International Journal of Psychosocial Rehabilitation, Vol. 24, Issue 05, 2020
ISSN: 1475-7192

# Studying the Swelling and Thermodynamic Functions of a Graft Co - polymer Using Different Molar Ratios of Acrylic Acid Monomer

Mazin F. Anad, Hamieda E. Salman and Mohammad N. AL-Baiati*

***Abstract---*** *In this work, the of graft co-polymer was prepared, by using glycerol as material containing the three alcoholic groups, and that reacted with terphthalic acid which have two carboxylic group as a first step, and then added 0.5 mole of fumaric acid to prepared graft co-polymer, as a second step. The acrylic acid monomer was added to the graft co-polymer in different number of moles (1.5, 2.0 & 2.5 mole). The swelling ratio measurements of the graft co-polymer, in three different buffer solution (2.2, 7.0 and 8.0), in the constant temperature at 310 K. The results showed that the increases of number of the moles of the acrylic acid monomer, Leads to increased of swelling ratio. Thermodynamic functions were calculated of the linear polymer.*

***Keywords---*** *Polyester Resin, Modified Polymer, Modified Polyester Resin, Condensation Polymerization, Interpenetrating Polymer Network, Swelling, Swelling of Polymer, Swelling of Modified Resin, Swelling of Co-polymer, Rate of Polymerization, Activation Energy, Thermodynamic Functions.*

## I. INTRODUCTION

Copolymerization is the joint polymerization of two or more monomer species. High–molecular mass compounds obtained by copolymerization are called copolymers [1]. The molecular chain of a copolymer is composed of different units, in accordance with the number of initial monomers [2]. If the reactants of a polycondensation have several different monomers, the result will be a copolymer [3]. The reaction of co-polycondensation has acquired great technical importance in recent years and is now widely used for the synthesis of various mixed polyesters and polyamides (e.g. containing ester and amide bonds simultaneously) and other copolymers. For instance co-polycondensation of hexamethylenediamine, adipic acid and terephthalic acid [4]; Polymers may be classified as hydrophobic or hydrophilic, according to whether or not they dissolve or swell in water. The polymers which contain hydrophobic groups (e.g. $C_2H_5$) are water insoluble. The polymers which contain a hydrophilic group (e.g. OH), are water soluble, in the case of linear polymers or swellable in the case of cross linked polymers. In other words, the hydrogel can be defined as a polymeric material which will swell in solvent and it contains a significant fraction of water (usually more than 20%) within its structure. The term xerogel is given to the polymer network alone (dry state) **[5]**, thus:

**Xerogel + Water → Hydrogel**

Hydrogels, are a coherent system rich in water; they are made up of two principal components; a constant solid component consisting of a polymer network, and a variable liquid component, either water or an aqueous solution.

---

*Mazin F. Anad, Department of Chemistry, College of Education for Pure Sciences, University of Kerbala, Holly Kerbala, Iraq.*
*Hamieda E. Salman, Department of Chemistry, College of Education for Pure Sciences, University of Kerbala, Holly Kerbala, Iraq.*
*Mohammad N. AL-Baiati*, Department of Chemistry, College of Education for Pure Sciences, University of Kerbala, Holly Kerbala, Iraq.*
*E-mail: Mohammad.nadhum@uokerbala.edu.iq*

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**

The aqueous component can undergo exchange with the environment by diffusion or evaporation [6, 7]. For getting materials combining biocompatibility with a good mechanical strength, two methods are used [8,9 ]: Copolymerization of hydrophilic monomers with hydrophobic monomers or with cross-linking agent or grafting of hydrophilic monomers on stronger polymer supports [10, 11, 12].

## II. EXPERIMENTAL

### *1. Chemicals*

All chemicals were used in this work analytical grade, imported from different companies.

### *2. Preparation of graft co-polymer* [13, 14]

**The first step**; In a 500 ml three-necked round bottom flask, (2.0 mole, 332gm) of terphthalic acid, and (1.0 mole, 92gm) of glycerol, were mixed together, this flask was equipped with a thermometer and a mechanical stirrer. The mixture warmed carefully with an electric heating mantle to 270C$^0$ until a clear liquor is formed and then about 25 ml of xylene was added carefully to the reaction flask, in the form of batch (two drops in each batch), Withdrawal of water formed in the esterfication process, and the flask was gently heated. Heating was stopped after 150 min. at 325 C$^o$, until no more water came off. **The second step**; The flask was allowed to cool to 110 C$^o$, and (0.5mole, 58gm), of fumaric acid, was added carefully to the reaction flask, and the flask was gently rise heated, after melting material, added the drops of xylene in the form of batch (two drops in each batch), until no more water came off at 275 C$^o$, and 125 min., to prepared of a new graft co-polymer. The flask was allowed to cool to 50C$^o$, and (1.36×10-3mole, 0.147gm) of hydroquinone was added to the reaction flask, with stirred by mechanical stirrer, and (1.5, 2.0 and 2.5 mole) about ( 108, 144 and 180 gm), respectively of acrylic acid monomer, was added to the graft co-polymer and stirred by mechanical stirrer, until a pourable syrup was formed. The viscosity and density of the prepared co-polymer were calculated using, Brookfild digital viscometer instrument and Hydrometer instrument respectively, and the average number of molecular weight ( $\overline{Mn}$ ) was determined using end group analysis method.. Table (1), represents the physical properties of modified polyester resin.

Table 1: Physical properties of the graft co-polymer

| Physical properties | Value |
|---|---|
| Molecular Weight ( $\overline{Mn}$ ) | Around 2800 gm/mole |
| Solid content | 61 % |
| Viscosity | 23 poise |
| Gel time | 15-20 min at 25C$^0$ |
| Acid Value | 26 |
| Density | 1.5 (gm/cm$^3$ ) |

### *3. Preparation of polymeric specimens*

The specimens of polymeric material containing different number of moles of the acrylic acid monomer were prepared by using Methylethylketone peroxide (MEKP) as a hardener and cutting as a disc in dimensions (thickness=3mm & diameter=10mm) and the weighted of the xerogel discs was exactly 0.4 gm of all specimens were used in the swelling study.

