Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(3):100-107

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

5-Indanyl methacrylate monomer: Synthesis, characterization and copolymerization with methyl methacrylate and its thermal properties

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ABSTRACT

A monomer of 5-indanyl Methacrylate (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.Copolymerization of 5-IMA with Methylmethacrylate (MMA) is carried out in benzene by free radical Solution polymerization at 70°C using Benzoyl Peroxide as initiator. 5-IMA–co-MMA Copolymers are characterized by Fourier transform infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopic Techniques (^{1}H-NMR) spectroscopy. Analysis of the thermal properties of the Copolymer by Thermogravimetric analysis (TGA)and Differential Scanning Calorimetry Analysis(DSC) are also reported.

Keywords: 5-indanyl Methacrylate, Methyl methacrylate and Benzoyl Peroxide.

INTRODUCTION

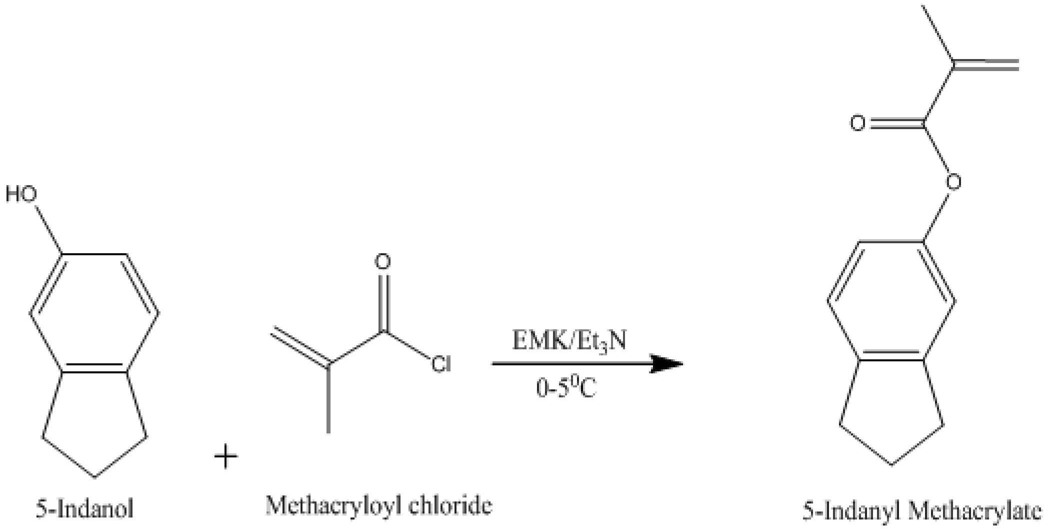
Incorporation of activated acrylates or methacrylate into polymers provides one of the most versatile routes for the preparation of reactive polymers. For example, copolymers of activated (meth) acrylates have been utilized to synthesize potentially electroactive polymers [l], macromolecular drug carriers [2] and polymeric reagents for peptide synthesis [3].The use of homopolymers and copolymers especially designed with functional active groups as lateral substituent’s of the main chain is a topic increasing activity and interest. Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties [4–9]. These kinds of macromolecules possess significant importance from both a fundamental and an applied point of view. 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°C.we have synthesized and characterized a new monomer, 5-Indanyl Methacrylate (5-IMA), which is further copolymerised with Methyl methacrylate. The copolymer is characterised by using IR, ^{1}H-NMR, TGA and DSC.

EXPERIMENTAL SECTION

Methyl methacrylate (Aldrich) was distilled under reduced pressure before use. 5-indanol (Aldrich) was used as received. Benzoyl peroxide was recrystallized from methanol at 0-10°C. Benzene and diethyl ether (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

