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Synthesis and Performance of Acrylic Acid Based Polymers As Scale Inhibitors for Industrial Water Applications.

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ABSTRACT

With increasing awareness and efforts on environmental protection, developing non-phosphorus and biodegradable scale inhibitors is becoming a hot research topic. In this work, an environmentfriendly scale inhibitor was synthesized by free radical polymerization with a series of acrylic acid homopolymerP(AA) using sodium persulphate as an initiator. The P(AA) was characterized using a Fourier transform infrared (FTIR) spectroscopy and Gel permeation chromatography (GPC).The physical properties of the P(AA) were evaluated and its application as eco-friendly phosphate-free scale inhibitor agent was investigated.

Keywords: acrylic acid, polymers, industrial water.

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INTRODUCTION

Social awareness and concern for environmental, health reasons and the state of our natural waters have been the major driving force to search for auxiliaries additives other than phosphates to reduce the amount of mineral acid used in thermal desalination by using lower molar mass polymers containing carboxylate [1-4].

Acrylic acid polymers and copolymers cover a very huge range of applications, such as hydrosoluble agents for dispersing agents, thickeners, flocculating and super-absorbent agents, detergent auxiliaries, organic synthesis, copolymer emulsion for paints, cosmetics, papers, varnishes and inks. In addition, dispersions for leather, textiles, non-woven fabrics, glues and adhesives, cleaning and waxing products. Besides, plastics, synthetic resins, synthetic rubbers and lattices [5-7].

Nano polymerization of acrylic acid systems can be prepared in many different ways. the method of preparation via nanotechnology play an important and significant role in the performance and use properties of the composition in question. (1-4) Aqueous polymerization of acrylic acid was carried out.(5). Continuous polymerization of acrylic salts were carried out. (6). Effects of various the scaling phenomenon may cause technical problems such as reduction of heat transfer efficiency in cooling systems and obstruction of pipes In industrial applications [13], The efficiency of scale inhibitors depends on their chemical properties (functionality, molar mass, polydispersity, and structure) and usage (concentration and method of application) [14] in addition to and the nature of the solids forming.) [15] , Polymers containing carboxylic acids such as poly(acrylic acid) and poly(maleic acid) are the most common groups of polymeric scale inhibitors[16], in addition to Aqueous dispersions of poly acrylates have excellent weather ability, water and alkaline resistance[17-18]Vinyl acrylic polymers are synthesized by copolymerization of acrylates with other materials, either monomers via direct polymerization [19] or with natural materials via graft copolymerization [20-22] using different polymerization techniques. Many countries have passed legislation to reduce the phosphate content of their products without reducing the level of performance expected by the customers. Thus the incentive to replace phosphates in the detergent industry led to the synthesis of polyacrylic acid (poly A A) with a high chelation capacity for calcium ions (Ca^{2+}) instead of phosphates in the detergent industry [23-25] Poly (AA) is an anionic polyelectrolyte [26] besides its chelation ability[27], (poly AA) has also dispersion properties [28], poly AA with molecular weights (Mw) in the range of (50 000 – 90 000) are effective species in preventing scale deposition in desalination [29].polyacrylic acid as antiscaling agent on heat exchangers, cooling water [30-33]. The aim of this study to prepare poly acrylic acid homo-polymers with high performance scale inhibitor, specifically develope to prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution .

EXPERIMENTAL STUDY

Materials

Acrylic acid ($CH_2 = CH - COOH$) Product of Elf Chem. .(ATO) Company (France) M.w (72) b.p at 1013 m bar (141 ºC) freezing point (13 ºC) , specific gravity at (25 ºC) = (1.043) , inhibitor content MEHQ (180-220 ppm) . Amm – Persulphate($(NH_4)_2S_2O_8$ white crystals Product of NBM Chem. Company (England) . - Sod – persulphate $Na_2S_2O_8$ white crystals product of NBM Chem. Company (England) - Iisopropanol Product of Life Chemical Company,(England).- Methanol Product of Life Chemical company (England)..

