STUDYING THE EFFECT OF IMETHYLFORMAMIDE AS INHIBITOR ON THE POLYMERIZATION OF ACRYLIC ACID

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ABSTRACT

Acrylic acid is very active, it can undergo polymerization even in absence of any initiators.Firstly theesterification of acrylic acid was carried out without DMF in presence of p-Toluenesulfonic acid (PTSA) monohydrate as a catalyst. The molecular weight of the product ester was found 127000 g/mol. Esterification of acrylic acid with different alcohol, n- Butyl [C_4H_9OH]*,n- Hexyl* $C_6H_{13}OH$*, Octyl* [C_8H_{17} OH]*, Decyl*[$C_{10}H_{21}OH$]*, Dodecyl* [$C_{12}H_{25}OH$]*, in presence of p-Toluenesulfonic acid (PTSA) monohydrate as a catalyst and Dimethylformamide (DMF) as inhibitor for the polymerization of acrylic acid wasdone. The molecular weight of the prepared esters were measured, it was found that all of them less than 600 g/moland the structures was confirmed by FTIR. Esterification of acrylic acid with alcohol in presence of benzoyl peroxide as an initiator was studded. The effect of molar ratio of DMF and concentration of both PTSAand benzoyl peroxide were studied .It was found that with increasing the molar ratio of DMF the degreeof polymerization decreased until certain ratio. On contrast with increasing the concentration of PTSA, the rate of the esterification increases.It is observed that at low concentration of benzoyl peroxide the polymerization process takes place Mw.591 g/molbut with increasing the concentration of benzoyl peroxide to 2.0 % the degree of the polymerization decreased Mw.157 g/mol.Accordingly DMF inhibits the polymerization of acrylic during the esterification and for the product esters with efficiency.*

Keywords: *Acrylic Acid, Alcohol, Dimethylformamide, Esterification, Inhibition, Molecular Weight and Polymerization.*

I. INTRODUCTION

Esterification is a chemically reversible reaction producing ester and water from two reactants of acid and alcohol. The desired product, ester provides useful applications in chemical industry [1]. Various acrylic esters are useful chemicals. Their excellent clarity, toughness, colour retention, UV stability and chemical inertness make acrylic ester emulsion polymers prime paint binders. Acrylics are widely used in all types of paint formulations, leather finishing, textile and fibre fill bonding and as adhesives [2].Especially butyl acrylate is widely used in industry as a precursor for varnishes, adhesives and finishes of papers and textiles [3]. Homogeneous catalysts such as sulfuric acid, hydrofluoric acid and para-toluene sulfonic acid are toxic, corrosive and often hard to remove from the products. Many works on esterification with different ion exchange resins have been studied. For example, esterification of acetic acid with n-amyl alcohol in the presence of Amberlyst 36 [4], propionic acid with 1-propanol [5]catalysed by Dowex 50Wx-400, lactic acid with ethanol using Amberlyst 15[6],and acetic acid with methanol in the presence of different ion exchange resins, Indion 130, Indion 190 and Amberlyst15 [7] were carried out at different reaction conditions[8].

Esterification reaction between acrylic acid and 2-ethylhexanol was investigated in an isothermal semi-batch reactor by using sulfuric acid as a homogeneous catalyst.Esterification of acrylic acid with 1-butanol has been studied in the presence of solid oxides and organic resins as heterogeneous catalysts. [9]. Among the other many acrylates, hydroxypropyl acrylates are used in production of acrylate polymers [10-12] and as a comonomer in adhesives, elastomers [13], inks, radiation curable[14], automotive top coating, nanocomposites materials [15], photo cure resins and oil additives and as a viscosity reducer [16,17].The properties of the resulting acrylics vary depending on the nature of the alkyl groups both on the alcohol and the acrylic acid. In addition, an inhibitor has to be used in the whole process to minimize polymerization of acrylic acid and acrylic ester. In order to avoid its local depletion, the inhibitor has to be added in every distillation column [18].

The addition of toluene, etherand n-hexane sharply reduces the polymerization rate and the fraction of syndiotactic polymer. The viscosity of acrylic acid also drops in the presence of these solvents. These results are in agreement with the assumption that he polymerization of acrylic acid is strongly controlled by linear monomer aggregates. The polymerization of acrylic acid are related to the fact that this monomer forms associated structures via hydrogen bonding.

In the present work, we study the inhibition of polymerization of acrylic acid during its esterification with different chain alcohols (n- Butyl [C_4H_9OH],n- Hexyl $C_6H_{13}OH$, Octyl [C_8H_{17} OH], Decyl[$C_{10}H_{21}OH$], Dodecyl [$C_{12}H_{25}OH$]) , in presence of p-Toluenesulfonic acid (PTSA) monohydrate as a catalyst and Dimethylformamide (DMF) as inhibitor. The effect of molar ratio of DMF and concentration of PTSA were studied.