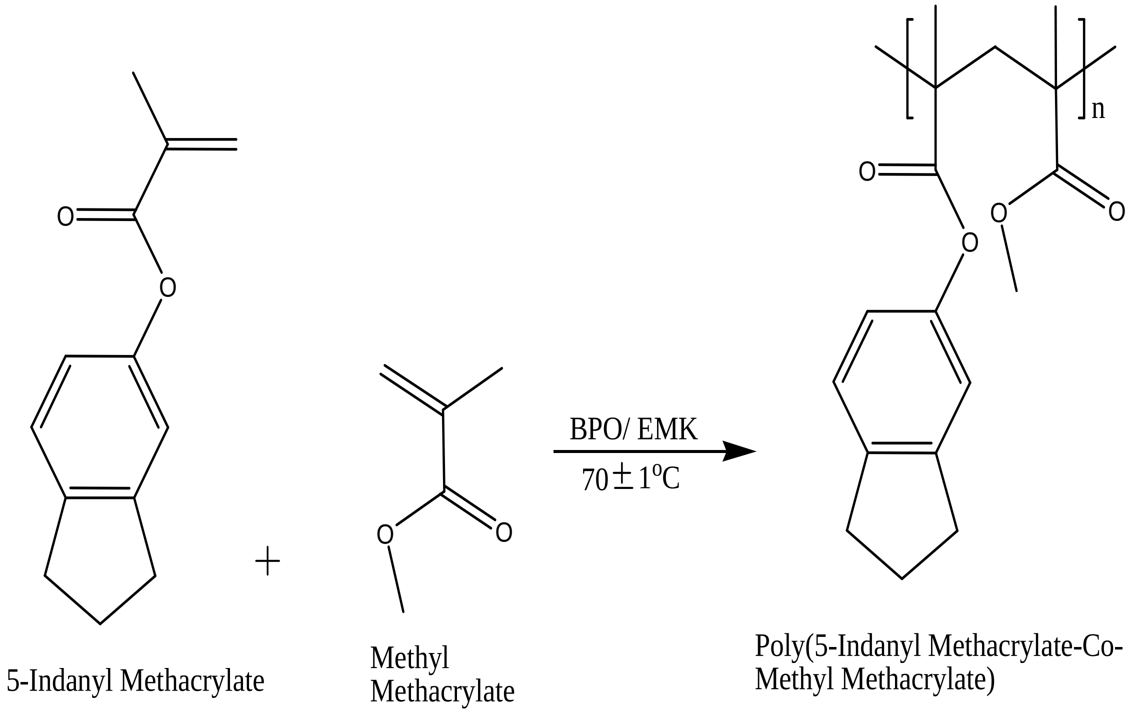
5-Indanol (27 g, 0.2 mol) dissolved in Ethyl Methyl Ketone was placed along with triethylamine (31 ml,0.22 mol) in a two-necked 500 ml flask. With continuous stirring of the reaction mixture at O^{0}C, the freshly distilled reagent Methacryloyl chloride (23 ml, 0.28 mol) was added slowly in drops from the addition funnel. After completion of addition, the contents were washed withwater 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 monomer 5-indanyl methacrylate was recovered (33 g, 88% yield) after Ethyl Methyl 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 Copolymerization

Required quantities of the monomer 5-Indanyl Methacrylate and Methyl 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 immersed in a thermostatic water bath maintained at 70 ± 1^{0}C.The copolymerization reaction was allowed to proceed for an appropriate duration. Then the solution was poured in ice-cold excess hexane to precipitate the copolymer. The copolymers 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-IMA-Co-MMA) is shown in **Scheme 2**



Scheme 2 Synthesis of poly (5-IMA-Co-MMA)

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, Fig.1.shows the characteristic peaks of the monomer. The C-H absorption of asymmetric and symmetric stretching vibrations are 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}.

