



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

**G.SenthilNathan^{1, 2}, K.Vetrivel³, I.Pugazhenth³, K.Anver Basha³,
I. Mohammed Bilal^{2*}**

¹Department of Chemistry, Sri Ganesh College of Engg and Tech, Puducherry, India.

²Departments of Chemistry, B.S. Abdur Rahman University, Vandalur, Chennai, India.

³Department of Chemistry, C.Abdul Hakeem College, Melvisharam, India.

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 ¹H-NMR and ¹³C-NMR. Copolymerization of 5-IMA with Glycidylmethacrylate (GMA) is carried out in benzene by free radical Solution polymerization at 70°C using Benzoyl Peroxide. 5-IMA –Co-GMA Copolymers are characterized by Fourier transform infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopic Techniques (¹H-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, Glycidyl methacrylate and Benzoyl Peroxide.

Introduction:

The copolymers of Glycidyl methacrylate have wide range of applications, comprising biological application for the binding of drugs and bio molecules, electronic application as a resistant negative electron beam, etc. This ability for GMA to enter into a vast number of chemical reactions is due to the reactive epoxide group it possesses. Glycidyl methacrylate (GMA) based copolymers have received more attention due to their versatile applications [1] and they are vinyl monomer carrying oxirane or epoxide group. Epoxy group has a unique reaction capability. They undergo ring opening when reacting with substances possess hydroxyl, amine or activated methylene groups. For these reasons, polymers with epoxide groups offer numerous functionalization possibilities in mild reaction conditions [2]. Addition reactions of alcohols, phenols, carboxylic acids and amines to pendant epoxide groups in poly(GMA) and its copolymers are well known [3,4]. The epoxide opening reaction with nucleophiles is generally performed with acidic or basic catalysis and in the absence of such catalysts, the reaction is moderately slow [5, 6]. The copolymers of Glycidyl methacrylate have been tested as adhesives for leather to leather and leather to rubber bonding. In continuation of our effort to synthesize new polymeric materials for industrial application, we have synthesized and characterized a new monomer, 5-Indanyl Methacrylate (5-IMA), which is further copolymerised with Glycidylmethacrylate. The Copolymer is characterised by using IR, ¹H-NMR, TGA and DSC.

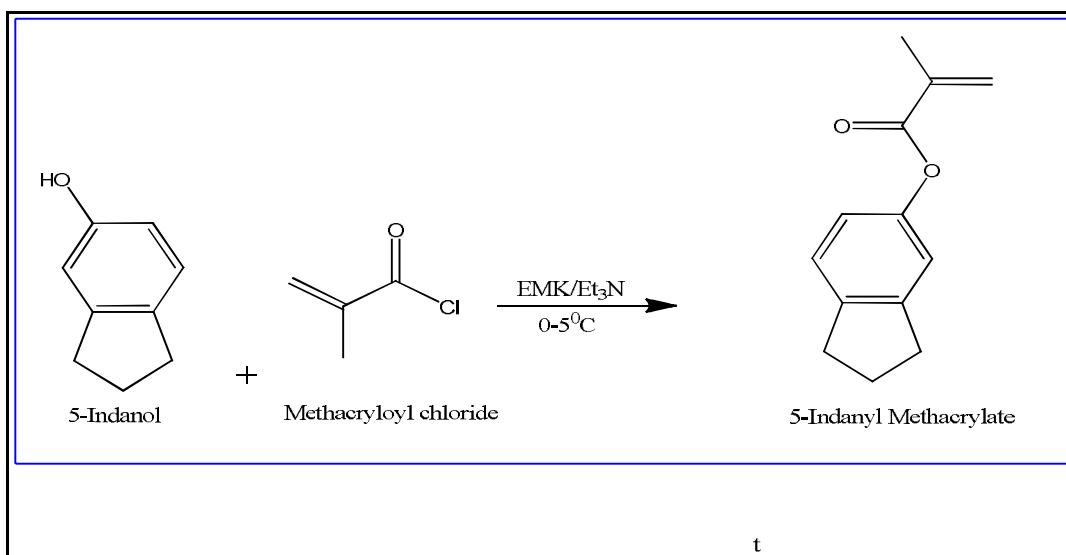
2. Experimental Section:

2.1 Materials and method:

Glycidyl 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:

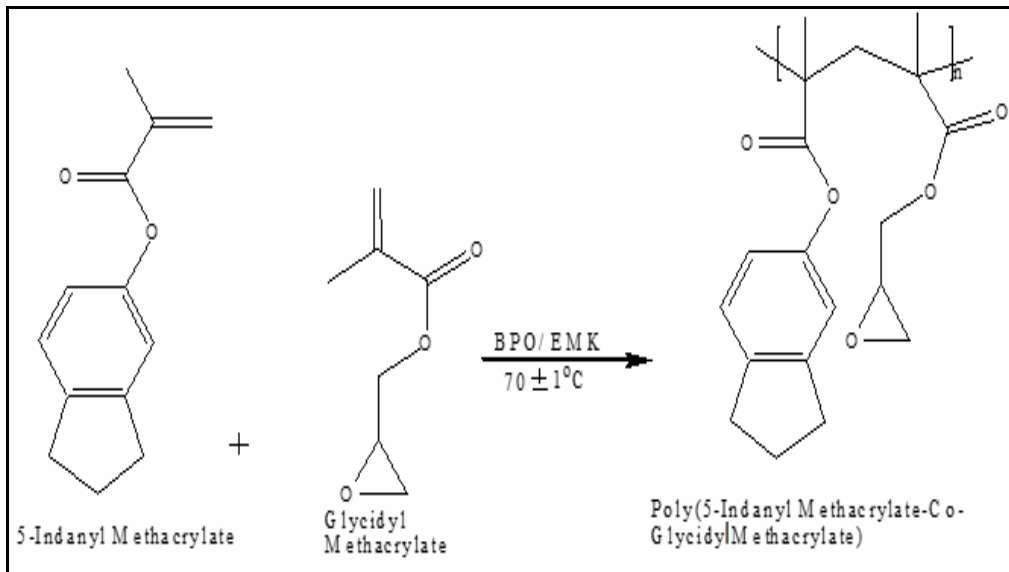
5-Indanol (27 g, 0.2 mol) dissolved in Ethylmethylketone was placed along with trimethylamine (31 ml, 0.22 mol) in a two-necked 500 ml flask. With continuous stirring of the reaction mixture at 0°C, the freshly distilled reagent Methacryloyl chloride (23 ml, 0.28 mol) was added slowly in drops from the 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 with 5% 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 Ethylmethylketone 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 Glycidyl 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 $70 \pm 1^\circ\text{C}$. 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-GMA) is shown in Scheme 2.



Scheme 2. Synthesis of poly (5-IMA-Co-GMA).

2.4. Solubility test:

Solubility of the copolymers were 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 are appeared at 2955.13 cm^{-1} . The =C-H out-of-plane bending in the range $1037.73\text{--}648.59\text{ cm}^{-1}$. The Peak due to -CH bending and -C=C- vinyl stretching appeared at 1292.85 and 1609.58 cm^{-1} . The ring stretching vibration often occurs at 1484.24 cm^{-1} . The main evidence of the monomer is the appearance of ester carbonyl group C=O stretching frequency at 1735.25 cm^{-1} .