### *4. Swelling*

The known weight and diameter of dried discs (Xerogel) were put in sample vials. The swelling time was counted when the solvent was added into the sample vials [10, 11]. The buffer solution contents of the hydrogels, were calculated according to the following equations [15] :

**Buffer solution % = (Wt. of hydrogel - Wt. of xerogel / Wt. of hydrogel) × 100**

### *5- Thermodynamic Functions*

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate of polymerization, at which a reaction proceeds. From the equation, the activation energy can be found through the relation [16]:

$$K = Ae^{-Ea/(RT)}$$

By using Van Huff complementary equation, the thermodynamic functions were determination of the linear co-polymer. The relationships below were used to calculate these functions [17]:

$$\ln K = -\left(\Delta H / RT\right) + \text{constant}$$

$$\Delta G = -RT.\ln K$$

$$\Delta S = (\Delta H - \Delta G) / T$$

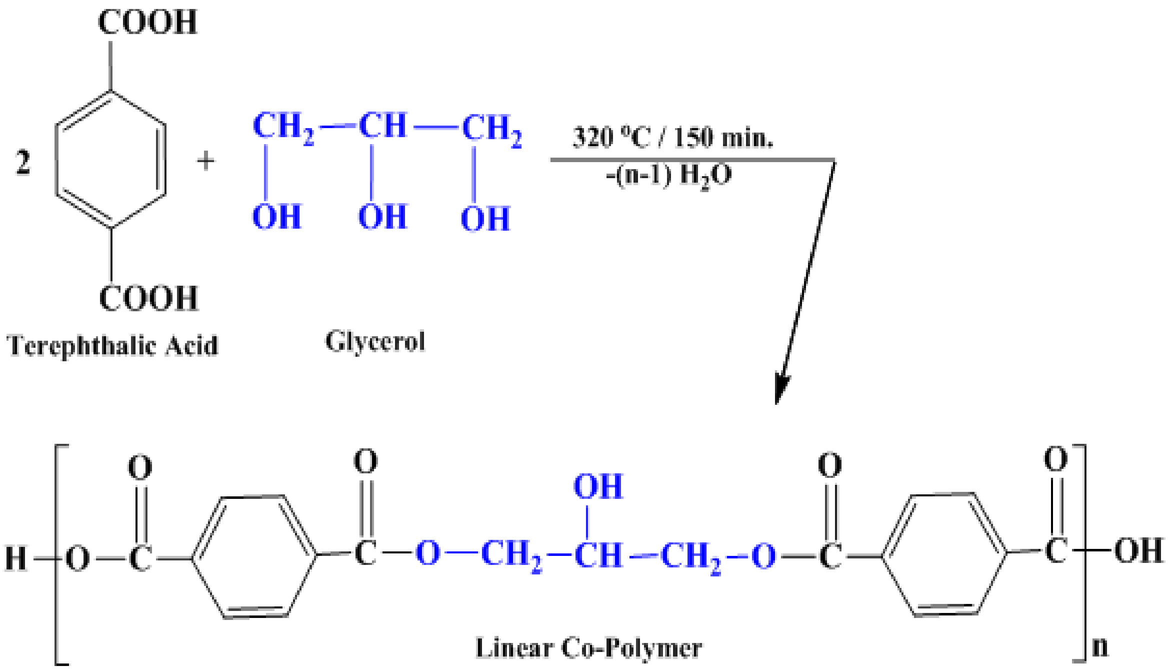
## III. RESULTS AND DISCUSSION

### *1. Preparation of graft co-polymer*

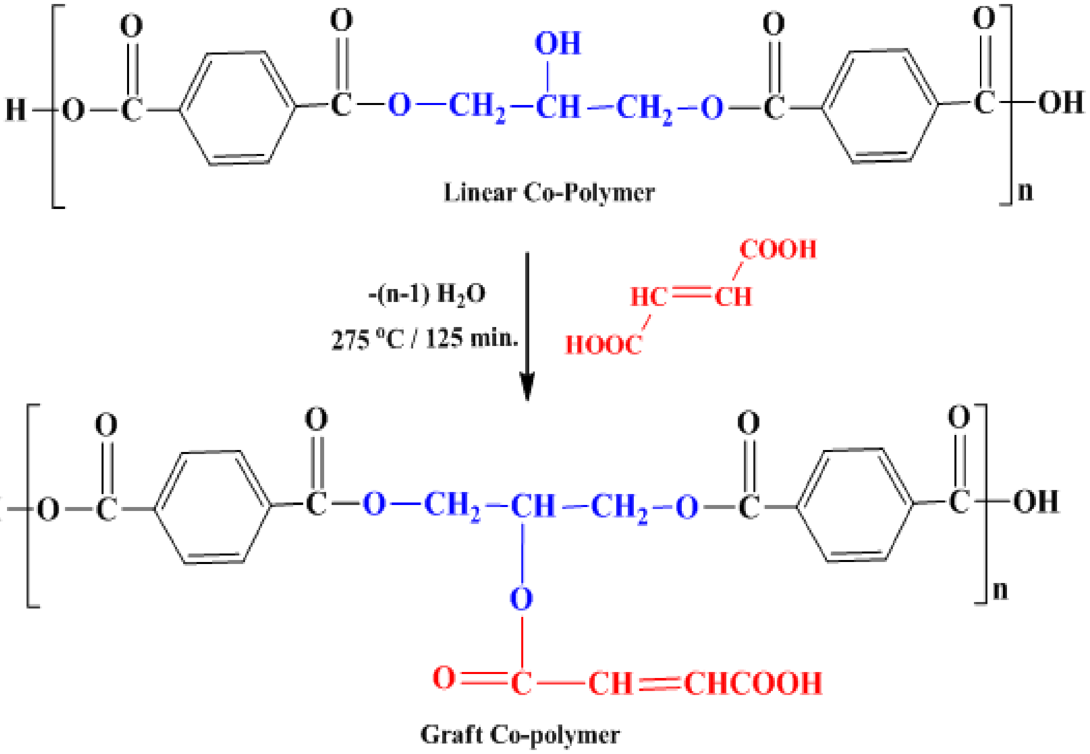
**The first step;** Figure (1), represent the FT–IR spectrum of the linear co-polymer, showed the appearance of a strong broad band at about 3423 cm$^{-1}$ for stretching alcoholic -OH with stretching (H–bond), and also showed a weak band at about 2902cm$^{-1}$ due to the -OH for Carboxylic acid, the C-H sp$^3$and sp$^2$hybridization absorption at about 2544 cm$^{-1}$, 2654 cm$^{-1}$respectively, and the spectrum also showed a strong band at about1726 cm$^{-1}$ assigned to a stretching band C=O for ester group.