Synthesis of homopolymerPoly Acrylic Acid p(AA)

The Poly –AA was synthesized in 4 -L, four -necked, round bottom flask that was partially submerged in controlled temperature water bath. In general, the procedure consisted of a load of 688 g of double – distilled water, placed in the round – bottom flask fitted with an over- head stirrer and an 18- in. reflux condenser. The pot temperature was typically maintained at 95 –98 º C. Glacial AA (211.6 g , 4.0 ml per minute) and also 60 ml of the initiator aqueous solution(1.0 ml per minute)were introduced. The amount of acrylic acid monomer varied in the range of 20 % (~ 3.7 M) to 25 % (~ 4.3 M) by weight during the experimental-design work. The initiator, sodium persulphate, was prepared by dissolving 2.50 g of the solid substance in 57.5 g of water. After the persulphate is delivered to the reactor, the concentration is ~ 0.01 M. the acrylic acid and initiator were metered simultaneously over a 60- min period .The heating with slow stirring was continued for another 60 min. Temperature readings were recorded every 15 min during the 2-h run. After the reactions were completed (2-h), the reactor was cooled and vented and the poly –acrylic acid solution was removed and cooled.

RESULT AND DISCUSSION

Effectsofreaction condition onhomopolymerization

The optimum conditions for preparing Homopolymerization acrylic acid by studying the effect of different factors, such as dosages of hydrogen peroxide, reaction temperature, reaction time and concentration of monomer. The effect of each factor on the viscosity of the obtained polymer was studied separately while the other factors being kept constant. Such that the optimum reaction conditions could be estimated on polymerization process.

Effect Of Acrylic Acid Percent

The yield was quantitative in each case. The calculated monomer quantity was added dropwise to the heated water in the three necked flask at 75 – 80 º C upon stirring simultaneously together with a constant percent of Na – persulphate as initiator (5 % of the weight of monomer) dissolved in a quantity of water equal in volume to that of the monomer . The addition time of the monomer and initiator was 1.5 hr , and the stirring continued for further 1 hr .

The results given in Table (1)and fig (2) show that at acrylic acid weight percentage of 5 and 10 %of the total weight of reactants , the obtained values of viscosity of the resulting polymer were too low to be determined with the help of the used apparatus . On the other hand at acrylic acid concentration of 35 % , the obtained polymer acquired very high viscosity , so that it was difficult for the mechanical stirrer to move .

The obtained results show that the obtained viscosity increases with the percentage of the added monomer within the range of (15 – 30%) of the total weight of the used reactants) . The viscosity reaches its highest possible value at monomer percentage of 30 % of the total weight of reactants. However monomer percentage of 25 % was preferred as convenient concentration in the further reactions carried out.

Table.1. Effect of acrylic acid concentration on solution viscosity

Acrylic Acid Quantity, gm and percentage relative to the total weight of reactants	Polymer Viscosity(Poise)
15 (15 %)	0.3
20 (20 %)	0.45
25 (25%)	2
30 (30 %)	3.8

Effect of Initiator Percentage

I - 2 (a) Acrylic acid percentage of 25% of the total weight of reactants (including water) which is the best obtained concentration (c.f. Table 1) was added to the heated water in the three-necked flask at (75 – 80 º C) , simultaneously with Na – persulphate as initiator in different percentages (of the weight of monomer) dissolved in water (wt . of aqueous soln. 25 % relative to the weight of total weight of reactants) in a period of 1.5 hr. The chosen appropriate percentage of initiator which is suitable for the easy stirring and conductance of the experiment was 5 % of the weight of monomer.

At initiator concentration of 10 % of the weight of monomer the obtained polymer acquired such high viscosity , that it was difficult for the mechanical stirrer to move.