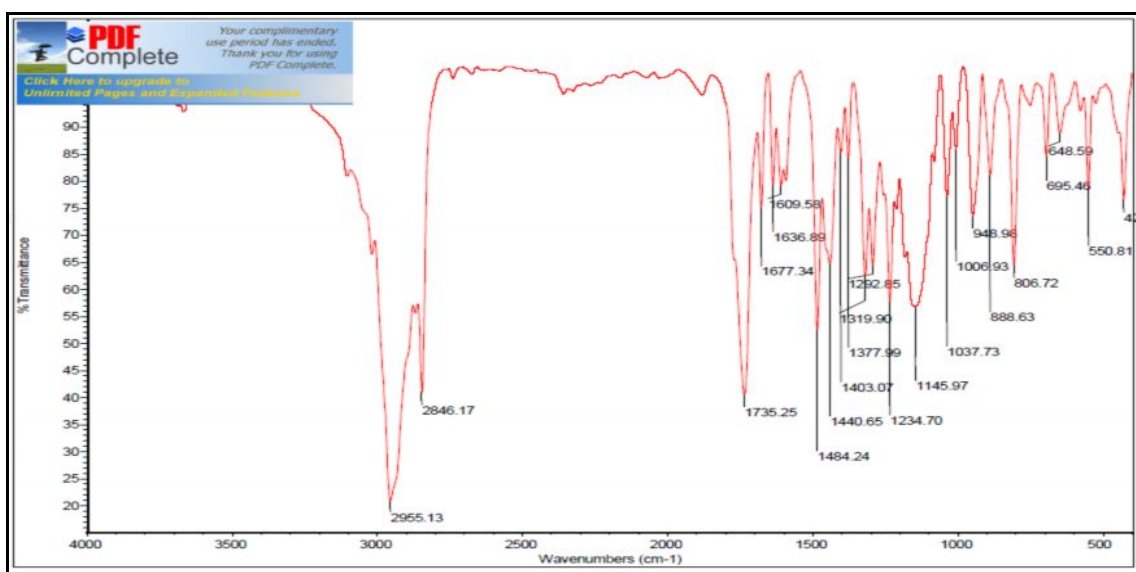


Figure 1 FT-IR spectrum of 5-Indanyl Methacrylate

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

The ¹H-NMR spectrum of the 5-IMA is shown in Fig. 2. The signals at 7.127 to 7.148 ppm for aromatic protons and δ 5.66 ppm (2H) for olefinic protons of the methacryloxy group. The α-methyl group protons are observed at δ 2.009 ppm. The methylene protons were observed at 6.18-6.43 ppm.