II. MATERIALS AND METHODS

2.1 Materials

In this work Acrylic acid [$H_2C=CH–COOH$] was esterified using a number ofalcohols, n- Butyl [C_4H_9OH],n-Hexyl $C_6H_{13}OH$, Octyl [C_8H_{17} OH], Decyl[$C_{10}H_{21}OH$], Dodecyl [$C_{12}H_{25}OH$], Benzoyl peroxide [$(C_6H_5CO)_2O_2$] was used as an initiator,p-Toluenesulfonic acid (PTSA) monohydrate [$CH_3C_6H_4SO_3HH_2O$] were used as catalyst. Dimethylformamide [$(CH_3)_2NC(O)H$]. All materials are from Aldrich Chemical Co. Ltd. (U.K.).All the prepared esters was characterized with Mass Spectra using thermo scientific trace GC ULTRA complex with single quadrupole (ISQ)and Fourier Transmission Infrared using a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique.

2.2 Experimental Procedure

2.2.1 Esterification of acrylic acid without DMF

2.2.1.1 Esterification of acrylic acid with hexyl alcohols [19]

Esterification has been carried out by reacting one mole of acrylic acid with one mole of the n-hexyl alcohol (as example) without dimethylformamide in presence of 1.5 % p-toluene sulfonic acid as a catalyst in dean-stark to monitor the amount of liberated water. The molecular weight was measured, it was 127000 g/mol .From the characterization of the product ester by FTIR, it was found that the peak of C=C which belongs to vinyl group of acrylic acid at 1600-1680 cm^{-1} was disappeared. However the peak of ester at 1730 cm^{-1}was appeared as shown in Fig. (1).

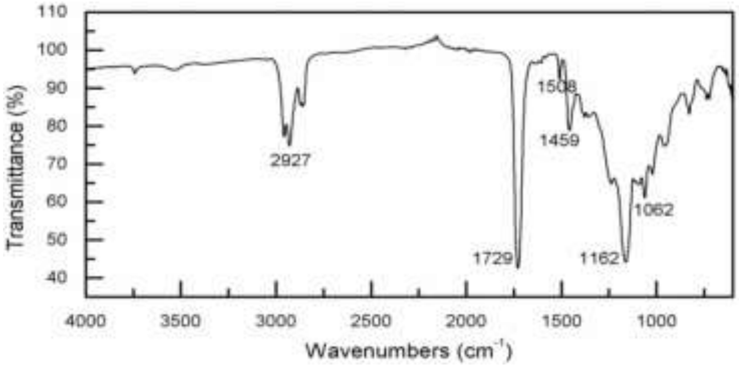


Fig (1): FTIR of Polyhexyl Acrylate

2.2.2 Esterification of acrylic acid with DMF

2.2.2.1Esterification of Acrylic Acid with Different Types of Alcohols [19]

Esterification has been carried out by reacting one mole of acrylic acid with one mole of the selected alcohol (n-Butyl, hexyl, octyl, decyl and dodecyl). The reactions were carried out in a resin kittle in presence of 1.5 % p-toluene sulfonic acid as a catalyst, Dimethylformamide (equal volume of used acrylic acid) as inhibitor for the polymerization of acrylic acid, and xylene as a solvent which used in dean-stark to monitor the amount of liberated water. The reactants heated gradually from the room temperature up to 130 ^{0}c. The molecular weight for all product esters were measured, it was found that they ranging from 120-300 g/mol and they characterized by FTIR, it was found that the peak of C=C which belongs to vinyl group of acrylic acid at 1600-1680 cm^{-1} was appeared and the peak of ester at 1730 cm^{-1}was found as shown in Fig.(2).

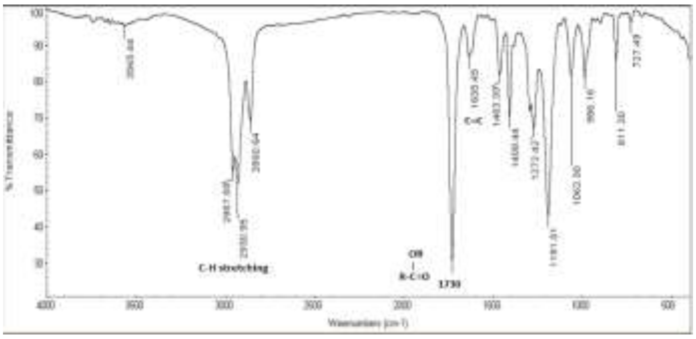


Fig (2): FTIR of Hexyl Acrylate

2.2.2.2 Esterification of Acrylic Acid with Hexyl Alcohol with Different Molar Ratio of DMF in Presence of PTSA

Esterification of acrylic acid (1 mol.) with hexyl alcohol (1 mol.)as example of the selected alcohols was occurred with the same condition in presence of 1.5 % p-toluene sulfonic acid with different molar ratio of DMF (0.25, 0.5, 1.0, and 2.0) as inhibitor.

2.2.2.3 Esterification of Acrylic Acid with Hexyl Alcohol with Different Molar Ratio of DMF in Presence of Benzoyl Peroxide

Esterification of acrylic acid (1 mol.) with hexyl alcohol (1 mol.) as example of the selected alcohol was occurred with the same condition in presence of 0.5% %benzoyl peroxide with different ratio of DMF (2.0, 3.0 and 4.0) as inhibitor.