Variation of the Viscosity of the obtained Polyacrylic acid with Initiator weight percentage relative to the weight of Monomer.

Table.2. Effect of acrylic acid concentration on solution viscosity

Initiator Percentage relative to the weight of the Monomer	Polymer Viscosity,
2%	5.5
3%	4.2
4%	3.5
5%	2
6%	1.7

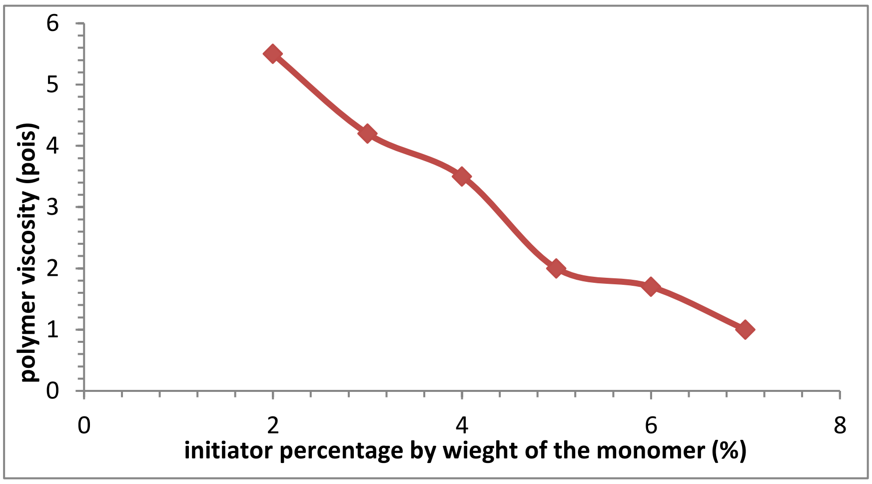


Fig. 2: Initiator percentage versus polymer viscosity (Poise)

Effect of Addition Time

Monomer percentage is 25 %, reaction temperature is (75 – 80 ºC), sodium persulphate as initiator = 5 % (of the weight of the monomer), and the monomer and the initiator solutions were added simultaneously within different addition times.

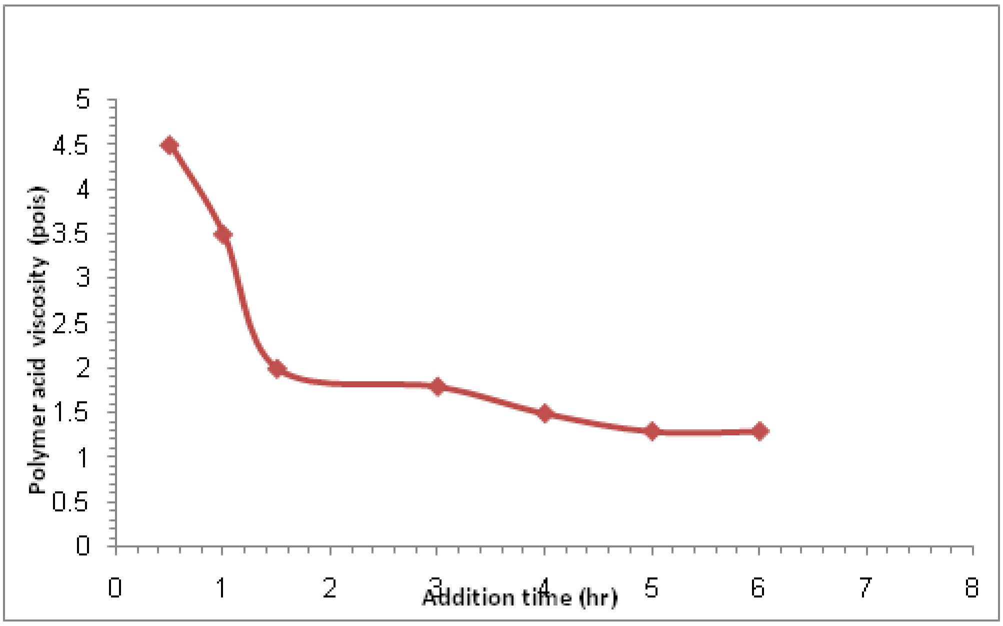
The results given in Table (3) and Fig. (3) show that the addition period of the monomer and initiator solutions to the reaction vessel have serious effect on the viscosity of the obtained product.