The spectrum appearance a weak sharp bands at about 1597cm$^{-1}$,1581cm$^{-1}$due to C=C for conjugated system of benzene ring and also showed a bands at about 1284 – 1259cm$^{-1}$ assigned to C-O absorption band [18]. Figure (2), The spectrum of $^1$HNMR showed, which explain the singlet signal at 13.24 ppm characteristic of proton in carboxylic acid group, furthermore the multiples in the region 7.53- 8.10 ppm back to all protons in aromatic ring, the signals at 6.27-6. 46 ppm for four protons of methylene in the structure of co-polymer, the multiples at 4.24-4.50 ppm of methyl protons, but the triplet signal in 3.44- 3.62 ppm dueto the proton of aliphatic alcohol so this spectrum was confirmed the structure of our target polymer [19].

DOI: 10.37200/IJPR/V24I5/PR201814
Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020



Equation (1): Reaction of step 1



Equation (2): Reaction of step 2

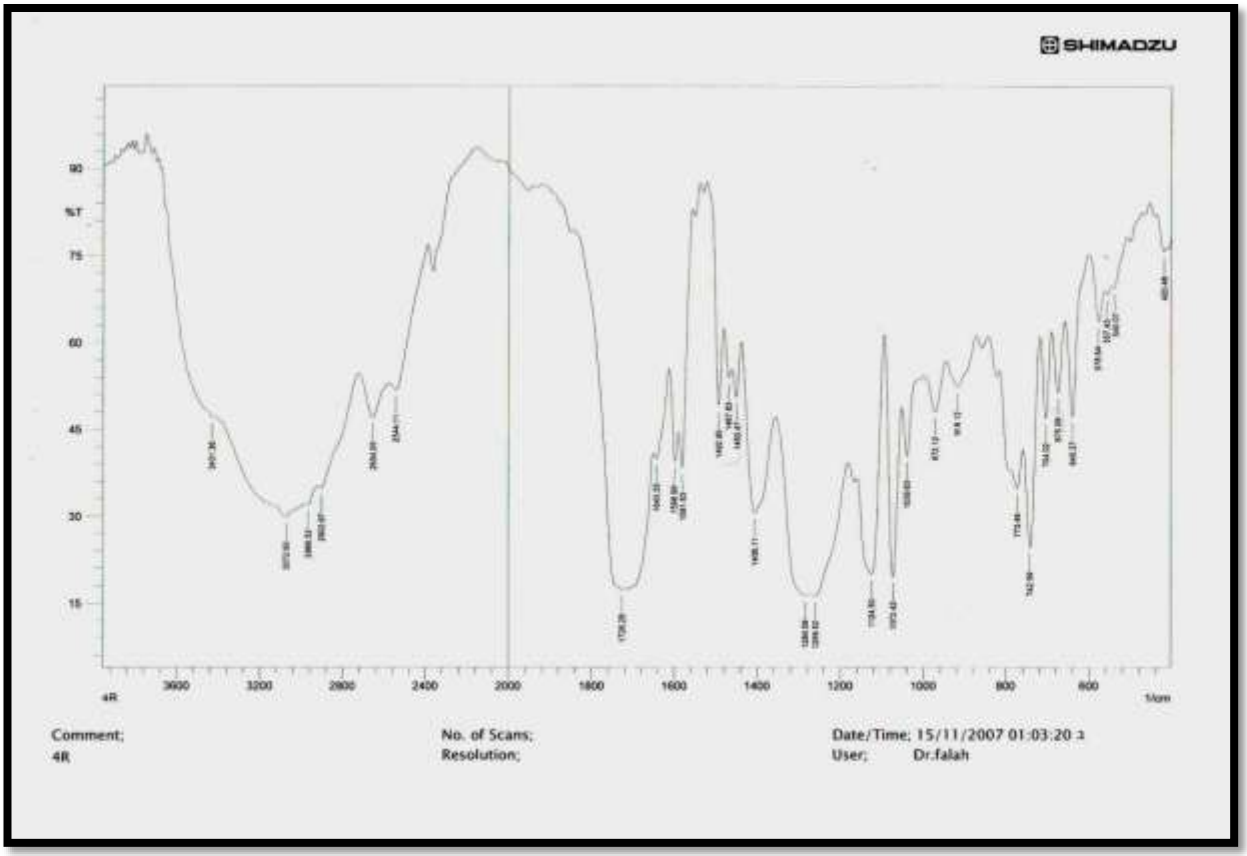


Figure 1: The FT-IR spectrum of linear co-polymer

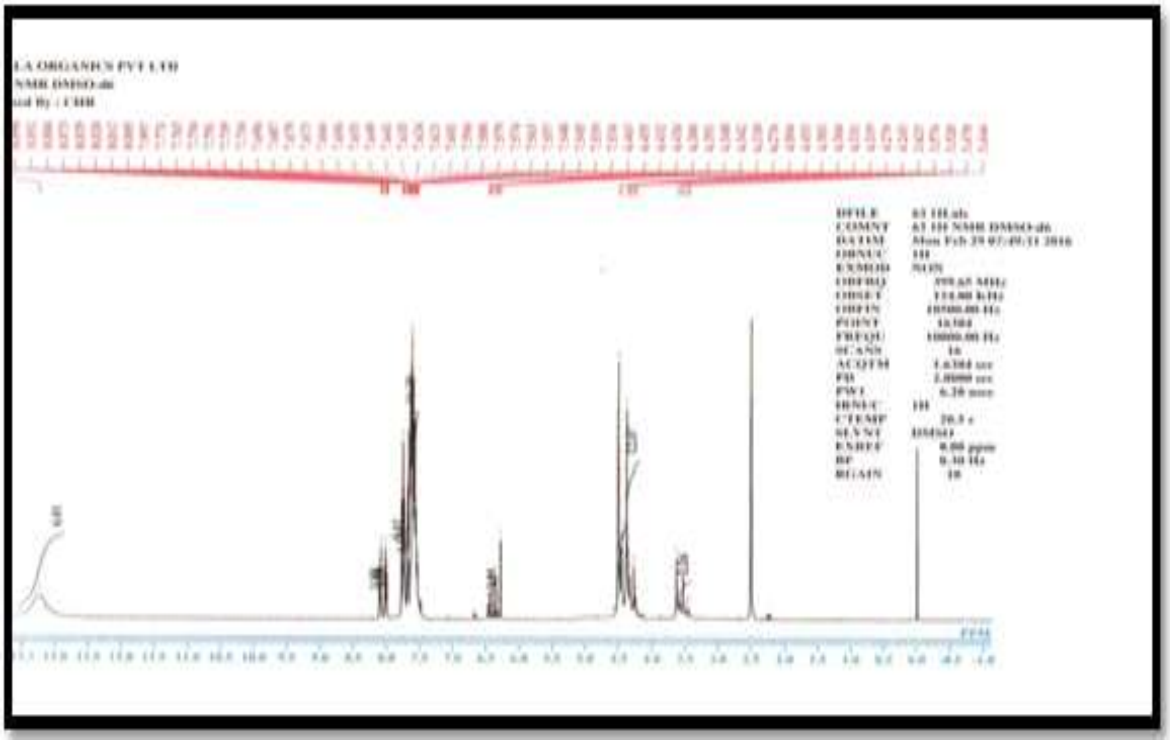


Figure 2: The $^1$HNMR spectrum of linear co-polymer

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**

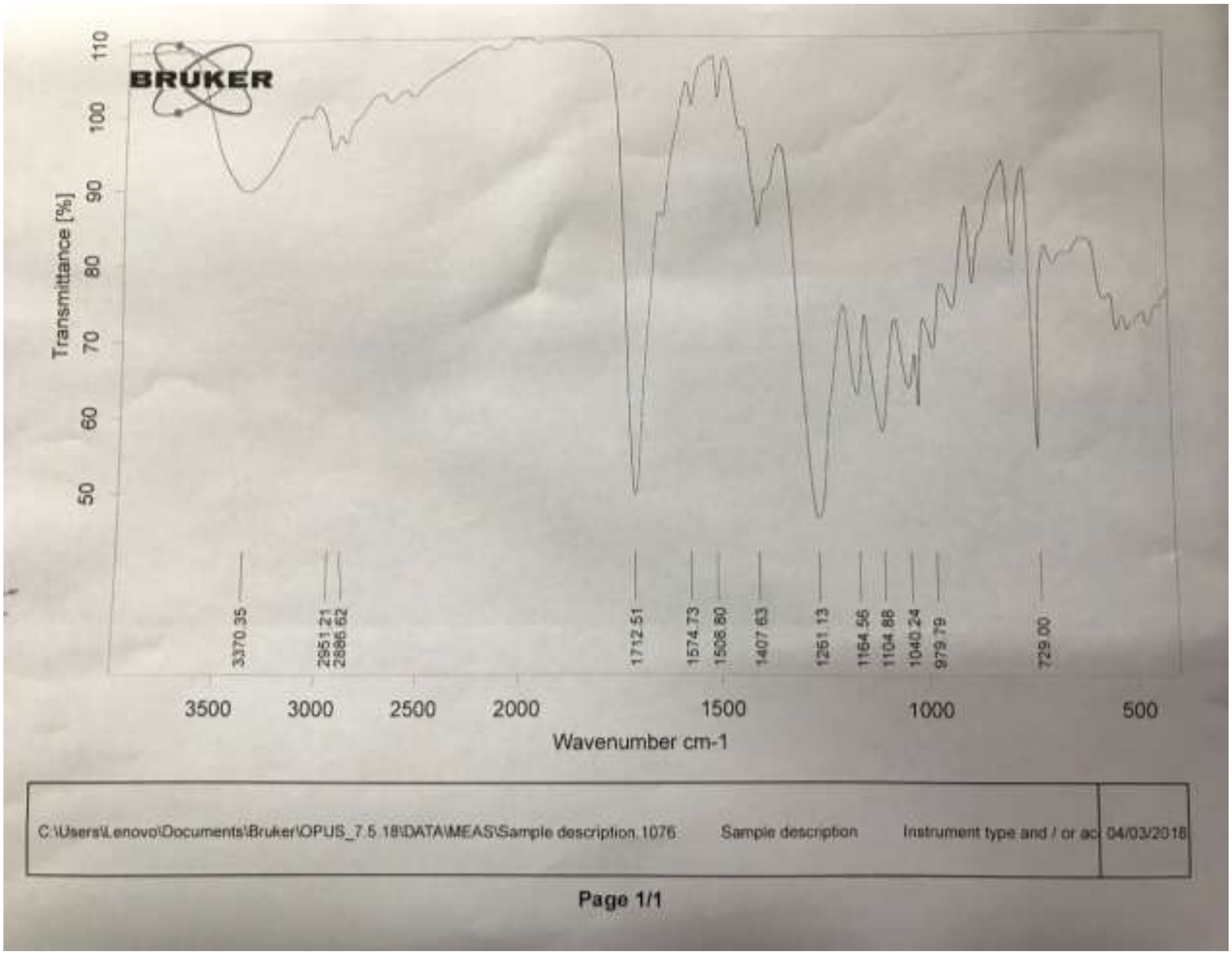


Figure 3: The FT-IR spectrum of graft co-polymer

The second step; Figure(3), showed the FT – IR spectrum of the graft co-polymer, its showed the appearance of a strong broad band at 3500 cm$^{-1}$ for stretching alcoholic -OH with stretching (H–bond), and the spectrum also showed the aliphatic C-H, aromatic =C-H and alkenes =C–H at approximately at 2880 cm$^{-1}$, 3140 cm$^{-1}$ and 3050 cm$^{-1}$ respectively, and the spectrum also showed a strong sharp band at 1740 cm$^{-1}$ and 1250 cm$^{-1}$ for a stretching band C=O ester and C-O ester respectively.