2.2.2.4 Esterification of Acrylic Acid with Hexyl Alcohol with Different Concentration of PTSA

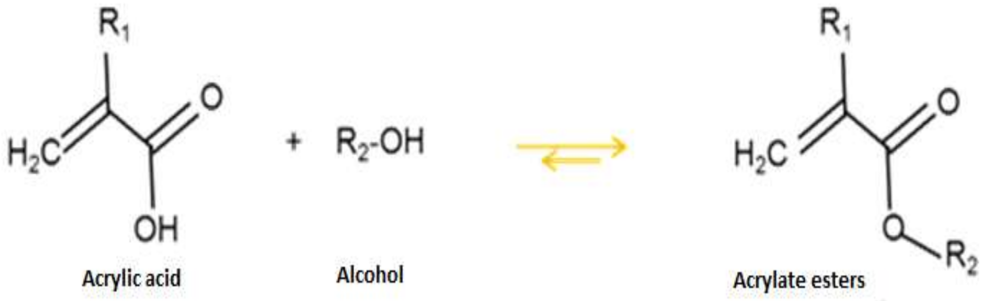
Esterification of acrylic acid (1 mol.) with hexyl alcohol (1 mol.) as example of the selected alcohol was occurred with the same condition in presence of 1mol. DMF with different concentration of PTSA (1.5, 3.0 and 6.0 %) as catalyst.

2.2.2.5 Esterification of Acrylic Acid with Hexyl Alcohol with Different Concentration Of Benzoyl Peroxide

Esterification of acrylic acid (1 mol.) with hexyl alcohol (1 mol.) as example of the selected alcohol was occurred with the same condition in presence of 1mol. DMF with different concentration of benzoyl peroxide (0.5, 1.0 and 2.0 %) as catalyst.

III. RESULTS & DISCUSSION

Acrylic esters are very important monomers that are widely applied in production of homo- and copolymers.A survey of the literature indicates that the important of hydroquinone to inhibit the acrylic acid to be polymerize [20].The synthesis of acrylic esters can be represented by the “equation 1”:



Therefore study was conducted to investigate the inhibition period of acrylic esters through studying some different parameters affected the esterification process with note that the timeof experiments specifiedexit the amount of liberated water:

3.1 The Effect of Carbon Chain Length of Alcohols

From the esterification of acrylic acid with different alcohol it was found that the long chain of alkyl group of alcohol (R-OH) don’t affect both esterification rate and degree of polymerization. Accordingly the molecular weight for all esters are related to the long chain of the alkyl chain as shown in Fig. (3).

