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Synthesis, Characterization and Thermal Studies of Poly(5-Indanyl Methacrylate)

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Abstract : A monomer of 5-indanylMethacrylate (5-IMA), has been synthesized from the precursor viz., 5-indanol and characterized by Fourier transform infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopic Techniques ^{1}H-NMR and^{13}C-NMR.Homopolymerization of 5-IMA is carried out in benzene by free radical Solution polymerization at 70°C using Benzoyl Peroxide. Then the Homopolymer of Poly (5-Indanyl Methacrylate) wascharacterized by Fourier transform infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopic Techniques (^{1}H-NMR) spectroscopy. Analysis of the thermal properties of the Poly(5-IndanylMethacrylate) by Thermogravimetric analysis (TGA) and Differencial Scanning Calorimetry Analysis (DSC) is also reported.
Keywords: 5-indanyl Methacrylate, TGA and DSC.

1. Introduction:

We have studied in a lot of poly (methacrylates) the influence of the chemical structure of the repeating unit on its conformational parameters. The rigidity of the chain is a property that determines many characteristics of the polymers in both solidstates as well as in solution. The use of homopolymers and copolymers especially designed with functional active groups as lateral substituent of the main chain is a topic increasing and interest. [1-2]. These kinds of macromolecules possess significant importance from both a fundamental and an applied point of view. Polymers aromatic acrylates and methacrylate are highly reactive monomers due to the presence of the aromatic ring and thus form and interesting class of polymers. Phenylmethacrylates find application in the preparation of many polymeric reagents and as electro - active polymers [3-4]. Methacrylate monomers consisting of an alkyl group, an acrylate ester group, and a functional carboxyl group can react with a wide range of monomers and functionalized molecules providing flexible polymer chains. Alkyl methacrylates are clear and volatile liquids that are slightly soluble in water and highly soluble in alcohols, ethers, and organic solvents (Wright, 1981; Braden et al., 1997; Parker et al., 1998).Aromatic acrylates and methacrylate are highly reactive monomers due to the presence of the aromatic ring and thus form an interesting class of polymers. Methacrylates based polymers are a type of important materials and wide applications drive efforts to prepare materials with highly improved properties. The advantage of methacrylate based polymers is its high thermal, chemical and mechanical stability, Which makes them best candidates for applications that require adhesion to various substrates, abrasion resistance, flexibility, toughness and excellent resistance to chemicals, solvents, and water. The degradation temperature of such Polymers could have high temperature as 500^{o}C.Aliphatic methacrylic ester containing ester group functionality [5] and the synthesis of bicyclic aromatics, such as isomeric acetonaphthyl methacrylate, and their polymers [6]

having long lived triplet states have been reported. Macromolecular derivatives of drugs can be prepared by the chemical transformation of the drug into a reactive derivative suitable for polymerization or by binding the drug into an existing natural or synthetic polymer [7, 8]. The aim of our research to study the synthesis[14-24] of 5-IndanylMethacrylate and its Homopolymer were characterized by Fourier transform infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopic Techniques (^{1}H-NMR) spectroscopy. Analysis of the thermal properties of the Poly (5-Indanyl Methacrylate) by Thermogravimetric analysis (TGA) and Differencial Scanning Calorimetry Analysis (DSC) are also reported.

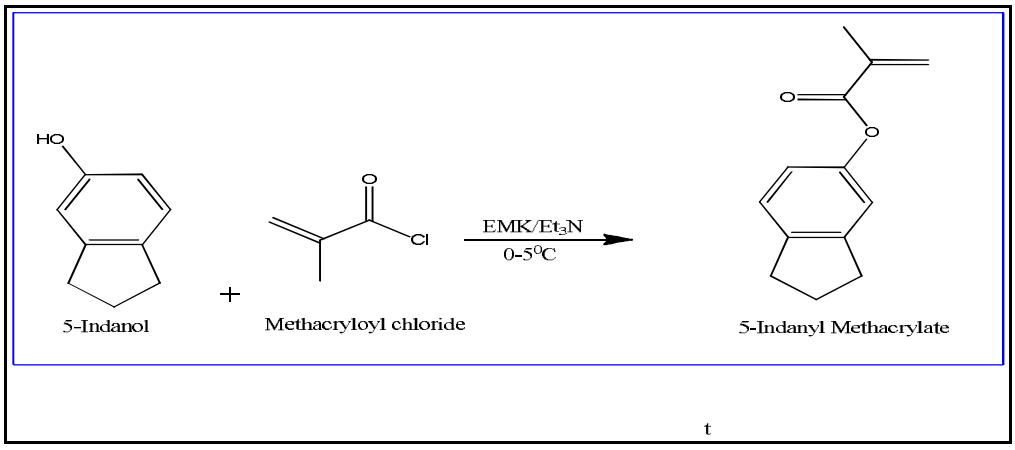
2. Experimental Section:

2.1Materials and method:

5-indanol (Aldrich) was used as received. Benzoyl peroxide was recrystallized from methanol at 0-5°C. Benzene and Ethyl Methyl Ketone (AR) and Methanol of LR grades were used without further treatment.Methacryloyl chloride was prepared by distilling a mixture of acrylic acid and benzoyl chloride.

2.2 Monomer synthesis:

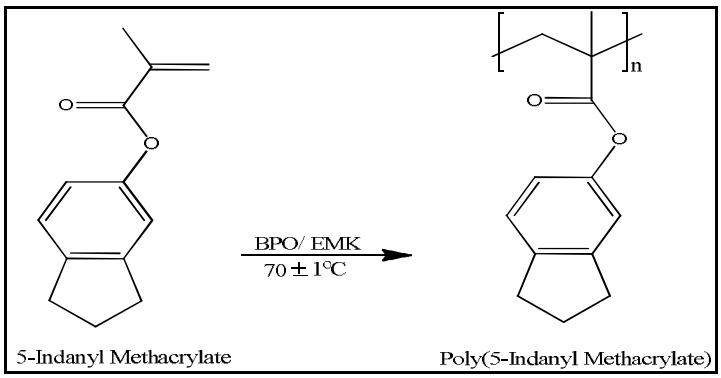
5-Indanol (27 g, 0.2 mol) dissolved in Ethylmethylketone was placed along with trimethylamine(31 ml,0.22 mol) in a two-necked 500 ml flask. With continuous stirring of the reaction mixture at 0-5^{0}C, the freshly distilled reagent Methacryloyl chloride (23 ml, 0.28 mol) was added slowly in drops from the addition funnel.After completion of addition, the contents were washed with water to remove the quaternary ammonium salt formed and the unreacted 5-indanol was then removed by washing with5% sodium hydroxide solution. The filtrate was then dried with anhydrous sodium sulphate and the monomer5-indanyl methacrylate was recovered (33 g, 88% yield) after Ethylmethyl Ketone evaporation. The reaction scheme for the synthesis of 5-Indanyl Methacrylate is shown in **Scheme 1**.



Scheme 1. Synthesis of 5-Indanyl Methacrylate

2.3 Homopolymerization:

Required quantities of the monomer 5-Indanyl Methacrylate along with BPO, were dissolved in 25 ml of Benzene placed in a standard reaction tube to obtain a homogeneous solution.. The mixture was flushed with oxygen free dry Nitrogen gas. The inlet and outlet of the reaction tube were closed by means of rubber tubing and pinch cork. The reaction vessel is then immersed in a thermostatic water bath maintained at 70 ± 1^{0}C.The Homopolymerization reaction was allowed to proceed for an appropriate duration. Then the solution was poured in ice-cold excess hexane to precipitate the Homopolymer. The Homopolymers were purified by repeated precipitation by hexane from solution in chloroform. It was then dried in a vacuum oven at 45 ° C for 24 h. The structure of the monomeric units of the poly (5- Indanyl Methacrylate) is shown in **Scheme 2**



Scheme 2. Synthesis of Poly (5-Indanyl Methacrylate)

2.4. Solubility test:

Solubility of the copolymers was tested in various polar and non-polar solvents. About 5–10 mg of the copolymer was added to about 2 ml of different solvents in a test tube and kept overnight with the test tube tightly closed. The solubility of the copolymers was noted after 24 h.