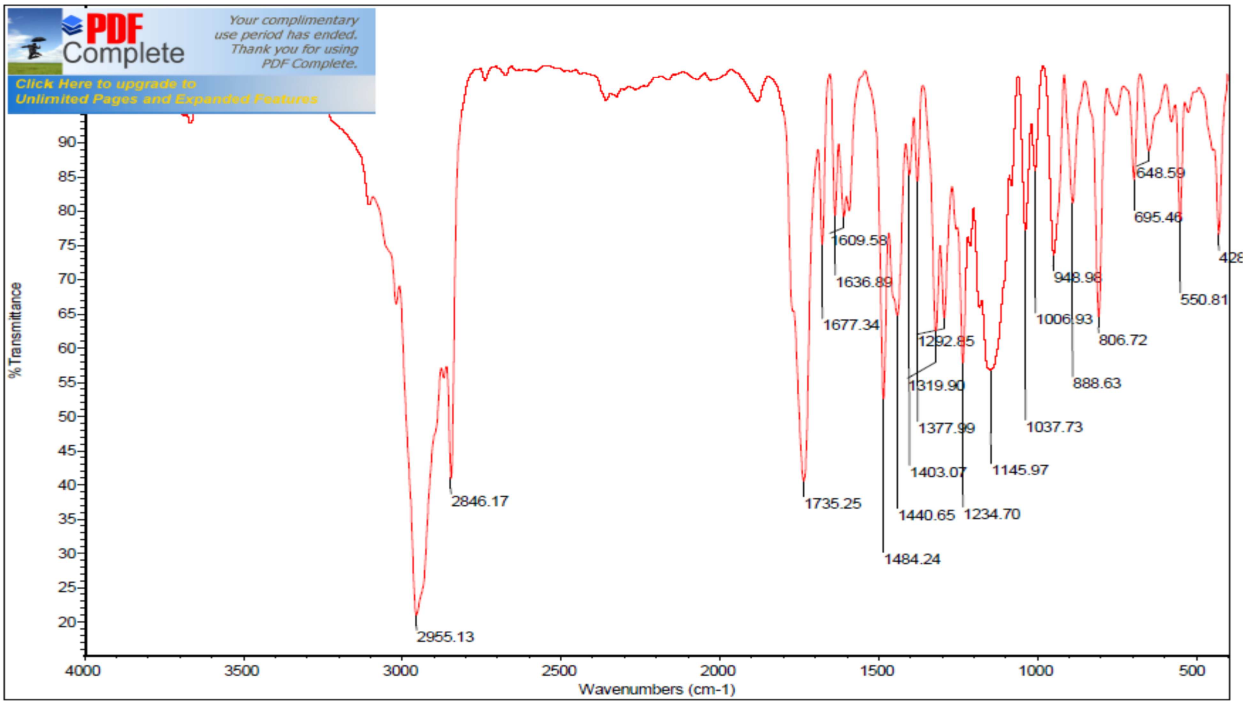


Figure 1 FT-IR spectrum of 5-Indanyl Methacrylate

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 δ 7.127to 7.148ppmfor 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.