In other words the highest value of viscosity is obtained at addition period of 1.5 hr and then decreases with increasing the addition time. The suitable chosen addition period was 1.5 hr addition and stirring continued for further one hr .[36]

Table.3. Effect of time on solution viscosity

Addition time, hr.	Polymer Viscosity ,Poise.
½	4.5
1	3.5
1	2
1 1/2	1.8
3	1.5
4	1.3
5	1.3

Fig.2.Poly acrylic Acid Viscosity ;Poise versus. Addition Time; hr.



Effect Of Overall Reaction Temperature

Acrylic acid percentage of 25 %, sodium persulphate as initiator = (5 % of the weight of the monomer) were used, and the monomer and the initiator solutions were added simultaneously within 1.5 hr . The polymerization reaction was carried out at different overall reaction temperatures. The results given in Table (10) and Fig. (4) show that the overall reaction temperature has serious effect on the viscosity of the obtained product. In other words at overall reaction temperature lower than 55 – 60 º C no product was obtained since the initiator did not dissociate into radicals. At reaction temperature higher than (50 - 60) the viscosity of the product decreased and the suitable value of viscosity was that obtained) at overall reaction temperature (75-80 º C).

Table (4): Variation Of The Viscosity Of The Obtained Polyacrylic Acid With The Overall Reaction Temperature.

Overall Reaction	
Temperature,º C	Polymer Viscosity,
55-60	4.1
65-70	3.3
75-80	2
80-85	1.5
90 – 95	1.3

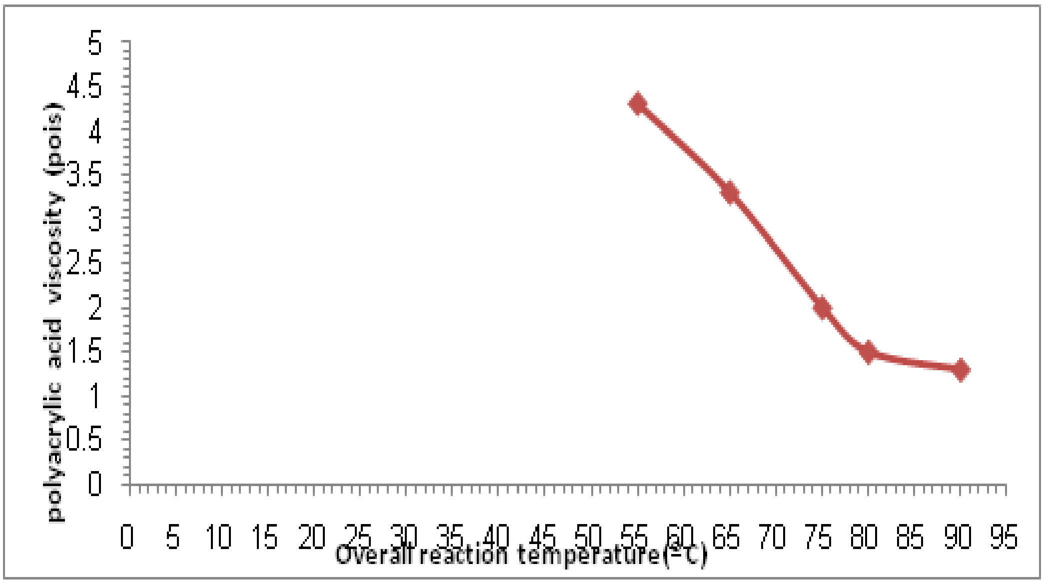


Fig.4.Polyacrylic Acid Viscosity ,Poise, versus Overall Reaction Temperature(ºC)