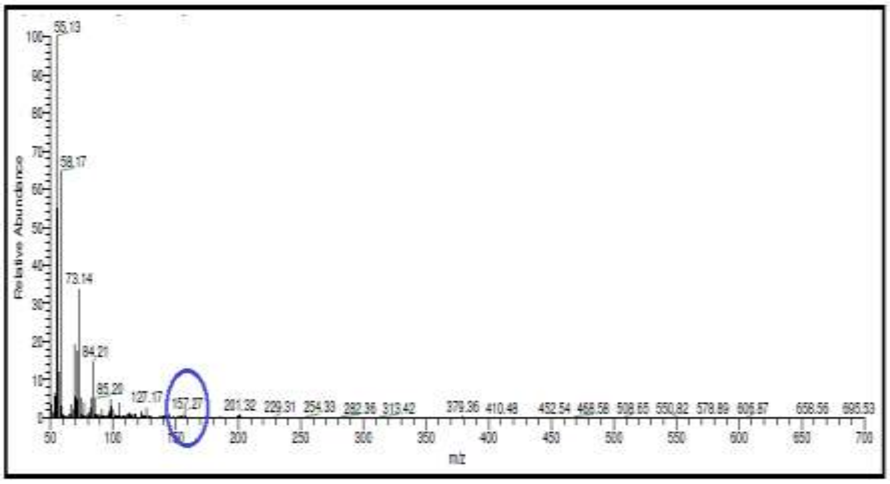


Fig. (3): Mass Spectroscopy of Hexyl Acrylate

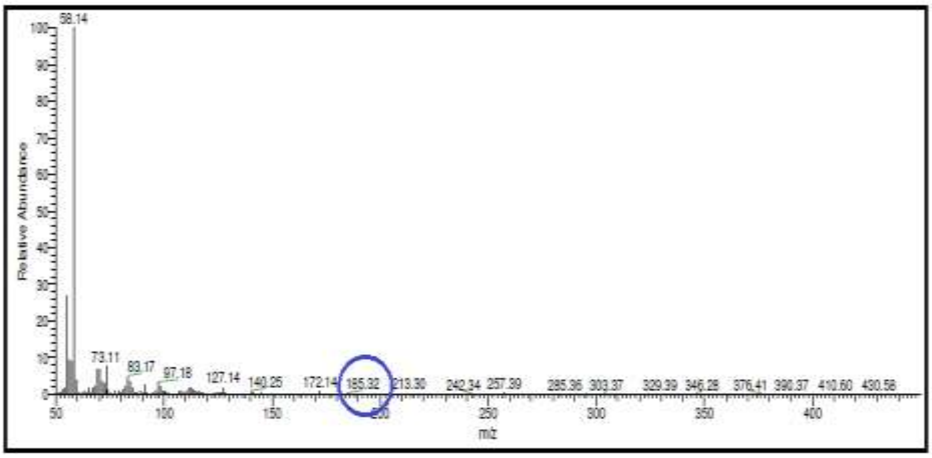
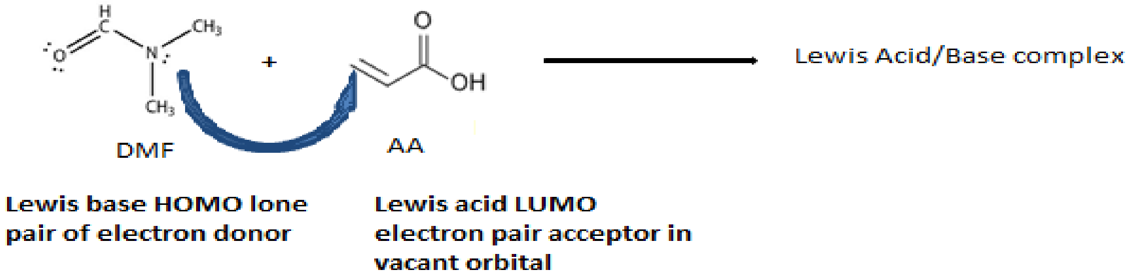


Fig. (4): Mass Spectroscopy of Decyl Acrylate

3.2 The Effect of Different Molar Ratio of DMF in Presence of PTSA

The different molar ratio of DMF (0.25, 0.5,1 and 2) with respect to the acrylic acid at constant concentration of PTSA (1.5%) plays an important rolein the competition between the processes of polymerization and esterification. The reliability and accuracy of the molecular weight produced by mass spectroscopy confirmed that increasing the molar ratio of DMF inhibit the polymerization process due to the lone pair of nitrogen of DMF(Lewis base)which blocking the π electrons of the double bond of acrylic acid (Lewis acid) accordingly the molecular weight of the esters are 470,274,157 and 157 g/molrespectively. It is clear that DMF at 1mole is sufficient to inhibit the polymerization process as shown in Fig.(5-8).The proposedinhibition mechanism of DMF as follow in “equation 2”:



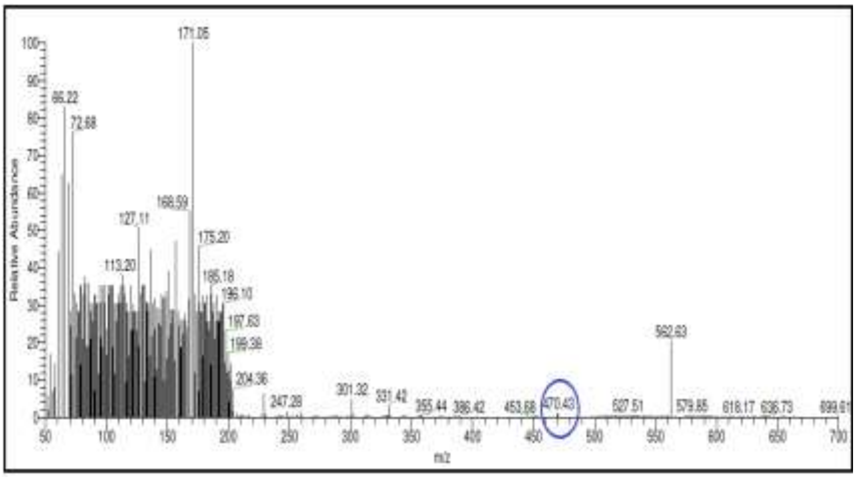


Fig. (5): Mass Spectroscopy of Hexyl Acrylate in Presence of 0.25mole DMF

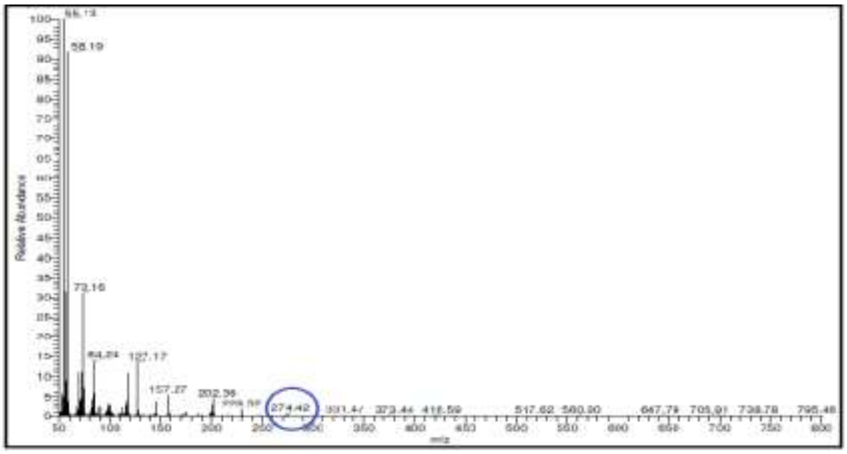


Fig. (6): Mass Spectroscopy of hexyl acrylate in presence of 0.5 mole DMF

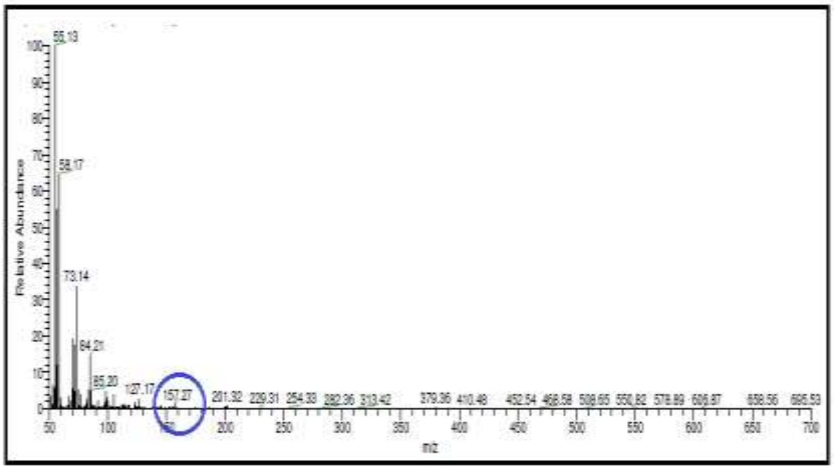


Fig. (7): Mass Spectroscopy of hexyl acrylate in presence of 1.0 mole DMF

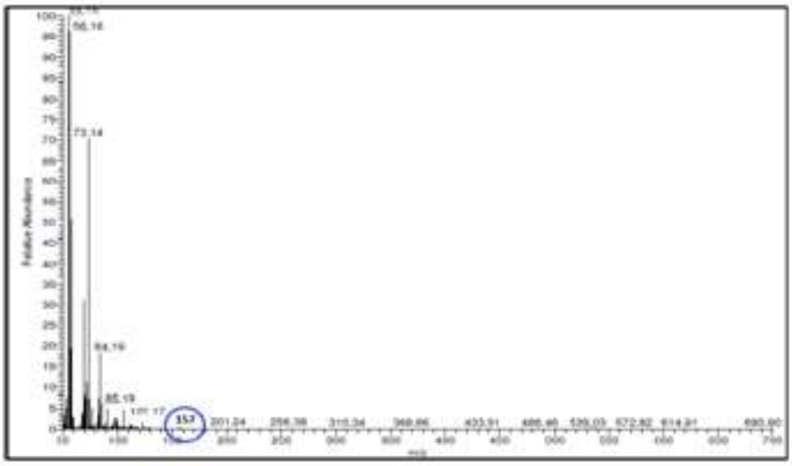


Fig. (8): Mass Spectroscopy of hexyl acrylate in presence of 2.0 mole DMF

There are two probabilities of the effect of DMF during the esterification:

1. Attacking the acidic proton of carboxylic group of the acrylic acid to the lone pair of nitrogen atom of DMF <u>or</u> Attacking the lone pair of nitrogen atom of DMF on π bond of the acrylic acid.
2. From the molecular weight results it is expected that the majority for second probability.

3.3 The effect of different molar ratio of DMF in presence of benzoyl peroxide

It is observed that with increasing the molar ratio of DMF (1, 2 and 4) in presence of 0.5 % of benzoyl peroxide the polymerization process was limited the rate and degree of polymerization although the benzoyl peroxide is strong initiator. The molecular weight of the product esters were 591,441 and 313 g/mol as shown in Fig. (9-11).