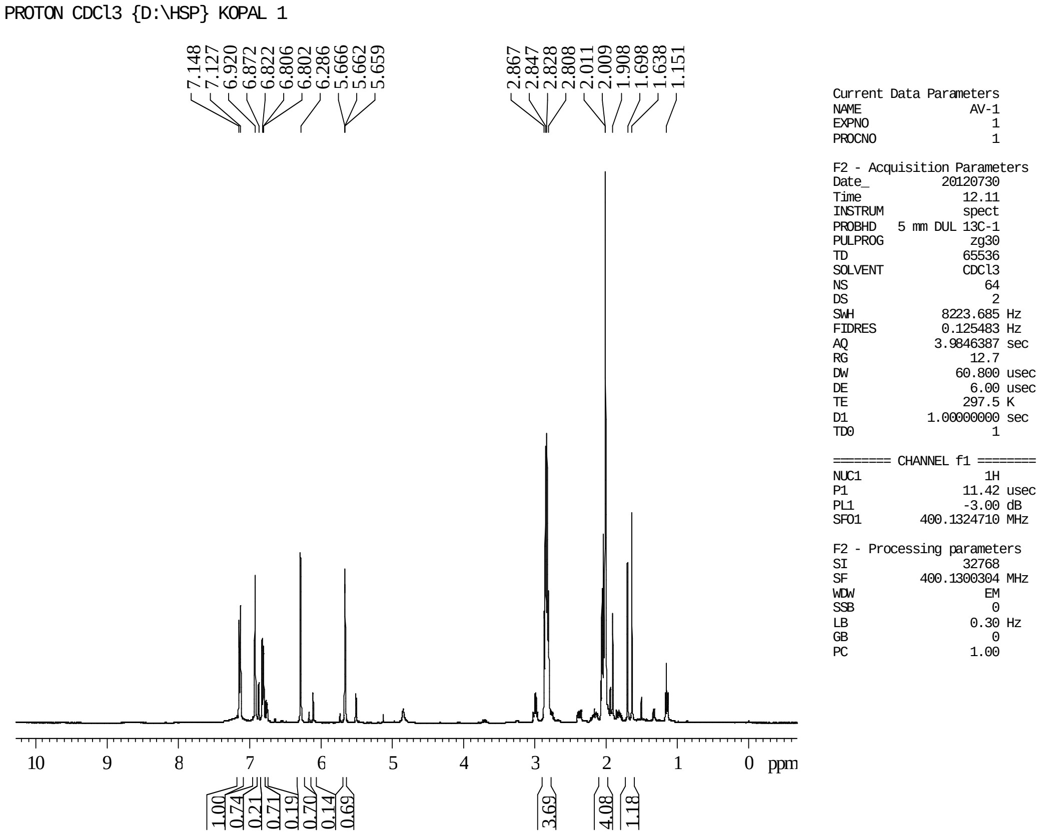


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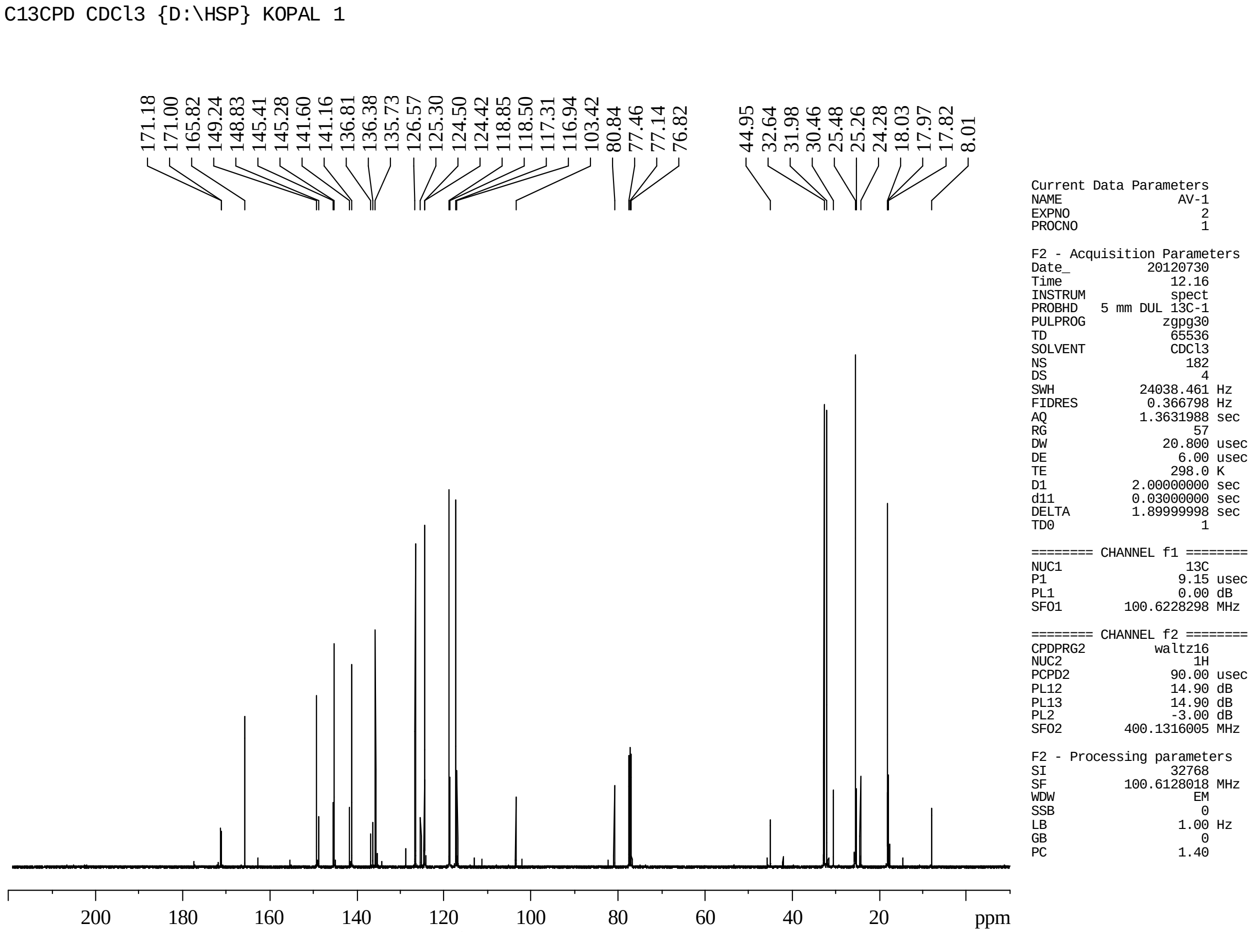
Figure 2 ^{1}H NMR Spectrum of 5-Indanyl Methacrylate