The data given in Table (4) show that the constitution of the reactants leading to the most suitable solution of the obtained copolymer for sizing process and leading to the best results of sized materials is that conducted according to the experiment in Table (4) where the product was characterized by accepted viscosity for sizing , no tackiness and resulted in good hardness on the sized fibers .The properties of the sized fiber are confirmed in **the Phoronia Tex Co. in the 10th of Ramadan City .**

Modified Method For The Synthesis of (AA) polymer For Application as Dispersing agent and as Chelant.

For the dispersion of high solids contents and mineral slurries , both the paint and paper industries are large user of fine particle size minerals. These minerals are used as pigments and provide opacity/hinding power in the finished products. Whilst most users of such fine particle size powders are well equipped to be handled , it is becoming increasingly common for mineral producers to supply their products in slurry form. This provides the end user with a number of advantages relating to easier handling of pigment, such as simpler mixing equipment and reduced dusting problems.The amount of initiator (wt. percentage of the weight of monomer) was gradually increased in order to obtained the suitable low molecular weight copolymer . The reaction mixture was the cooled and its pH adjusted to 7.5 with the help of NH_4OH (22%)sol-utioThvalidity of both PAA homopolymer and also copolymer (obtained from AA and MAA in different ratios) as dispersing agent were estimated from the results of the determination of the viscosity (poise) , appeahomogeneityoobtained dispersion. Dispersions were found to change according to the ratios of the monomer constitutions in the obtained polymer and co-polymer and ratio of the volume of added isopropanol. .

The data given in Table (14) show that the homopolymer PAA gave bad results concerning dispersion. In case of copolymer the best suitable product as dispersant and chelant was that prepared at AA : MAA ratio = 4 : 1 , isopropanol ratio = 20 % relative to the total volume , water in flask = 30% ,water dissolving initiator = 25% relative to the total volume and initiator percent = 2 % of the weight of monomer (exp No 7) .

A)Procedure For The Evaluation Of Polymer Solution As Dispersion.

In the absence of dispersing agent, it is impossible to introduce a necessary high percentage of the powder into water in the factories for paints when dealing with the formulations of emulsion paints or paste paints . Practically it was possible to introduce quantities of dispersing agents (co-polymer) ranging from 0.2 – 0.6 % relative to the added powder percentage (Talc + TiO_2 + $CaCO_3$)till about 60% of the total weight of paint , to obtain suitable formulation .

The following steps were followed prepared

1- Mixture consisting of water (25% by wt), binder MTB (10% by wt) was prepared in a beaker and mixed together by low velocity stirrer.
2- Small percents (0.2 -0.5 %) of silicon antifoam, and also 0.1 -0.3 % (formaldehyde) anti – bacteria were added.
3- A few quantity of wetting agent (nonyl phenol 0.5 – 1%) was introduced, and noticing that the medium was alkaline (pH =8) with the help of NH_4OH (22%) solution in order to prevent coagulation of the binder as a result of increase of temperature upon stirring.
1. 4-An amount of the prepared polymer (dispersing agent) ranging between 0.5- 1.0 of the total weight % was added with stirring, followed by a quantity of filler (TiO_2 + $CaCO_3$+ talc) , about 60% of the total weight of the used reactants , with vigorous stirring for 5-10 min.
4- The viscosity of the whole mixture was measured using viscometer, notice that the low value of viscosity indicates that the dispersion proceeds progressively taking care that the amount of dispersing agent is small (0.5 -0.8 % of total weight) .

B) Polyacrylic Acid As Chelating Agent .