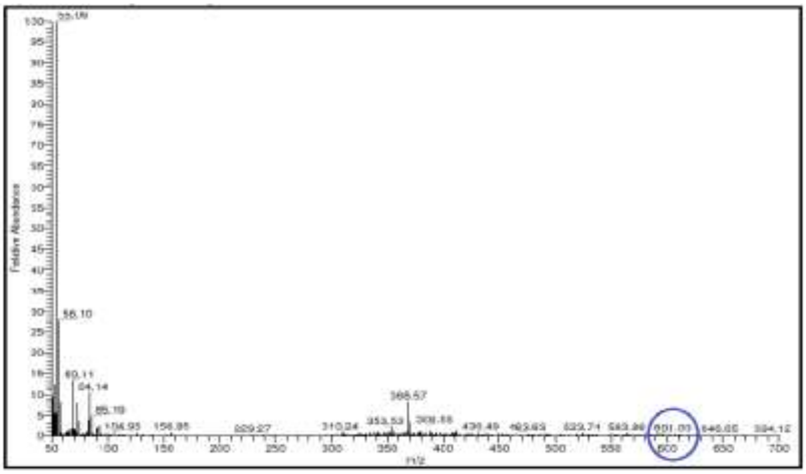


Fig. (9): Mass Spectroscopy of hexyl acrylate in presence of 1.0 mole DMF

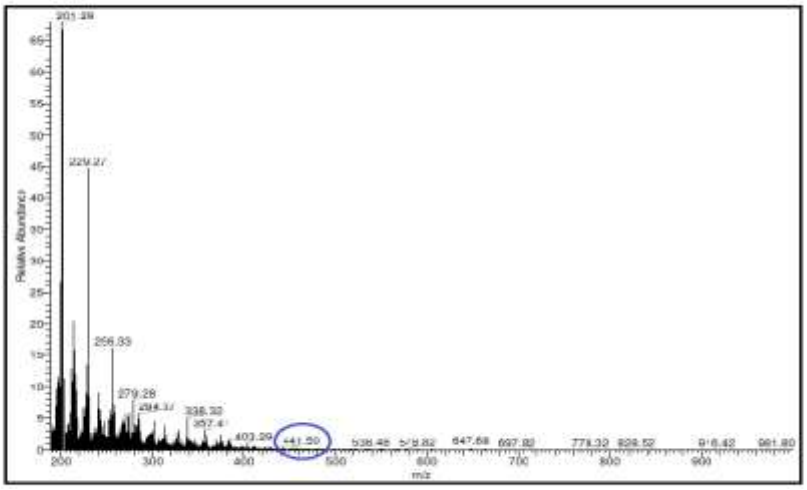


Fig. (10): Mass Spectroscopy of hexyl acrylate in presence of 2.0 mole DMF

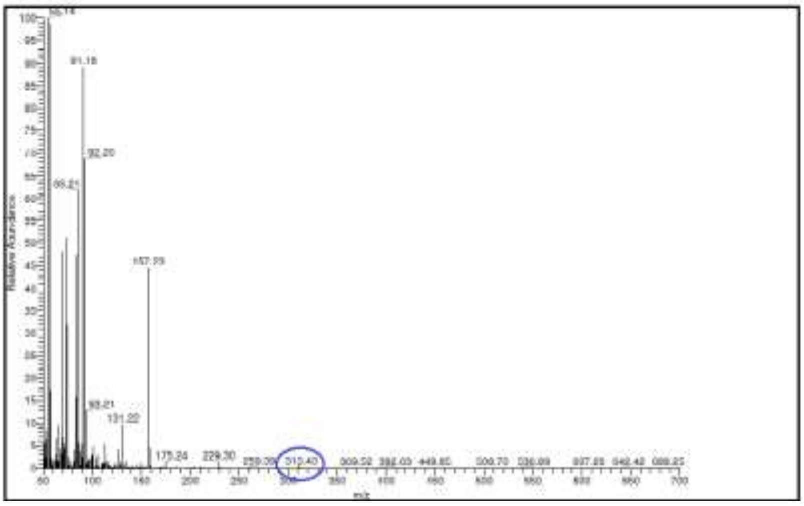
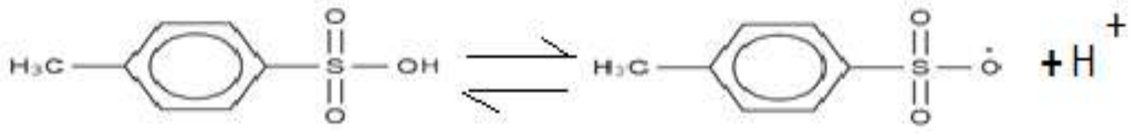


Fig. (11): Mass Spectroscopy of hexyl acrylate in presence of 4.0 mole DMF

3.4 The effect of different concentration of PTSA



ρ-Toluenesulfonic acid ρ- Toluenesulfonate

At constant molar ratio of DMF to acrylic acid 1:1 the catalyst PTSA loading on conversion of acrylic acid to acrylate ester was studied .The catalyst loadings were varied as 1.5, 3.0 and 6.0 %.It was found that the rate of esterification reaction increases due to increase of acid sites available for the reaction with the increase of catalyst loading [21-23]as shown in “equation 3”and has no effect on the polymerization of acrylate which was inhibited by DMF as shown in Fig.(12, 13, 14).