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TE                298.0 K
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d11          0.03000000 sec
DELTA        1.89999998 sec
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PL1                0.00 dB
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======== CHANNEL f2 ========
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PL12              14.90 dB
PL13              14.90 dB
PL2               -3.00 dB
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F2 - Processing parameters
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SF          100.6128018 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

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

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

The ^{13}C-NMR spectrum of the monomer 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 carbonylcarbon is appeared at 166.0ppm. The peak at17.97ppm shows the presence of alpha methyl carbon.

RESULTS AND DISCUSSION

3. Characterisation of Copoly (5-IMA-Co-MMA)

3.1FT-IR spectrum of the Copoly (5-IMA-Co-MMA)

The FT-IR spectrum of the copoly (5-IMA-co-MMA) is shown Fig.4. The two methyl group between two phenyl rings have a characteristic bending frequency at 1388.5cm^{-1} and C-H absorption of asymmetric and symmetric stretching vibrations are appeared at 2950.8 cm^{-1}. The main evidence for the formation of the copolymer is appearance of broad ester carbonyl group C=O stretching frequency at 1732.0cm^{-1}. The C-O stretching frequency of ester group is appeared at 1149.3cm^{-1}. The disappearance of alkanes =C-H stretching frequency at 3057.16cm^{-1}confirms the copolymer formation.

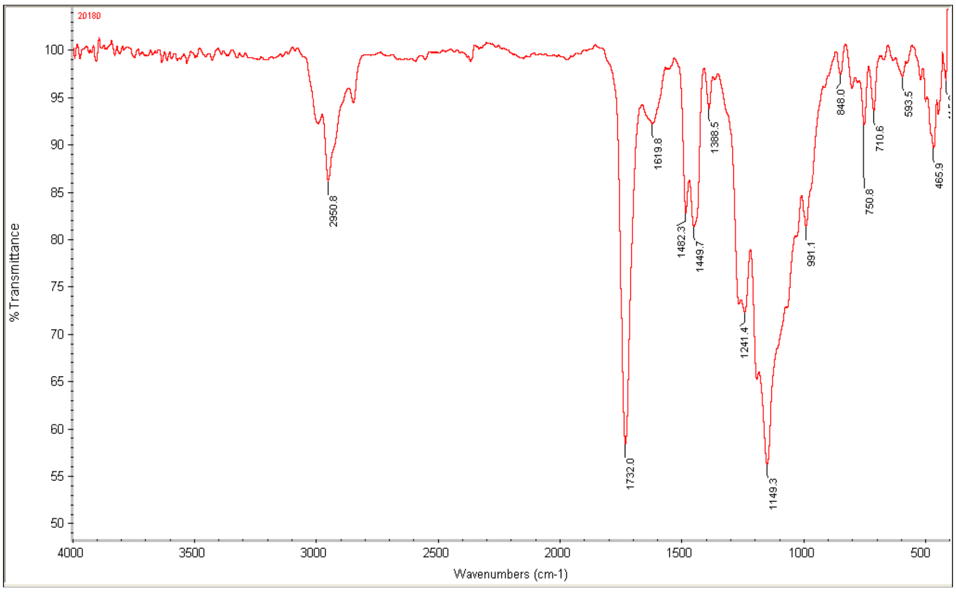

Figure 4 FT-IR spectrum of Copoly (5-IMA-co-MMA)

3.2. ^{1}H-NMR spectrum of the Copoly (5-IMA-Co-MMA)

The ^{1}H-NMR spectrum of the copoly (5-IMA-co-EMA) is shown in Fig.5. The signals at 7.45-7.98ppm (m, 9H) are of aromatic protons. The CH_3 proton of MMA group is appeared at δ 1.33ppm. The peak at 1.90 ppm is due to the backbone methylene proton. The alpha methyl protons of MMA observed at 1.29ppm.The beta methyl protons of MMA are observed at1.90ppm.