***2-Thermodynamic Functions***

The rate of polymerization in different times (Sec.) at a constant temperature was calculated by measuring the acid value. The slope of a plot of acid value (A.V.) versus time (Sec.) represents the rate of polymerization Figure (4). Table (2), showed the acid value in different times at different temperatures. The rate of polymerization of the modified unsaturated polyester resin, was (120 Sec.$^{-1}$) at a constant temperature in 583 K. The activation energy (Ea) of polymerization of the modified unsaturated polyester resin was calculated from Arrhenius equation and it was found (2.9 × 10$^{6}$ J/mole) at a constant temperature in 583K.

Table 2: Represent the acid value of linear co-polymer in different times at different temperatures.

| Time (Sec.) | Acid Value | Slope | Temp. (K) |
|---|---|---|---|
| 120 | 240.0 | 3.254472 | 563 |
| 240 | 220.0 | | |
| 360 | 198.8 | | |
| 480 | 182.0 | | |
| 120 | 176.4 | 3.254472 | 568 |
| 240 | 162.4 | | |
| 360 | 147.0 | | |
| 480 | 135.0 | | |
| 120 | 126.0 | 3.254472 | 573 |
| 240 | 114.6 | | |
| 360 | 103.6 | | |
| 480 | 92.4 | | |
| 120 | 81.2 | 3.254472 | 578 |
| 240 | 73.0 | | |
| 360 | 64.4 | | |
| 480 | 57.4 | | |
| 120 | 47.9 | 3.254472 | 583 |
| 240 | 42.8 | | |
| 360 | 37.0 | | |
| 480 | 30.0 | | |

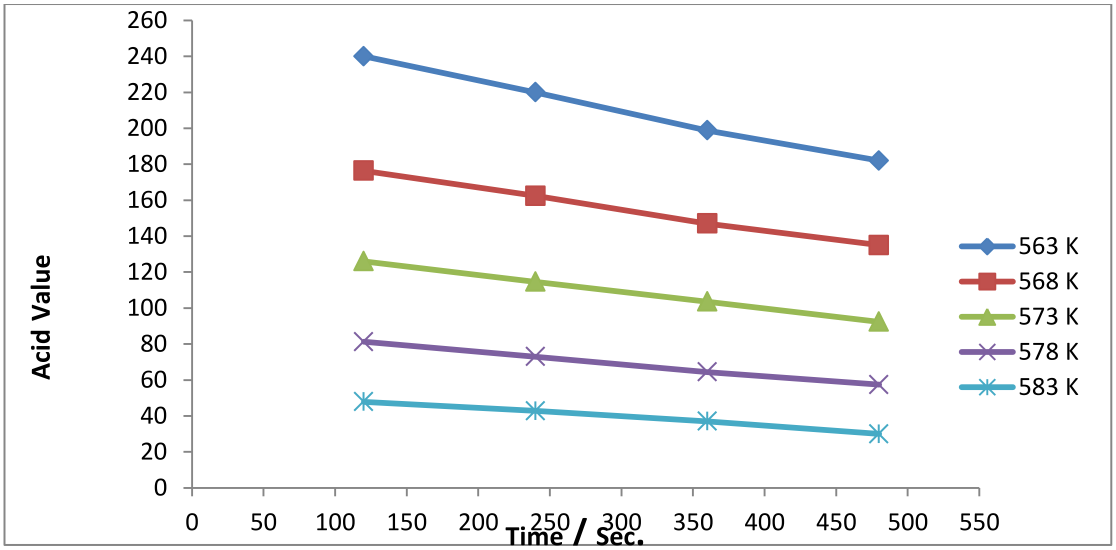


Figure 4: Acid value Vs. Time (Sec.) in different temperatures

By using Van Huff complementary equation, the thermodynamic functions were determination of the linear co-polymer. Table (3), showed the thermodynamic functions.

Table 3: The thermodynamic functions of the linear co-polymer

| no | T (K$^o$) | 1/T | lnK | ΔH (J/mol) | ΔG (J/mol) | ΔS (KJ/mol.K) |
|---|---|---|---|---|---|---|
| 1 | 563 | $1.776 \times 10^{-3}$ | -0.1003 | $2.9 \times 10^{6}$ | 469.482 | 5.150 |
| 2 | 568 | $1.7605 \times 10^{-3}$ | -9.2992 | | 43914.095 | 5.097 |
| 3 | 573 | $1.7452 \times 10^{-3}$ | -10.733 | | 51131.174 | 4.971 |
| 4 | 878 | $1.7301 \times 10^{-3}$ | -15.232 | | 73197.254 | 4.890 |
| 5 | 583 | $1.7152 \times 10^{-3}$ | -24.063 | | 116634.852 | 4.774 |

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**

### *3. Measured of swelling*

The swelling curves of graft co-polymer showed a plot of buffer solution content for different compositions against swelling time (hour and day). The initial swelling rate was medium, the maximum being reached within the first few hours of the swelling. The shape of the swelling curves indicated that buffer solution–soluble molecules were being released from the xerogel upon swelling. [14].