2.5. Characterization of Monomer:

2.5.1. FT-IR spectrum of the 5-Indanyl Methacrylate:

The FT-IR spectrum of 5-IMA is shown in Fig.1. The C-H absorption of asymmetric and symmetric stretching vibrations is appeared at 2955.13 cm^{-1}. The =C-H out-of-plane bending in the range 1037.73-648.59 cm^{-1}. The Peak due to –CH bending and –C=C- vinyl stretching appeared at 1292.85 and 1609.58cm^{-1}.The ring stretching vibration often occurs at 1484.24cm^{-1}. The main evidence of the monomer is the appearance of ester carbonyl group C=O stretching frequency at 1735.25 cm^{-1}.

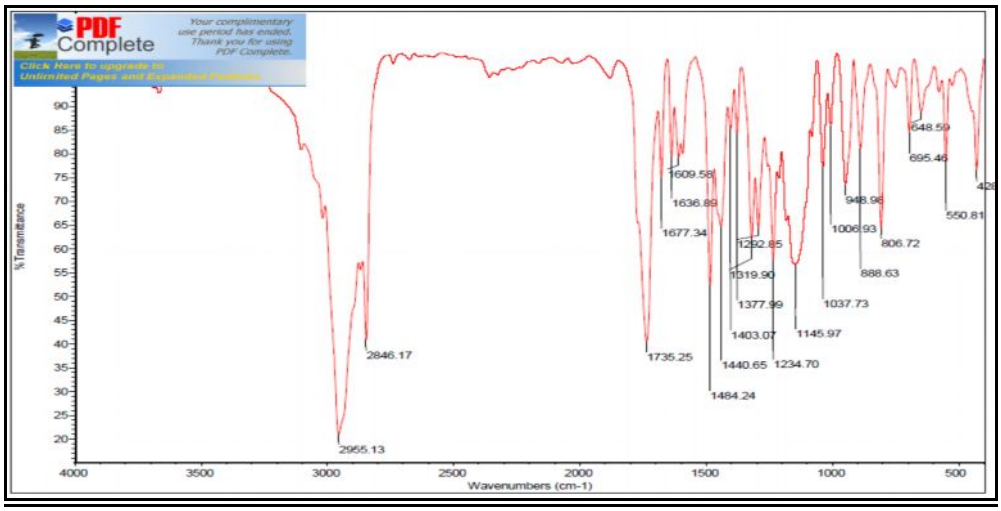


Figure 1 FT-IR spectrum of 5-Indanyl Methacrylate

2.5.2. ^{1}H- NMR spectrum of the 5-Indanyl Methacrylate:

The ^{1}H-NMR spectrum of the 5-IMA is shown in Fig. 2. The signals at 7.127to 7.148 ppm for aromatic protons and δ5.66ppm (2H) for olefinic protons of the methacryloxy group. The α-methyl group protons are observed at δ 2.009 ppm.The methylene proton were observed at 6.18-6.43ppm.