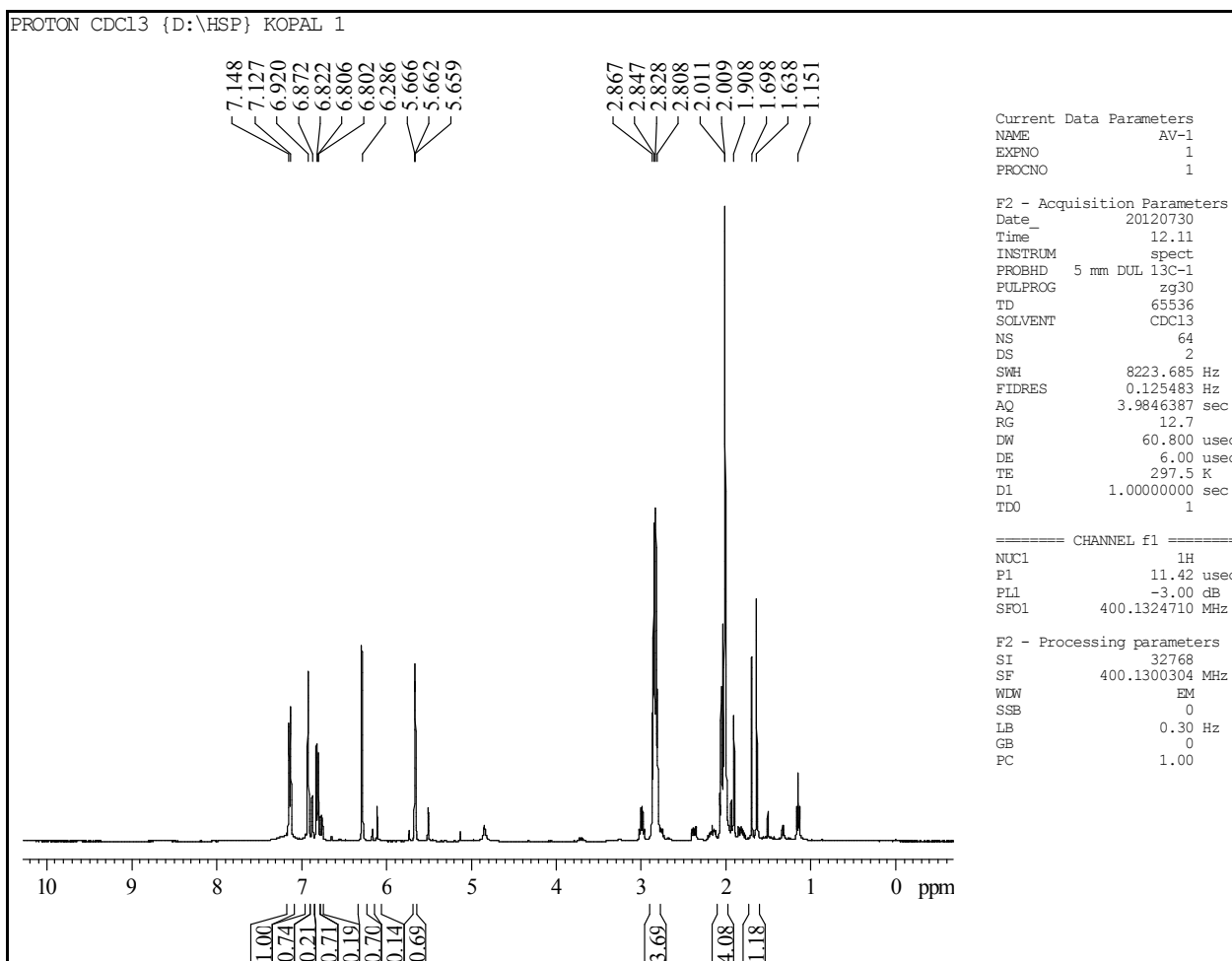


Figure 2 ¹H NMR Spectrum of 5-Indanyl Methacrylate

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

The ¹³C-NMR spectrum of the 5-IMA is shown in Fig. 3. The signal at 18.03 ppm is due to the presence of α-CH₃ carbon of methacryloxy unit. The signals at 122.94 to 148.7 ppm for aromatic ring carbons and 128.0 ppm for olefinic carbon peak (=CH₂) of the methacryloxy group. The ester carbonyl carbon is appeared at 166.0 ppm. The peak at 17.97 ppm shows the presence of alpha methyl carbon.