A plot of buffer solution content versus time showed hydration curves of graft co-polymer for three different numbers of moles from acrylic acid compositions ranging from 1.5, 2.0 and 2.5 mole, against swelling time at constant temperatures, as shown in Tables (4) to (6) and Figures (5) to (10) respectively.

Table 4: Swelling ratio (%) in different time, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

| Time | Swelling ratio (%) | | |
|---|---|---|---|
| | Number of moles acrylic acid monomers | | |
| (hour) | 1.5 moles | 2 moles | 2.5 moles |
| 1 | 5.0111 | 5.1241 | 5.2356 |
| 2 | 5.0433 | 5.1468 | 5.2582 |
| 3 | 5.0660 | 5.1695 | 5.2708 |
| 4 | 5.0887 | 5.1822 | 5.2930 |
| 5 | 5.1114 | 5.2149 | 5.3156 |
| (day) | | | |
| 1 | 6.0165 | 6.1600 | 6.2875 |
| 2 | 6.0580 | 6.1855 | 6.3130 |
| 3 | 6.0835 | 6.2110 | 6.3385 |
| 4 | 6.1090 | 6.2365 | 6.3640 |
| 5 | 6.1345 | 6.2620 | 6.3895 |

Table 5: Swelling ratio (%) in different time, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

| Time | Swelling ratio (%) | | |
|---|---|---|---|
| | Number of moles of acrylic acid monomers | | |
| (hour) | 1.5 mole | 2.0 mole | 2.5 mole |
| 1 | 7.0160 | 7.2455 | 7.4555 |
| 2 | 7.0590 | 7.2890 | 7.5084 |
| 3 | 7.1035 | 7.3230 | 7.5421 |
| 4 | 7.1374 | 7.3640 | 7.5859 |
| 5 | 7.1692 | 7.4192 | 7.6299 |
| 6 | 7.2023 | 7.4325 | 7.6690 |
| (day) | | | |
| 1 | 8.0180 | 8.2526 | 8.4931 |
| 2 | 8.0571 | 8.2917 | 8.5381 |
| 3 | 8.0963 | 8.3308 | 8.5831 |
| 4 | 8.1323 | 8.3699 | 8.6281 |
| 5 | 8.1744 | 8.4090 | 8.6731 |
| 6 | 8.2135 | 8.4481 | 8.7181 |

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**

Table 6: Swelling ratio (%) in different time, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

| Time | Swelling ratio (%) | | |
|---|---|---|---|
| | Number of moles acrylic acid monomers | | |
| (hour) | 1.5 moles | 2.0 moles | 2.5 moles |
| 1 | 9.1011 | 9.2439 | 9.3854 |
| 2 | 9.1218 | 9.2642 | 9.4056 |
| 3 | 9.1423 | 9.2844 | 9.4258 |
| 4 | 9.1627 | 9.3046 | 9.4460 |
| 5 | 9.1831 | 9.3248 | 9.4662 |
| 6 | 9.2033 | 9.3450 | 9.4864 |
| 7 | 9.2236 | 9.3652 | 9.5066 |
| (day) | | | |
| 1 | 10.0190 | 10.6150 | 11.2185 |
| 2 | 10.1040 | 10.7010 | 11.3060 |
| 3 | 10.1890 | 10.7870 | 11.3935 |
| 4 | 10.2740 | 10.8730 | 11.4810 |
| 5 | 10.3590 | 10.9590 | 11.5685 |
| 6 | 10.4440 | 11.0450 | 11.6560 |
| 7 | 10.5290 | 11.1310 | 11.7435 |