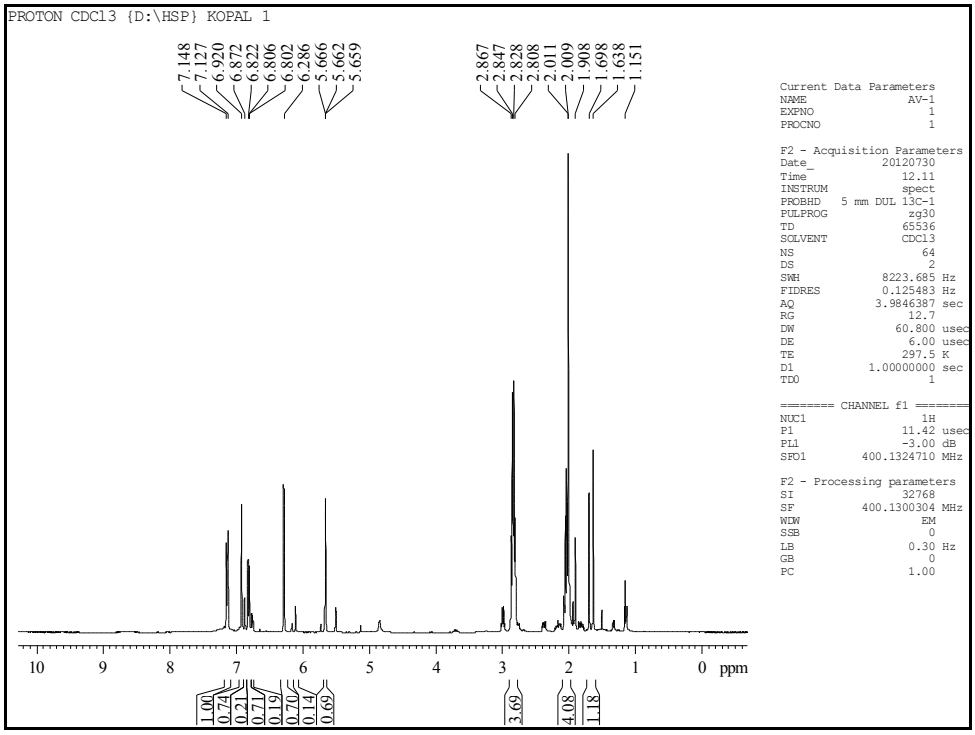


Figure 2 ^{1}H NMR Spectrum of 5-Indanyl Methacrylate

2.5.3. ^{13}C- NMR spectrum of the 5-Indanyl Methacrylate:

The ^{13}C-NMR spectrum of the5-IMA is shown in Fig. 3. The signal at18.03ppm is due to the presence of α-CH_3 carbon of methacryloxy unit. The signals at 122.94 to 148.7ppm for aromatic ring carbons and 128.0 ppm for olefinic carbon peak (=CH_2) of the methacryloxy group. The ester carbonyl carbon is appeared at 166.0ppm. The peak at17.97ppm shows the presence of alpha methyl carbon.

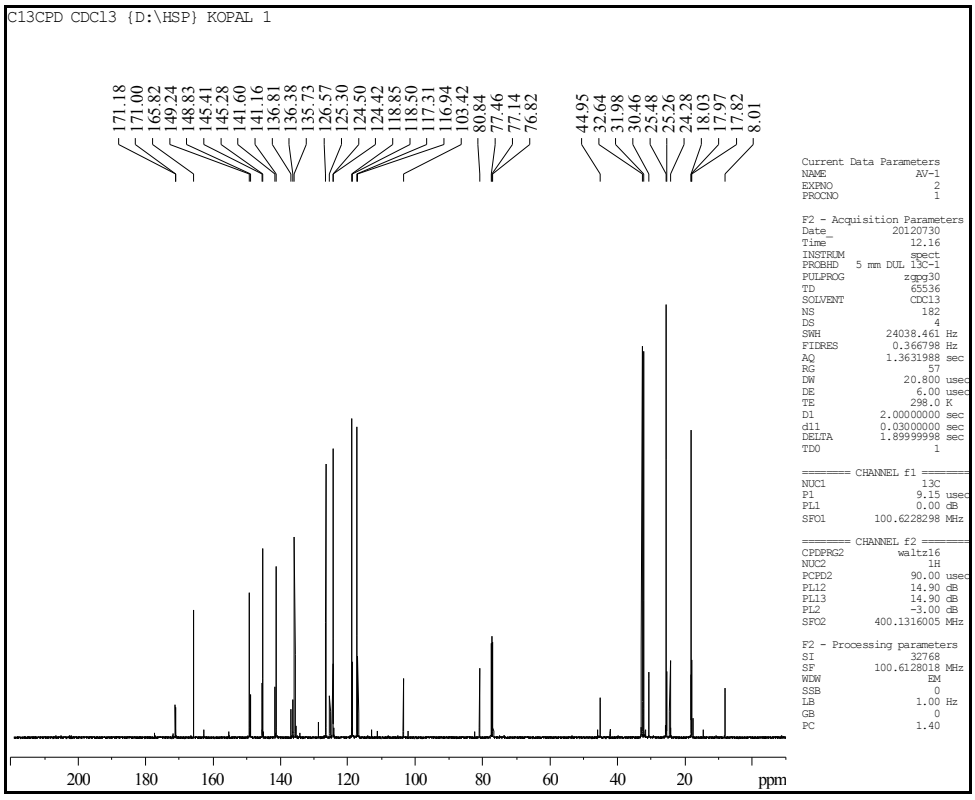


Figure 3^{13}C NMR Spectrum of 5-Indanyl Methacrylate

Results and Discussion:

3. Characterisation of Poly (5-Indanyl Methacrylate):

3.1.FT-IR spectrum of the Poly (5-Indanyl Methacrylate):

The FT-IR spectrum of the Poly(5-Indanyl Methacrylate) is shown Fig.4. The C-H absorption of asymmetric and symmetric stretching vibrations are appeared at 2945.6 cm^{-1}. The main evidence for the formation of the copolymer is appearance of broad ester carbonyl group C=O stretching frequency of the copolymer at 1746.9cm^{-1}. The C-O stretching frequency of ester group is appeared at 1134.9cm^{-1}. The disappearance of alkanes =C-H stretching frequency at 3057.16cm^{-1}confirms the Homopolymer formation.

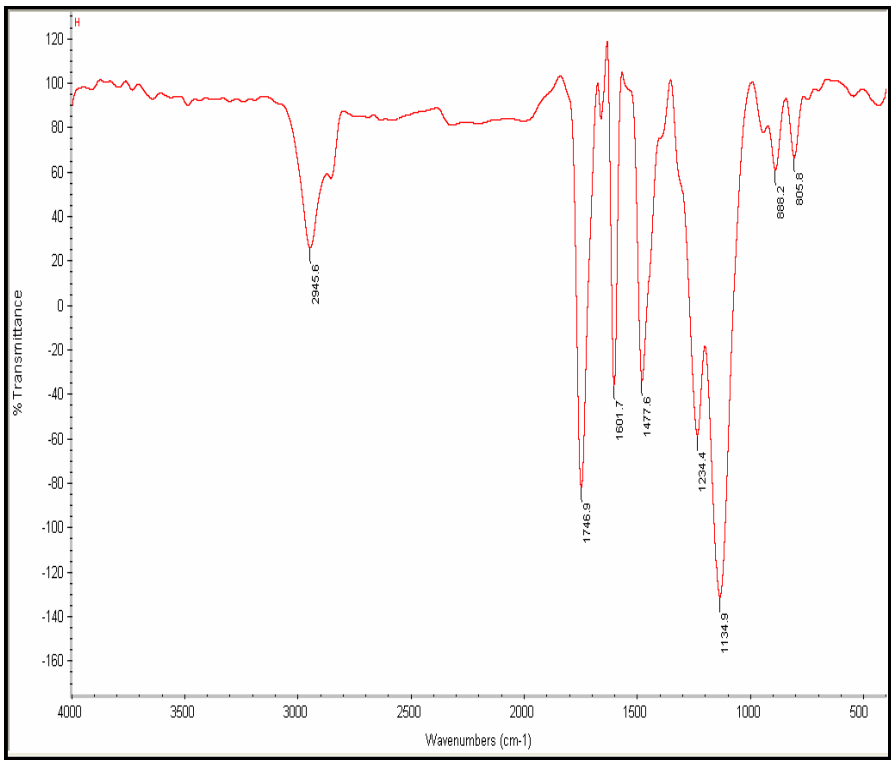


Figure 4 FT-IR spectrum of Poly (5-Indanyl Methacrylate)

3.2. ^{1}H-NMR spectrum of the Poly (5-Indanyl Methacrylate):

The ^{1}H-NMR spectrum of the Poly (5-Indanyl Methacrylate)is shown in Fig. 4. The signals at δ 6.827-7.266ppm (m, 9H) are of aromatic protons. The CH_3 proton of group is appeared at δ 1.63ppm. The methylene Proton of the epoxy group show signals at 2.334 and 2.829ppm.The alpha methyl proton of poly (5-IMA) areobserved at 1.693ppm respectively.