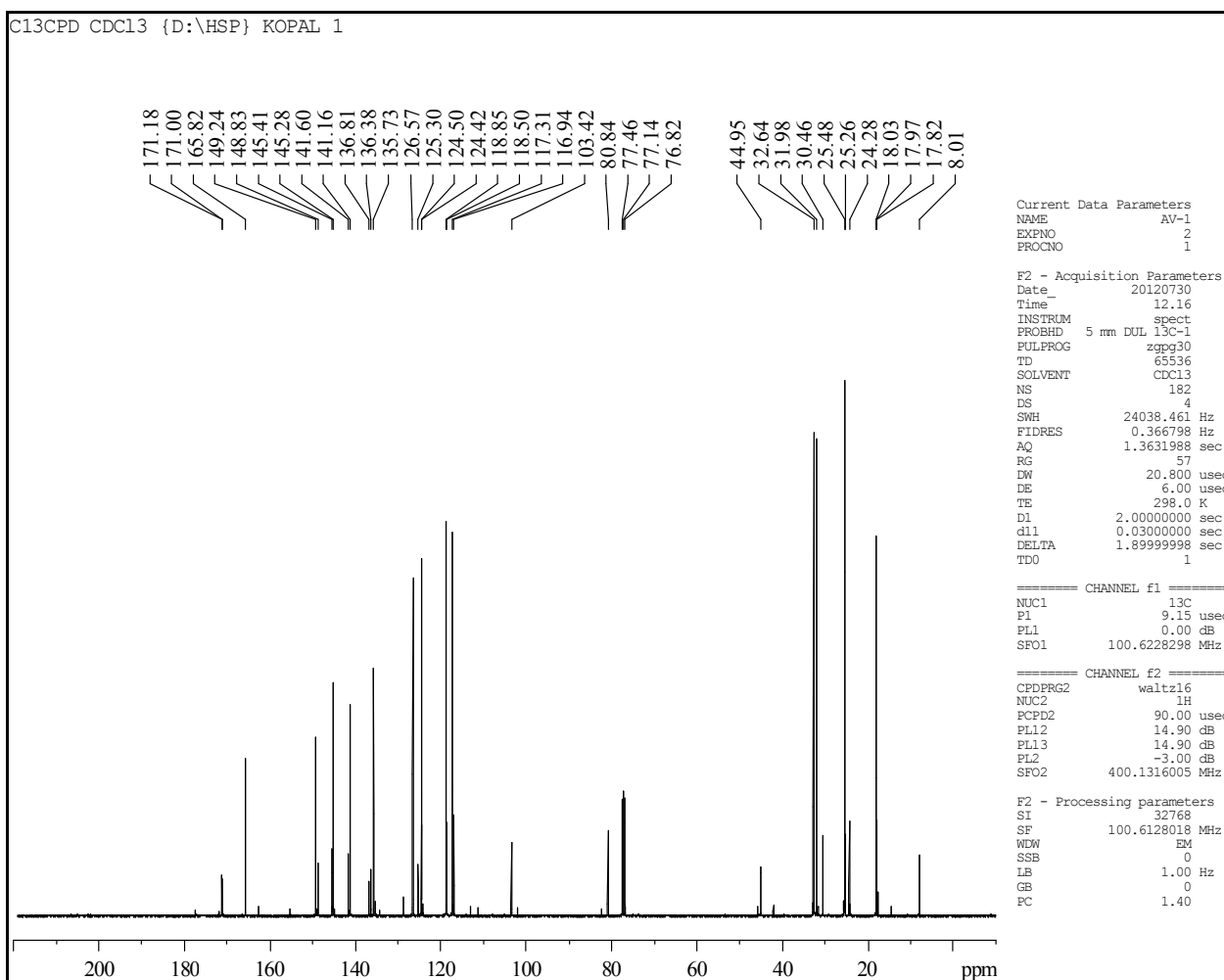


Figure 3 ^{13}C NMR Spectrum of 5-Indanyl Methacrylate

Results and Discussion:

3. Characterisation of Poly (5-IMA-co-GMA):

3.1 FT-IR spectrum of the POLY (5-IMA-co-GMA):

The FT-IR spectrum of the copolymer (5-IMA-co-GMA) is shown Fig.4. The two methyl group between two phenyl rings has a characteristic bending frequency at 1393.4 cm^{-1} and C-H absorption of asymmetric and symmetric stretching vibrations are appeared at 2946.5 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 1735.9 cm^{-1} . The C-O stretching frequency of ester group is appeared at 1136.4 cm^{-1} . The disappearance of alkanes =C-H stretching frequency at 3057.16 cm^{-1} confirms the copolymer formation.