3.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used in estimating the percent weight loss of the copolymer which undergoes decomposition. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in copolymer. The thermal stability of the IMA: MMA polymers is shown in Figure 6, which depicts that there is an increase in initial decomposition temperature (IDT) with decrease of MMA content. It is also inferred that overall thermal stability of the polymers increases with decrease of MMA content (Table 1).

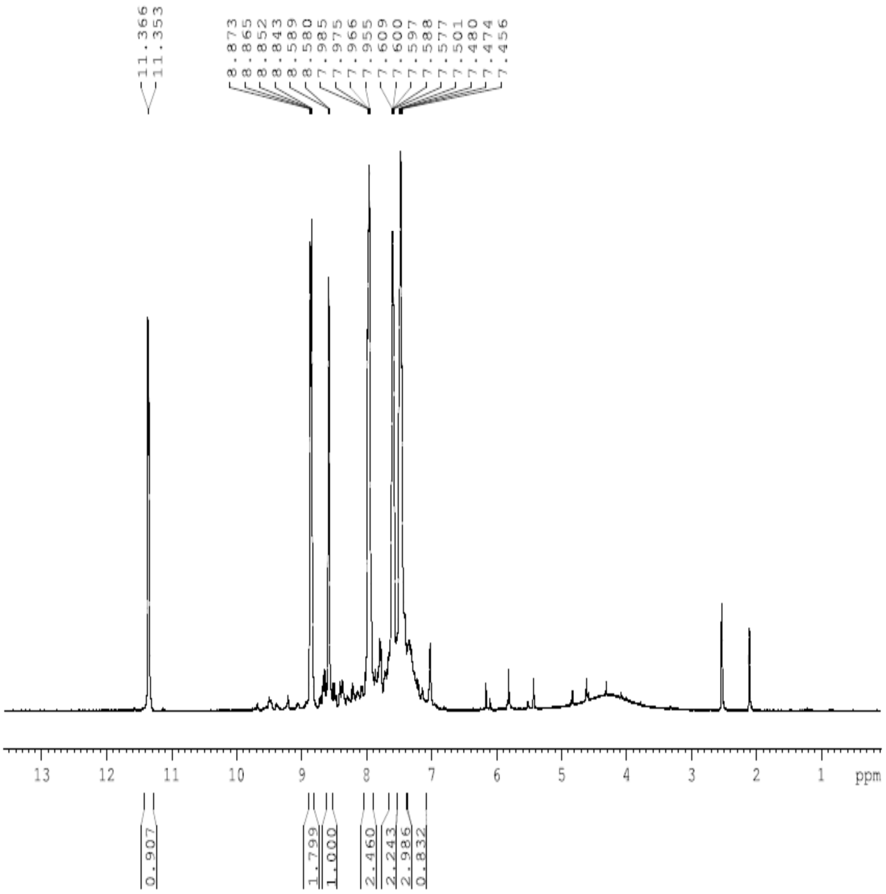

Figure 5^{1}H NMR spectrum of Copoly (5-IMA-co-MMA)