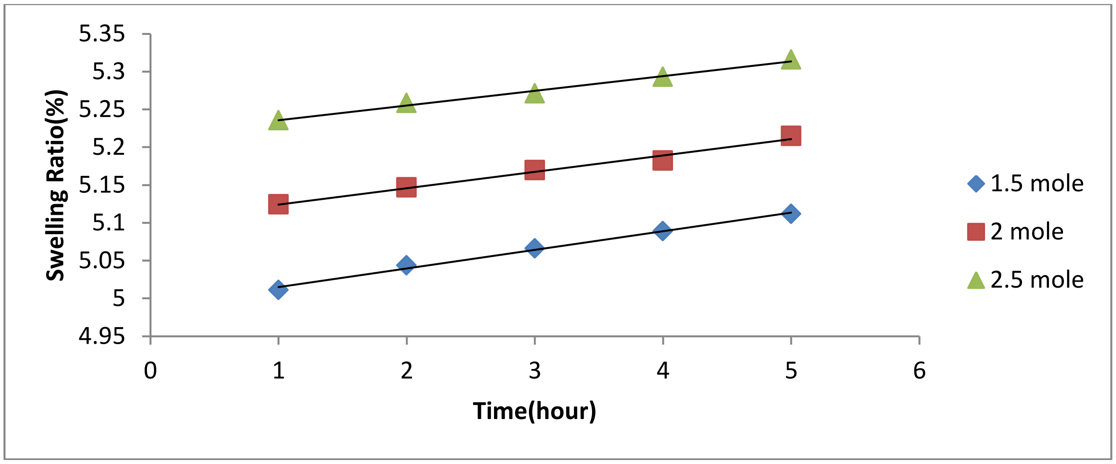


Figure 5: Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

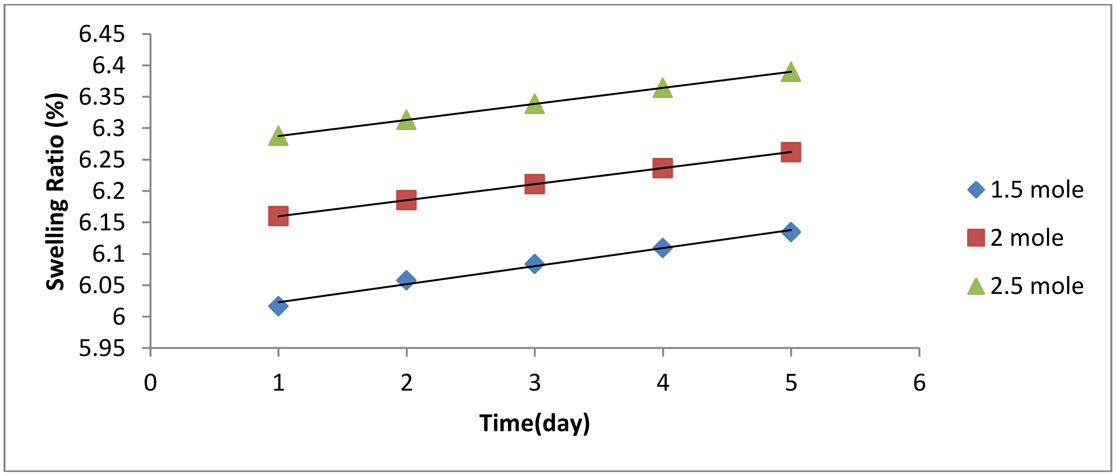


Figure 6: Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=2.2 at 310 K

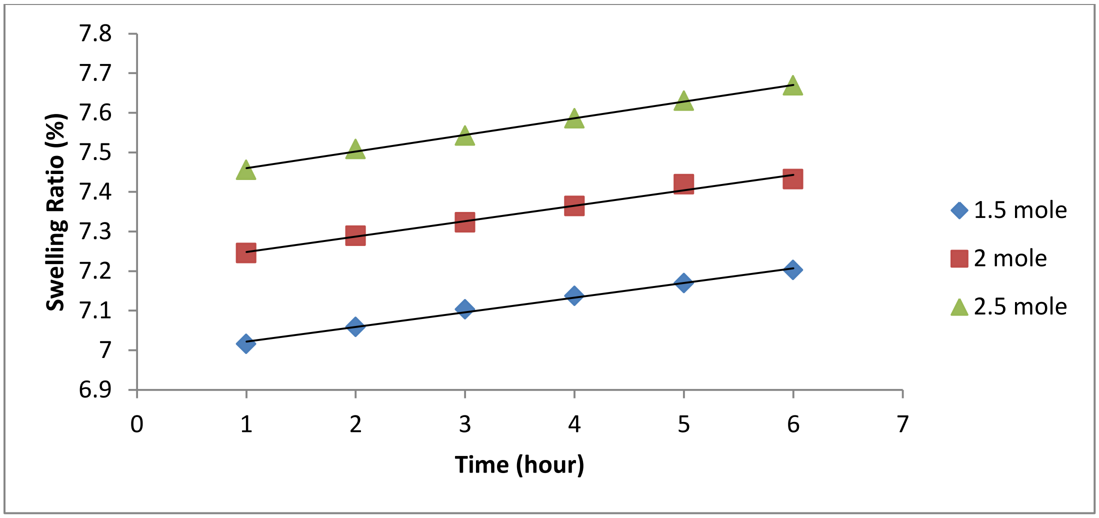


Figure 7: Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

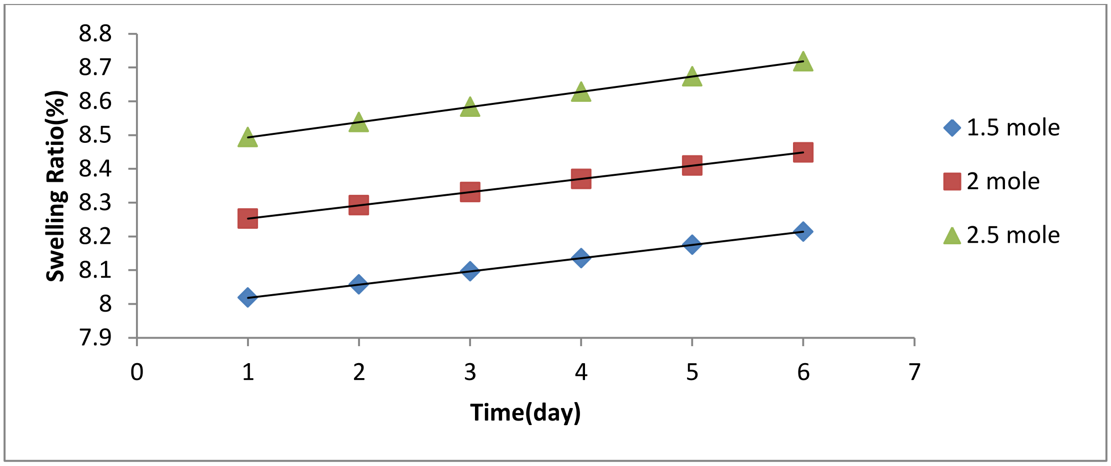


Figure 8: Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=7.0 at 310 K

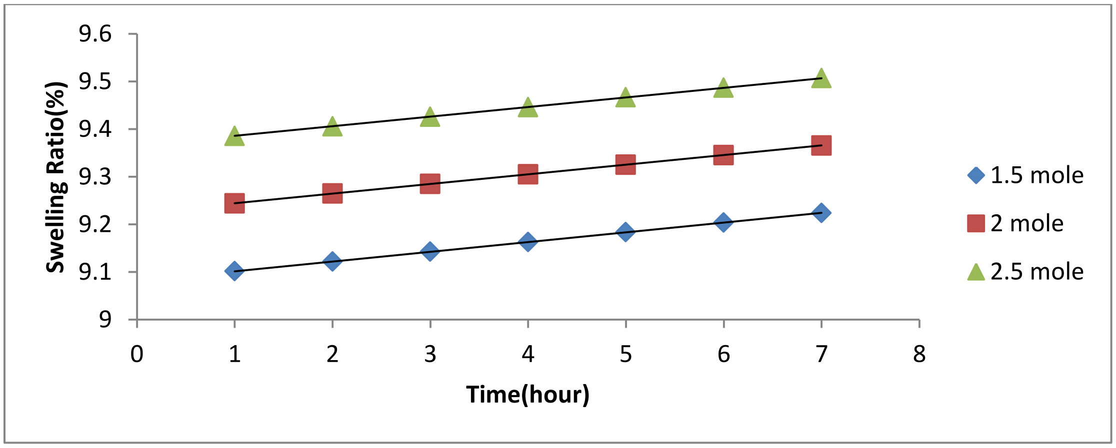


Figure 9: Swelling ratio (%) in hour, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**