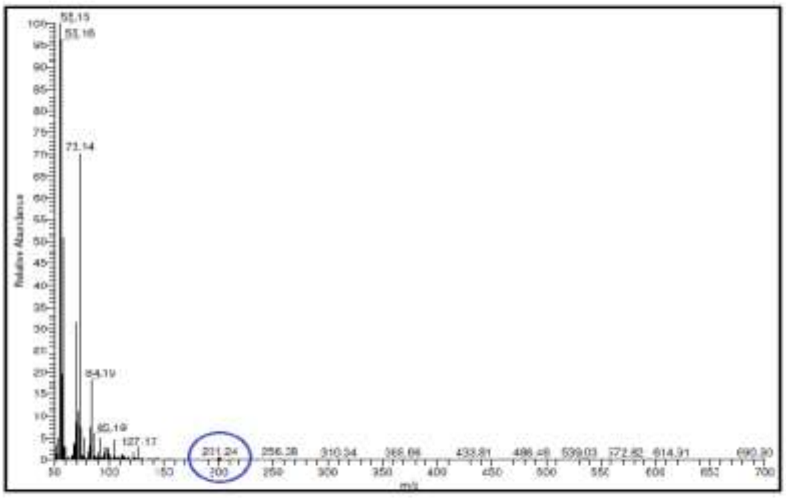


Fig. (12): Mass Spectroscopy of hexyl acrylate in presence of 1.5 % of PTSA

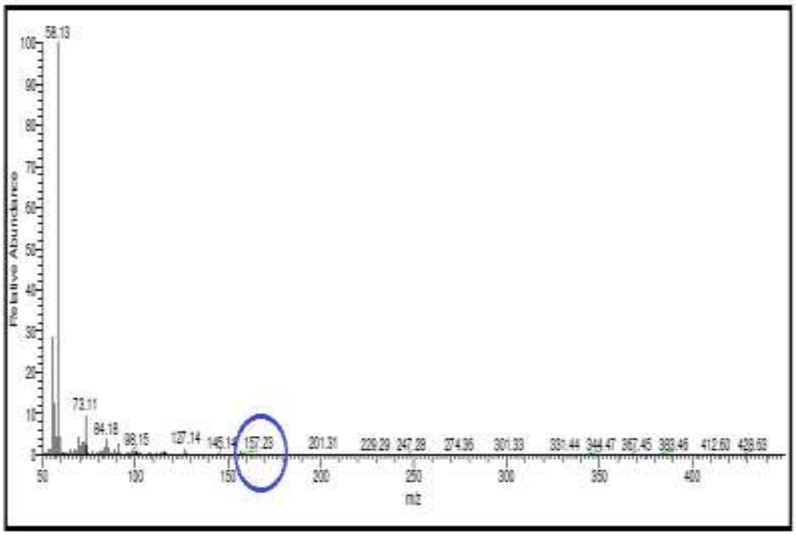


Fig. (13): Mass Spectroscopy of hexyl acrylate in presence of 3 % of PTSA

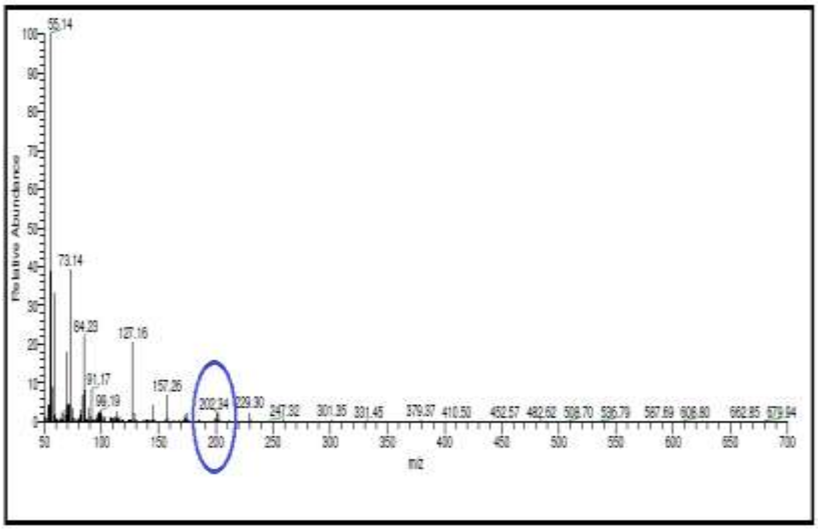
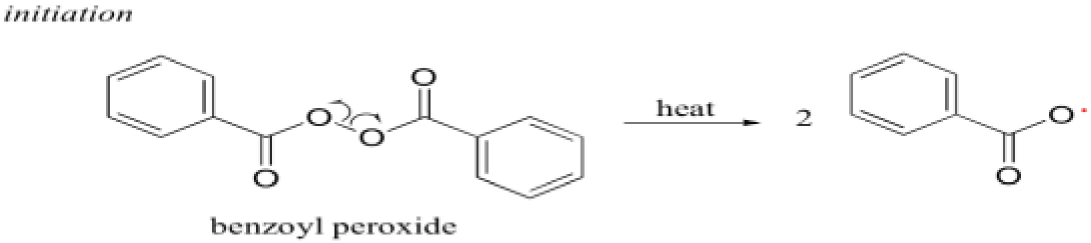


Fig. (14): Mass Spectroscopy of hexyl acrylate in presence of 6 % of PTSA

3.4 The Effect of Different Concentration of Benzoyl Peroxide



To investigate the effect of the concentration of benzoyl peroxide as initiator at constant molar ratio of DMF to acrylic acid 1:1 the concentration was changed as 0.5, 1.0 and 2.0 % in absence of PTSA as catalyst. The results are given in Fig. (15-17).It is observed that at low concentration of benzoyl peroxide the polymerization process takes place Mw.591 butwith increasing the concentration of benzoyl peroxide 2.0 % the degree of the polymerization decreased Mw.157 g/mol.This results due to the excess of benzoyl peroxide free radical as shown in “equation 4”which block the propagation process with addition the effect of DMF which already block on π bond of acrylic acid.