Chelating agent forms soluble complexes with earth alkali salts (calcium , magnesium) and at the same time has an anticatalytic effect in the presence of heavy ions (iron , copper) when bleaching with hydrogen peroxide .

i) Chelating agent permits the following especially noteworthy effects : forms complexes with earth alkali salts (calcium ,magnesium even in a strongly alkaline medium , thus preventing precipitation of hydroxides , oxides , carbonates soaps and other insoluble compounds
ii) Prevents the formation of insoluble compounds silicates when bleaching with hydrogen peroxide , thanks to its inhibiting action (threshold effect inhibition) , thus avoiding troublesome deposits on the textile goods ad machine parts .
iii) Demineralizes cotton and other natural fibers during treatments in an aqueous medium : the ash content is correspondingly low has a very good anticatalytic effect against heavy metal ions (iron , copper) during bleaching with hydrogen peroxide
iv) Softens water , thus counteracting formation of insoluble calcium deposits in pipes , tanks , machines , etc .
v) Has a good dispersing effect on an accompanying substances released during treatment and /or impurities in the cotton , which become easier to release and wash off in the subsequent rinsing process , with positive effects on the absorbency , whiteness and handle of the textile material
vi) Alkali- resistant in caustic soda solutions up to and over 30 ◦ Be , thus highly suitable for use in highly concentrated bleach reinforcing liquors . vii) corrosion inhibitor on metal viii) Non-foaming .
Chelating agent is used for the following purposes.
i) Complexing calcium and magnesium ions in a aqueous medium
ii) Preventing formation of insoluble silicate deposits on textile goods and machine parts .
iii) Demineralizing cotton and other natural fibers
iv) Preventing catalytic damage to cellulosic fibers when bleaching with hydrogen peroxide in the presence of heavy metal ions softening mains water .
v) This polymer is used in textile and coating factories , swimming pools and water boilers . it was tested as chelating agent in Alpha factory for water treatment and it was approved .

The addition of the prepared co-polymer (c.f Table 13, exp. No 8) to ordinary tap water (2-4 gm /liter) in the textile factories is found to eliminate the hardness of water (which results for the presence of excess amounts of Ca^{++} and Na^{+} ions and salts) .

It was therefore possible to use the obtained soft water for washing process .

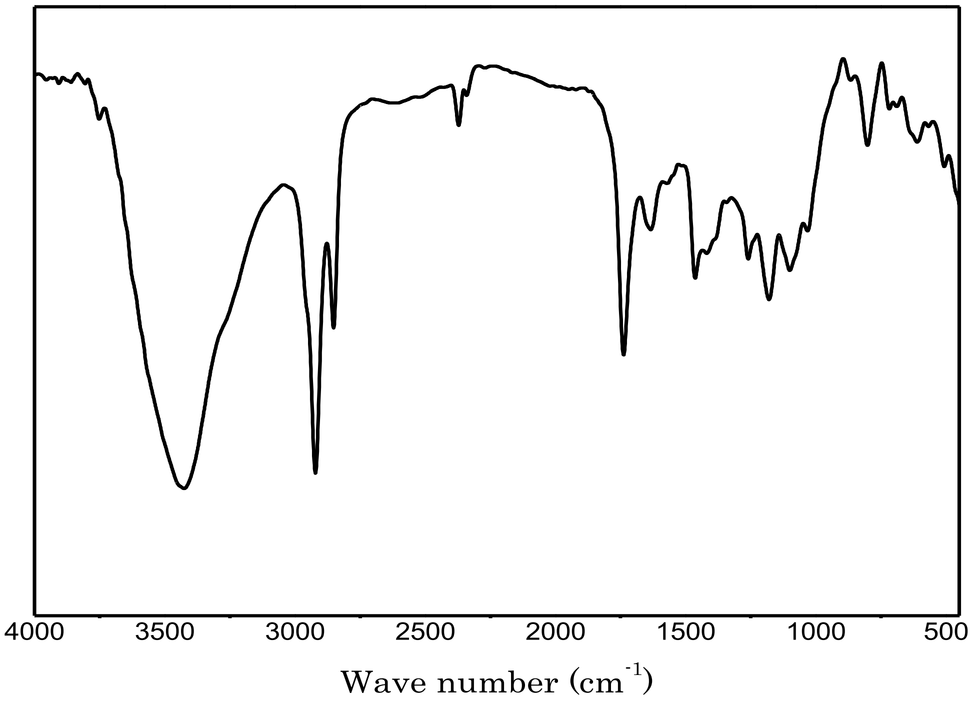
When added to boilers5 gm / liter , the used chelating agent was found to remove the salts formed on the surface of the boiler , otherwise the efficiency of the boiler is lowered