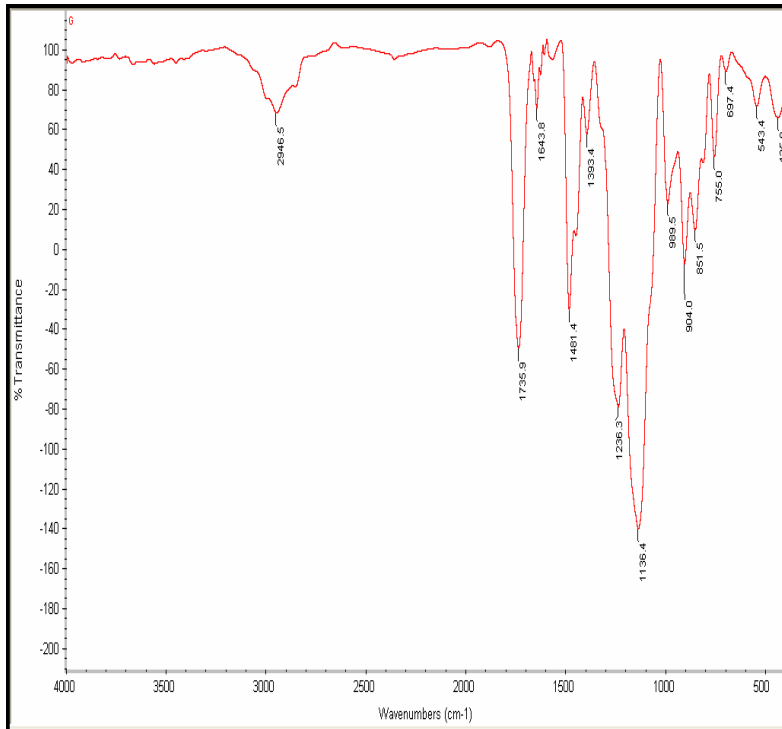


Figure 4 FT-IR spectrum of POLY (IMA-Co-GMA)

3.2. ¹H-NMR Spectrum of the POLY (5-IMA-co-GMA):

The ¹H-NMR spectrum of the Copoly (5-IMA-co-GMA) is shown in Fig. 4. The signals at δ 6.906-7.260ppm (m, 9H) are of aromatic protons. The CH₃ proton of GMA group is appeared at δ 1.33ppm. The methylene Proton of the epoxy group show signals at 2.63 and 2.38ppm. The alpha methyl proton of 5-IMA and GMA are observed at 1.28 and 1.33ppm respectively.