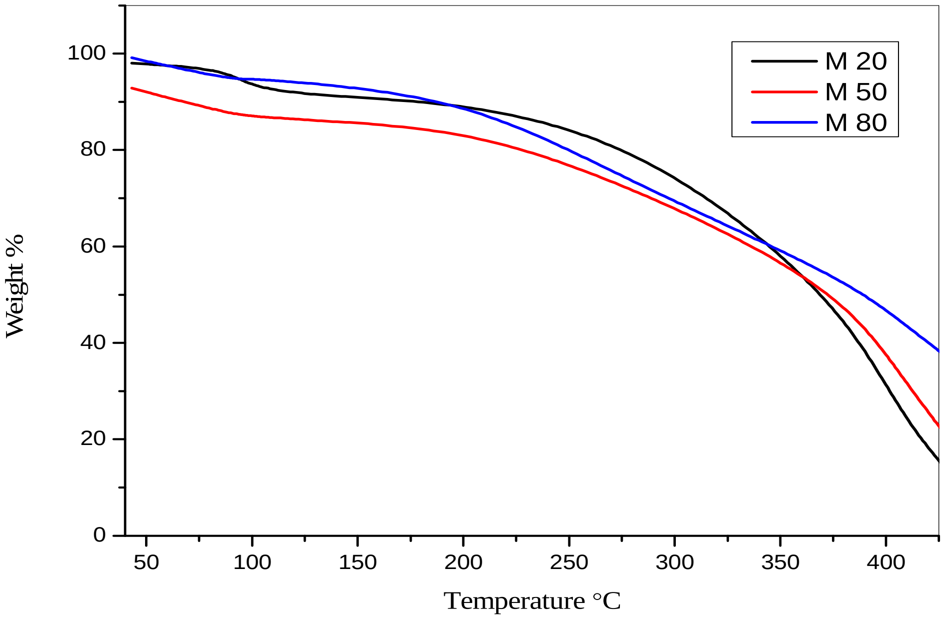

Figure 6 TGA curve of different composition of poly (5-IMA-co-MMA)

Table 1 Thermal stability of developed polymers

POLYMER	IDT (°C)
5-IMA-co-MMA(20:80) M20	316.47
5-IMA-co-MMA(50:50) M50	370.29
5-IMA-co-MMA(80:20) M80	393.49

3.5. Differential Scanning Calorimetry Analysis (DSC)

The DSC Spectrum of poly (5-IMA-co-MMA) is shown Fig.7**.** 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 copoly (5-IMA-co-MMA) is**70.39**^{0}C. Actually by the incorporation of MMA unit in the copolymer, there is a visible increase in the 'Tg' value.

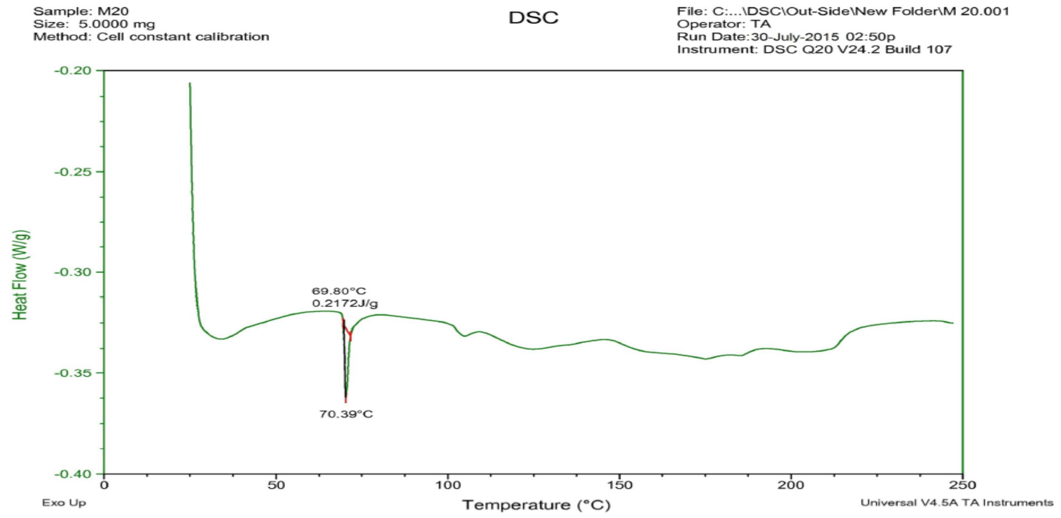

Figure 7 DSC of Copoly (5-IMA-co-MMA)

3.6. Solubility test

The solubility of the newly prepared copolymers 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	Completely soluble
Acetone	Completely soluble
Toluene	Completely soluble
Chloroform	Completely soluble
Benzene	Completely soluble

CONCLUSION

An attempt has been made to synthesize copolymer with reactive functional groups. Therefore, copolymers of 5-IndanylMethacrylate-co-Methylmethacrylate having different compositions were synthesized by free radical solution polymerization mechanism. Characterizations of the copolymer were performed by FT-IR and ^{1}H NMR spectroscopic techniques. The thermal stability of the copolymers was measured by TGA and DSC. The Electrochemical studies of this copolymer is in Progress.

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