Characterization of the prepared polymers

Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectroscopy was used as an analytical technique for the estimation of the functional groups presented in Polymers [42]. In this study, FTIR spectroscopy was able to differentiate the chemical bonds in the molecular structure of P(AA). The P(AA) sample was analyzed using KBr pellet technique. In this technique, The film of the polymer was obtained by blending the solid samples with KBr to obtain transparent discs. It was then scanned by the Perkin Elmer system 2000 FT-IR spectrometer in the range from 4000 cm-1 – 400 cm-1 IR spectrum of polyacrylic acid P(AA) Show that characteristicγC = 0 stretching vibration at 1714.68 cm-1and very broad band having a medium value at 3429.14 cm-1 characteristic for γ CHaliphatic of methylene and methine coupled with that of γ OH of carboxylic group and that of γ H2O [43], (Water of crystallization) stretching vibrations with appearing a 6 CH deformation at 1457.86 cm-1 .and OH out of plan at 1097.23 cm-1 [44]

Fig(6)FT-IR spectra of polyacrylic acid homopolymersP(AA)



TGA was recorded on , Shimadzu, Thermo Gravimetric Analyzer

The TGA analysis was done in the presence of air .Results of TGA for the prepared polymers PAA, PMAA, PAA-PMAA co-polymer and PAam systems are given in Table (15) and Figs. (21-24) . The first stage decomposition of PAA (wt loss = 21.6 %) started at about 240 ºC which is ascribed to be due to the formation of anhydride linkages $^{(56)}$. Similar values were reported for PAA $^{(57)}$.

Heating at 300 ºC and higher results in wt loss = 32.4 % where possible decompositions to monomer, carbon dioxide, and volatile hydrocarbons are reported at temperatures higher than 300 ºC

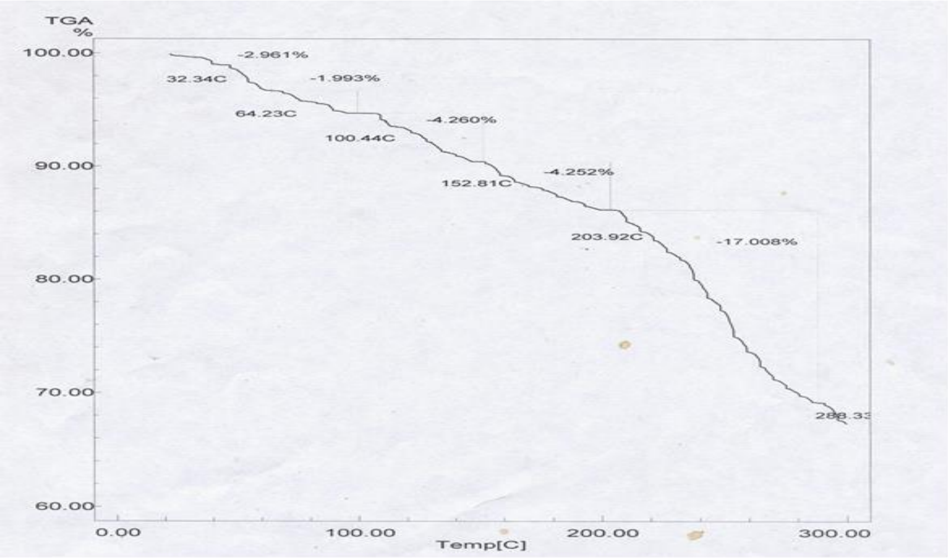


Figure (7) Thermo gravimetric Diagram for The prepared P.A.A

Gel Permeation Chromatography (GPC) analysis

GPC spectra of modified P(AA)homopolymer (The weight average (Mw),number average(Mn), andpolydispersity are given in in table (7) and figure (7).