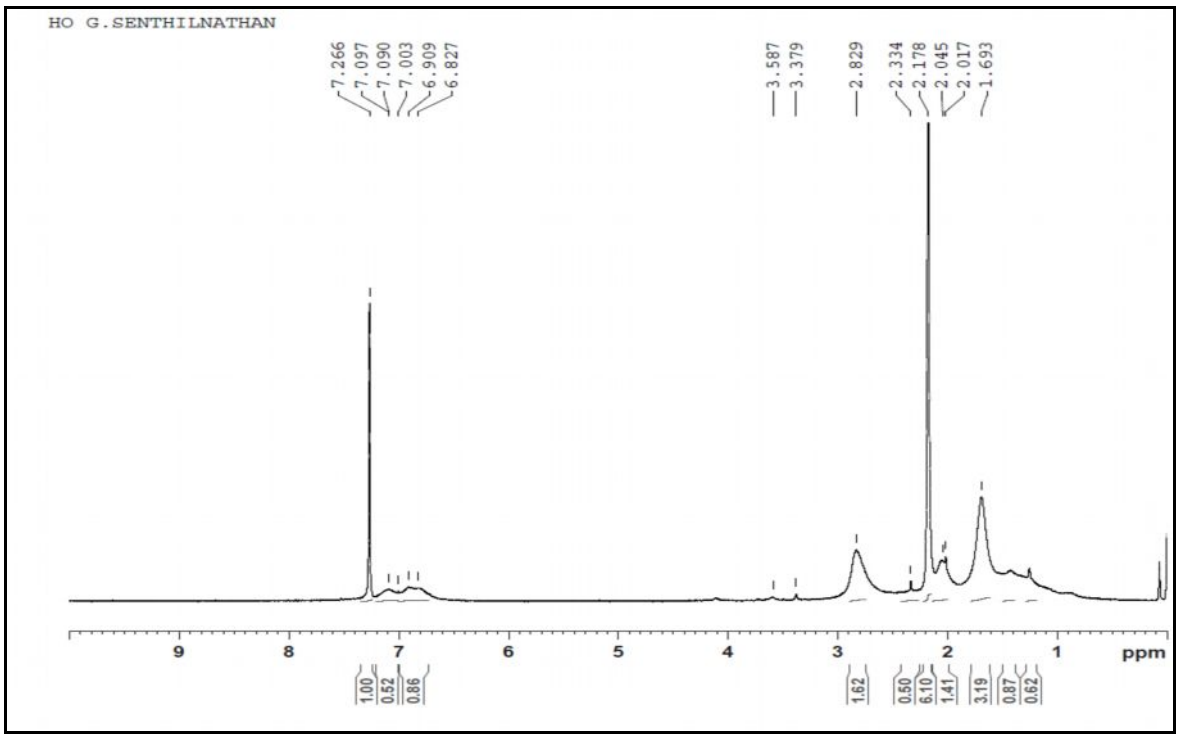
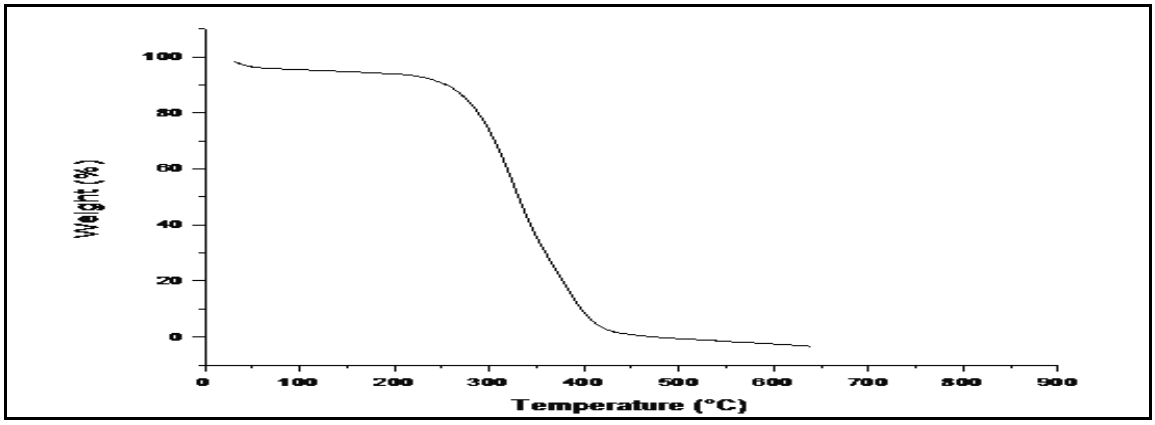


Figure 4 ^{1}H NMR spectrum of Poly (5-Indanyl Methacrylate)

3.3. Thermogravimetric Analysis (TGA):

Thermogravimetric analysis is used in estimating the percent weight loss of the Poly (5-Indanyl Methacrylate) which undergoes decomposition. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in Poly (5-Indanyl Methacrylate). The thermogravemetric analysis results of Poly (5-Indanyl Methacrylate) shown inTable1. The initial decomposition temperature (IDT) was determined from TGA thermogram and was found to be in the rage of **231^{0}C**.

