at different concentration before and after radiation.

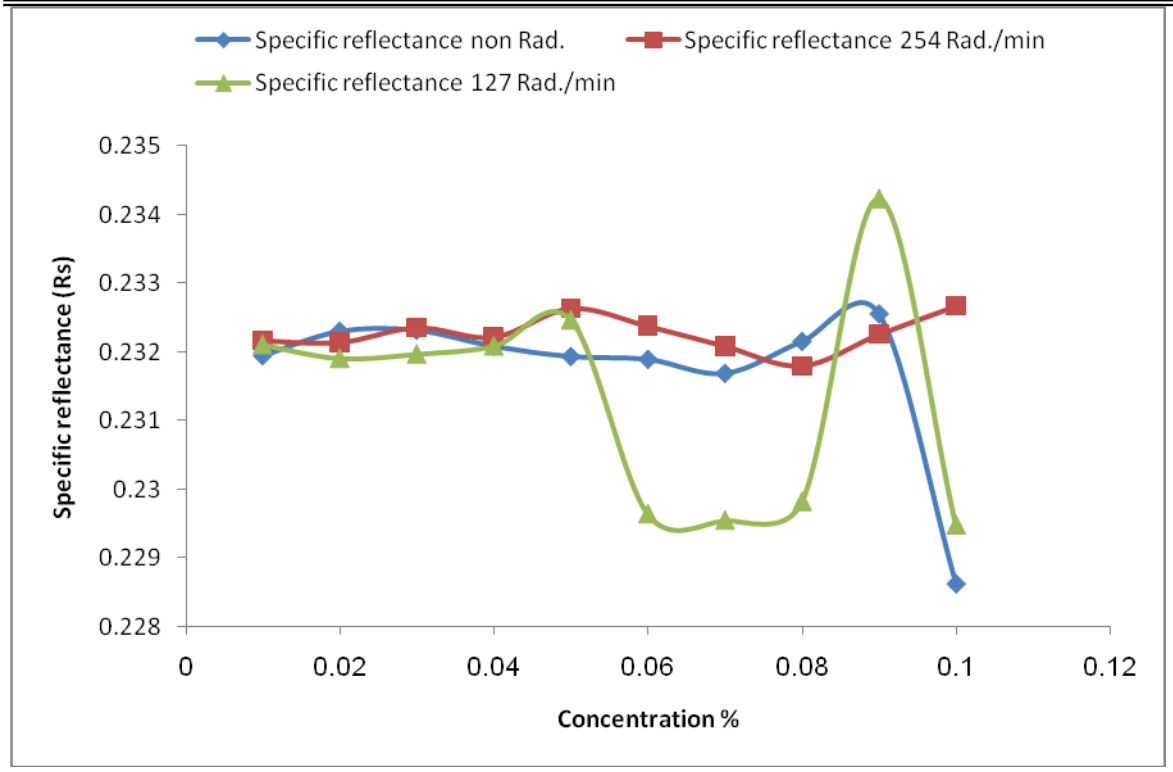

Figure 10: Specific reflectance of polyacrylamide in ethylene glycol at different concentration before and after radiation.

الخلاصة:

هدف البحث دراسة تاثير اشعاع كاما على الخواص الريولوجية والبصرية لبولياكريل امايد المذاب في اثلين كلايكول. ثم تشعيع البوليمر بجرعتين اشعاعيتين ٢٥٤ rad/min ، ١٢٧ rad/min ولمدة ١٠ دقائق وكانت العينات على شكل اقراص.

الخصائص الريولوجية اللزوجة(القصية ، النسبية، النوعية، المختزلة، ذاتية) معدل اللزوجي للوزن الجزيئي ونصف القطر فعال للبوليمر اضافة الى الخواص البصرية (الامتصاصية، معامل الانكسار معامل الامتصاص المولاري) الانعكاسية ، معامل الرقة، والانعكاسية النوعية).

النتائج اظهرت تناقص في قيمة كل من اللزوجة(القصية ، النسبية، النوعية، المختزلة، ذاتية)' الوزن الجزيئي اللزوجي واللزوجة الاصيلة ومن ناحية اخرى ظهرت تباين في قيم نصف القطر الجزيئي الفعال ' معامل الامتصاصية 'معامل الانكسار ' انعكاسية'معامل الرقة والانعكاسية النوعية بزيادة الجرعة

لقد كان لجرعة الاشعاع التاثير الواضح على التركيب الكيميائي للبوليمر لذلك فان خصائصه دالة للجرعة الاشعاعية