7.Gell Permeation chromatography Data for P(AA)			
Sample	***Mn*(g/mol)**	***Mw*(g/mol)**	***Mw/Mn(polydispersity)***
P(AA)	**5.7911e4**	**9.0861e4**	**1.56**

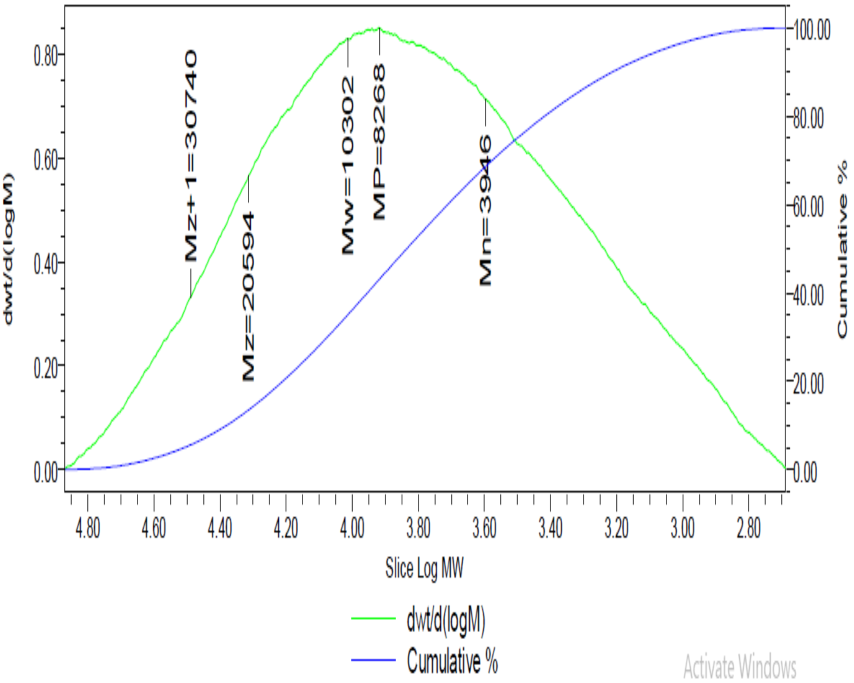


Fig (7) Gell Permeation chromatography(GPC)for P(AA)

CONCLUSIONS

- The optimum conditions for the polymerization of homopolymers from Poly acrylic acid P(AA).such as the concentrations of monomer, concentration ofinitiator, time of addition of both monomer and initiator effect of time reaction on the conversion of monomers can conclude that viscosity of the polymer solutions and hence their molecular weight increases by increasing monomer concentration, but decreases with increasing initiator concentration, time of addition and reaction temperature after a certain degree.

- At higher monomer concentration for example more than 30% the polymerization solution becomes very viscous, so the stirring becomes too difficult, on the other hand lowering the viscosity can be attained by increasing the initiator percentage, time of addition and reaction temperature, which results in decreasing the viscosity and enhance decreasing molecular weight of the obtained hom-polymer.

- The experimental results showed thatmodifiedpoly acrylic acid had an excellent efficiency of scale inhibition for calcium sulfate, nearly 95.% of scale inhibition efficiency, This product,Poly acrylic acid can replace phosphonates as scale control agents to prevent the formation of calcium sulfate and other scales such as calcium carbonate,The recommended dose couid be in the range (50-100ppm).

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