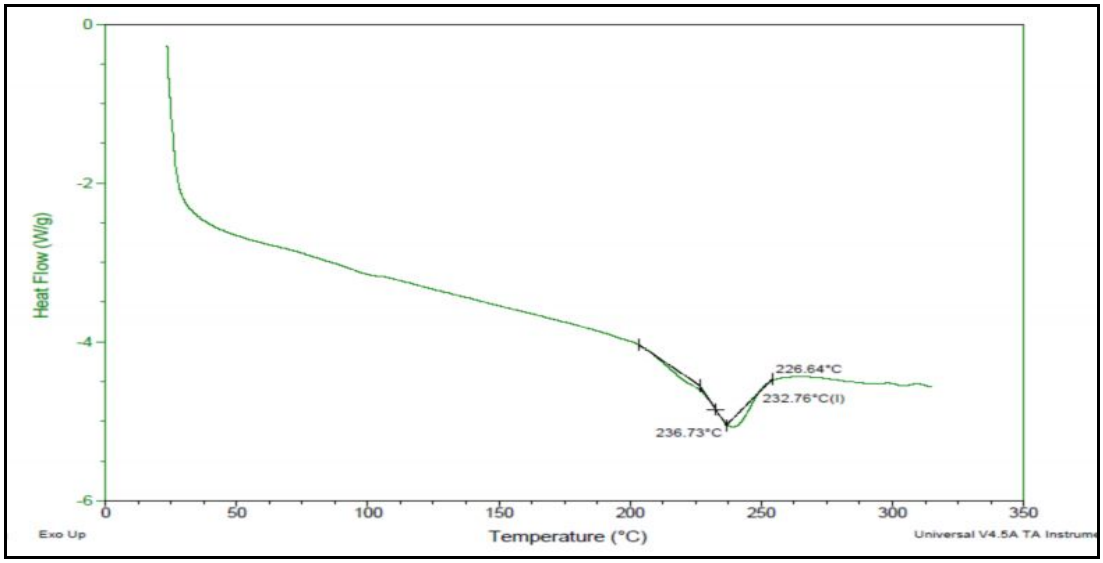


"Figure 5- TGA curve of Poly (5-Indanyl Methacrylate)

Table 1

Homopolymer	Initial Decomposition Temperature (^{o}C)
Poly (5-Indanyl Methacrylate)	231

3.4. Differencial Scanning Calorimetry Analysis (DSC):



The DSC Spectrum of **Poly (5-Indanyl Methacrylate)**. DSC is a standard tool for measuring the melting and freezing points of polymers. Initially, the solid polymer is heated from room temperature to its melting point. As it melts from solid to a molten liquid, the temperature is constant. After phase change is complete, the temperature starts rise again. All polymers exhibit a glass transition at a particular temperature or range of temperatures. The glass transition temperature is well marked in the amorphous polymers, whereas in semi crystalline polymers it is less conspicuous because it only occurs in the non-crystalline amorphous parts of the polymer. The 'Tg' value for **Poly (5-Indanyl Methacrylate)**is **236.73^{0}C**. Actually by the incorporation of 5-IMA there is a visible increase in the 'Tg' value.

3.5. Solubility test:

The solubility of the newly prepared Poly (5-Indanyl Methacrylate) in various solvents was tested at room temperature. The polymers were easily soluble in various solvents, namely toluene, benzene, chloroform, acetone and acetonitrile. The solubility test clearly shows that the polar solvents are more suitable for the copolymers to be used in coating applications.

Solvent	Solubility
DMSO	Partially soluble
Acetonitrile	Partially soluble
Acetone	Completely soluble
Toluene	Completely soluble
Chloroform	Completely soluble
Benzene	Completely soluble

4. Conclusion:

The poly (5-IndanylMethacrylate) was synthesized by free radical solution polymerization mechanism. Characterizations of the poly (5-IndanylMethacrylate) were performed by FT-IR, ^{1} H NMR, spectroscopic techniques. The thermal stability of the poly (5-IndanylMethacrylate) was measured by TGA and DSC.

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