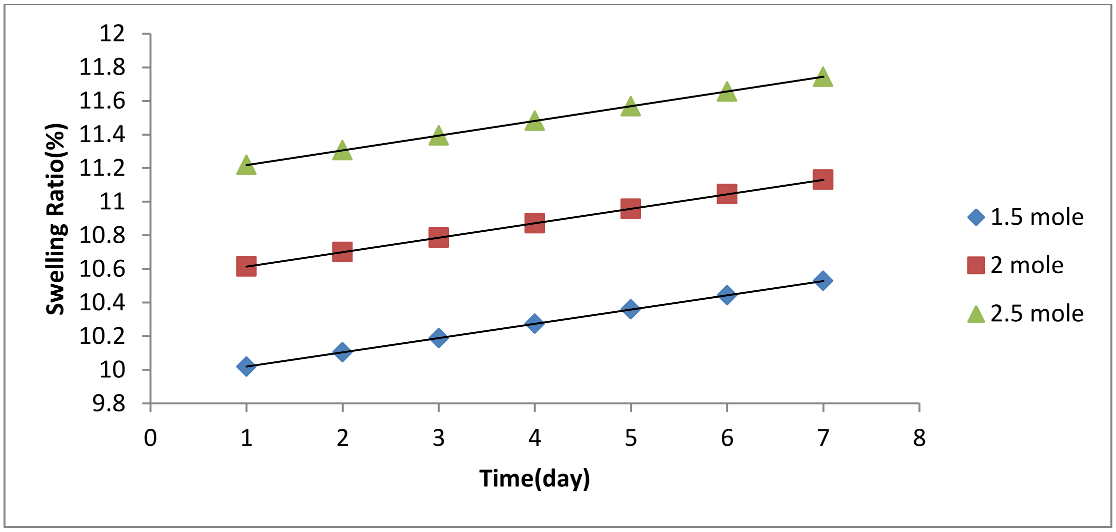


Figure 10: Swelling ratio (%) in day, of graft co-polymer with different moles of acrylic acid monomers in pH=8.0 at 310 K

As clearly shown in these figures increasing the time with increases of the buffer solution content (%), this behavior can be explained due to, the pH of buffer solution and the structure of polymer, i.e., present of the hydrophilic groups in the xerogel, concentration and nature of the pH of buffer solution. All these factors will increase the buffer solution content (%) with the increased of time [14]. The low values of swelling process were affected by High chain flexibility and the degree of cross linking, i.e., in the graft co-polymer with 1.5 mole of acrylic acid, the values will be low comparing with the values in the graft co-polymer with 2.5 mole of acrylic acids.

## IV. CONCLUSIONS

Increasing of the number of moles of the acrylic acid monomer due to, increases the hydroxyl content ratio of the product co-polymer, and thus leads to increases the swelling graft co-polymer, and the results also showed that the effect of the pH of buffer solution on swelling.

## REFERENCES

[1] Jin G. & Dijkstra J.; Hydrogels for Tissue Engineering Applications; *Springer*, p.59, (2010)
[2] Ebewele R.; Polymer Science and Technology; CRC Press., *New York*, P.71&35. (2000).
[3] Robert A.M.; Handbook of Petrochemicals Production Process; McGraw-Hill Publisher; *New York*, P.110&84, (2006).
[4] Reddy C. & Swamy B.; *Inter. J. Phar. and Pharma. Sci.;* 3 (1), p. 215, (2011).
[5] Boydston A., Xia Y., Kornfield J., Gorodetskaya I. & Grubbs R.; *J. Am. Chem. Soc.;* 130 (38), p.12775, (2008).
[6] You N., Higashihara T., Yasuo S., Ando S. & Ueda M.; *J. Polym. Chem.*; 1, p.480, (2010)
[7] Bastiurea M., Rodeanu M., Dima D., Murarescu M. & Andrei G.; *Digest J. Nanomaterials and Biostructures;* 10, p.521, (2015).
[8] Jin T., Zhu J., Wu F., Yuan W. & Geng, L.; *J. Cont. Rele.;* 128,p.50, (2008).
[9] Mohammad AL-Baiati, Nadhir J. and Rawaa H; *Res. J. Pharma., Bio. and Chem. Sci.;* 7(5); P. 1452; (2016)
[10] Dinarvand R.; *Int. J. Pharm.;* 349, p.249, (2008)
[11] Puapermpoonsiri U., Spencer J. & Van der Walle C. ; *Eur. J. Biopharm. ;* 72, p.26 &33, (2009)
[12] You N., Higashihara T., Yasuo S., Ando S. & Ueda M.; *J. Polym. Chem.;* 1, p.480, (2010)
[13] Mohamed F. & Van der Walle C. ; *J. Pharm. Sci.;* 97, p.71, (2009)

[14] ZahraaM. & Mohammad AL-Baiati; *J. Global Pharma Techno.;* 2017; 12 (9): 50-56
[15] Chaupart N., Serpe G. & Vedn *J.; Polymer*; 39, p.1375,(1998).
[16] Mohammad AL-Baiati; *pH.D. Thesis; University of Baghdad;* (2008); p. 45.
[17] Liu J., Zheng X.& Tang K.; *Rev. Adv. Mater. Sci.;* Vol. 33, p. 428, (2013)
[18] Pretsch E., Buhlmann P.& Baderscher M.; Structure determine of Organic compound; *Springer, 4thEd,* p.244, (2009).
[19] Pavia L., Lampman L., Kris S. & Vyvyan R.; *Introduction to Spectrophotometer; 4th Ed,* (2009)

**DOI: 10.37200/IJPR/V24I5/PR201814**
**Received: 13 Feb 2020 | Revised: 07 Mar 2020 | Accepted: 23 Mar 2020**