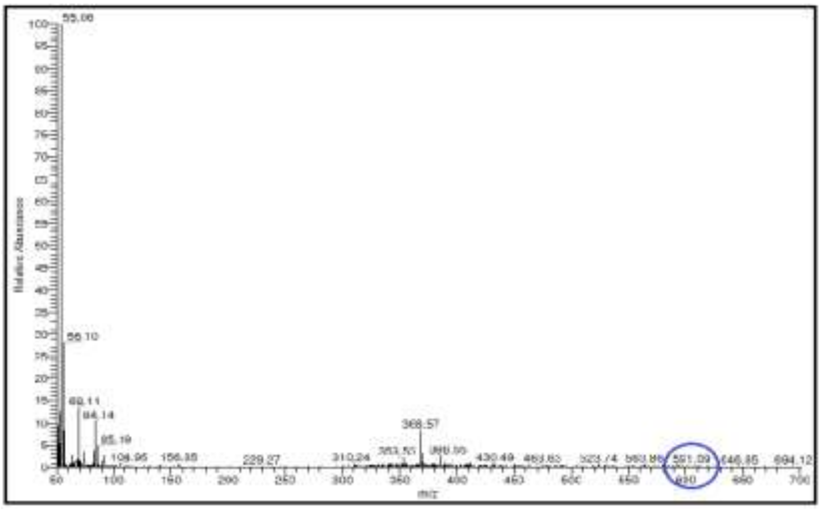


Fig. (15): Mass Spectroscopy of hexyl acrylate in presence of 0.5% of benzoyl peroxide

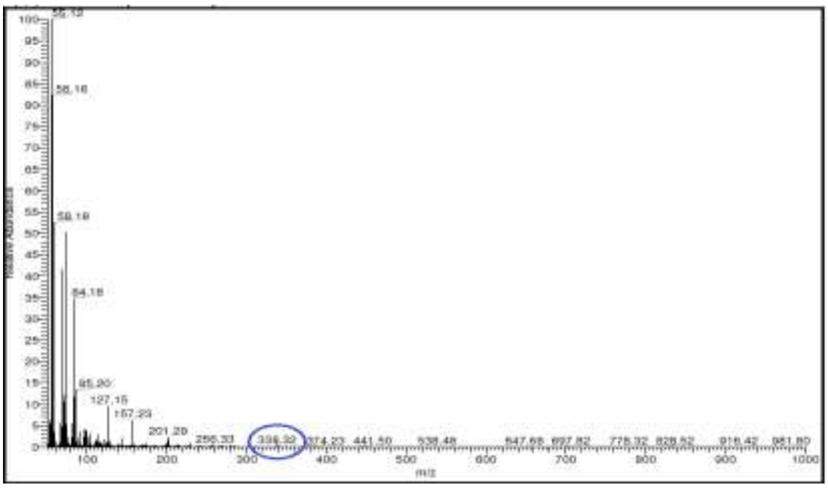


Fig. (16): Mass Spectroscopy of hexyl acrylate in presence of 1.0% of benzoyl peroxide

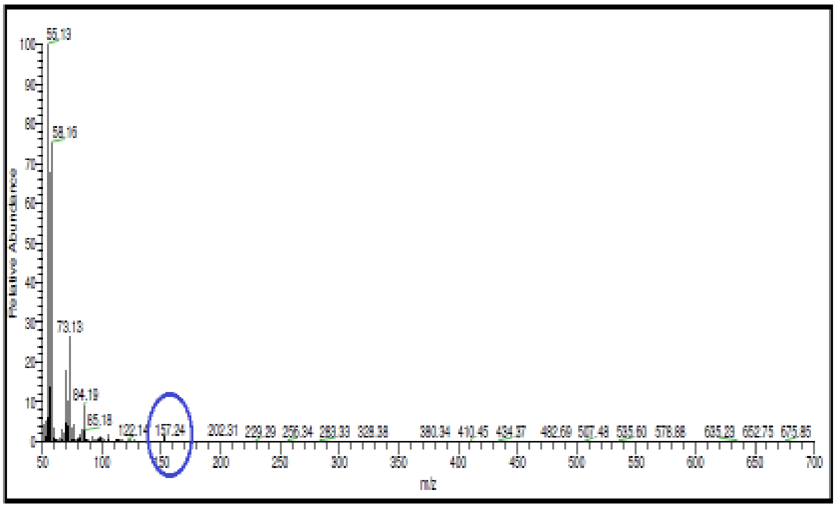


Fig. (17): Mass Spectroscopy of hexyl acrylate in presence of 2.0% of benzoyl peroxide

IV. CONCLUSION

The esterification of acrylic acid with different alcohols was studied and it was found that the different long chain of the alkyl group don't affect the role of DMF as an inhibitor on the polymerization process.The effect of different molar ratio of DMF in the presence of PTSA as a catalyst or benzoyl peroxide as initiator shows that the DMFdiscouraged efficient polymerization process. But when the molar ratio of DMF was constant to acrylic acid 1:1 in the presence of different concentration of PTSA as a catalyst, it was found thatthe rate of esterification reaction increases due to increase of acid sites available for the reaction with amount of catalyst loading and has no effect on the role of DMF as inhibitor of polymerization.

On contrast in case of different concentration of benzoyl peroxide as an initiator, the results confirmed that the excess of benzoyl peroxide free radical helps DMF to inhibit the polymerization processes during the esterification. All these result confirmed that the dimethylformamide inhibit the double bond of acrylic acid or formed acrylate to be polymerized.

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