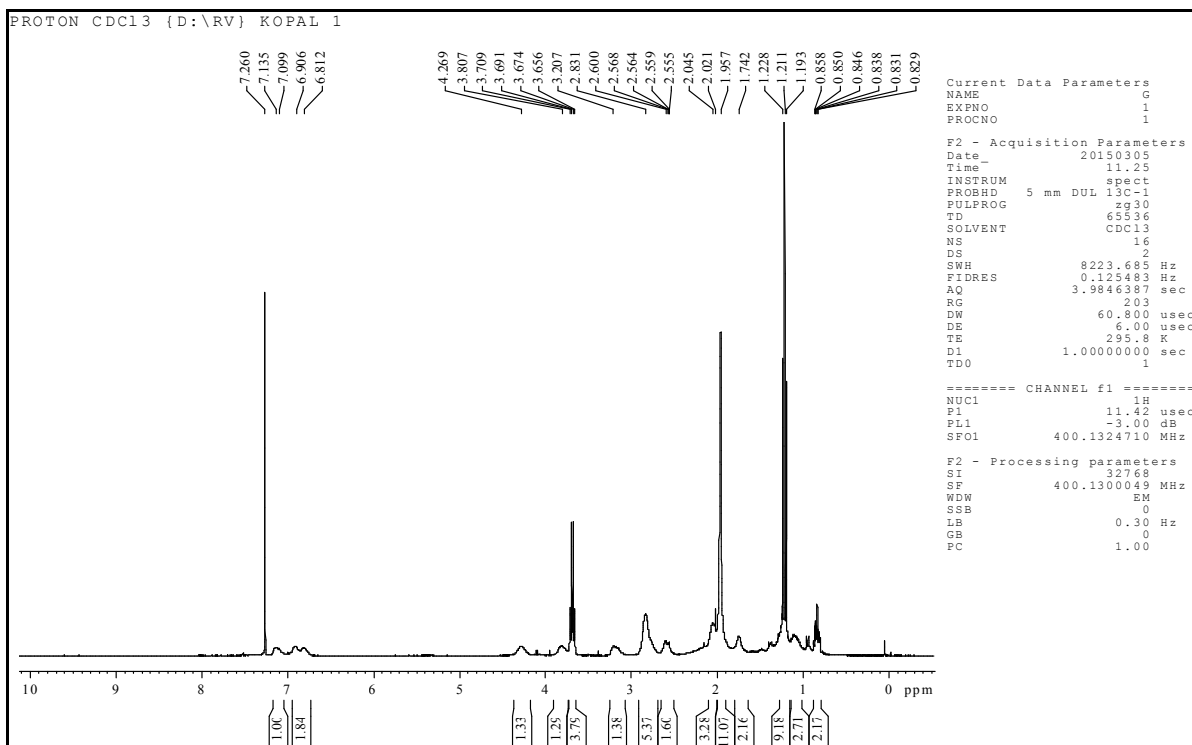


Figure 4 ¹H NMR spectrum of POLY (5-IMA-co-GMA)

3.3. Thermogravimetric Analysis (TGA):

Thermogravimetric analysis is 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 thermogravimetric analysis results of Copolymers are shown in Table 1. The data clearly indicates that all polymers undergo Single-step decomposition. Initially the initial decomposition temperature (IDT) increases, later it decreases with increase of 5-IMA content in the Copolymer. The initial decomposition temperature (IDT) were determined from TGA thermogram and were found to be in the range of $107.12 - 282.85^{\circ}\text{C}$. The decomposition of copolymer at high temperature may be due to the breakage of main chain accompanied by volatilization of the cleaved Products.

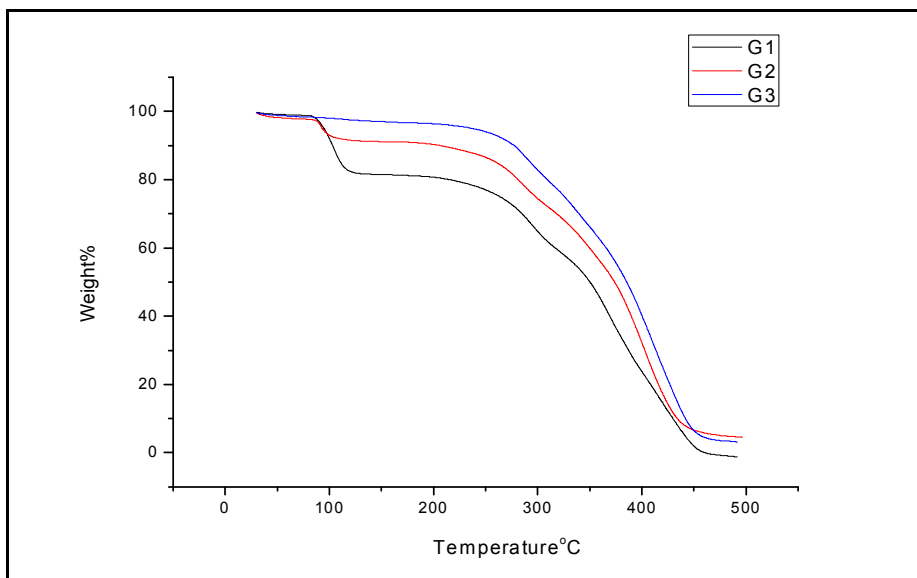


Figure 5- TGA curve of different composition of poly (5-IMA-co- GMA)

Table 1

Poly(5-IMA-co-GMA)	IDT ($^{\circ}\text{C}$)
5-IMA:GMA (20:80) G1	107.12
5-IMA:GMA (50:50) G2	282.85
5-IMA:GMA (80:20) G3	277.34

3.4. Differential Scanning Calorimetry Analysis (DSC):

The 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 rises 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 'T_g' value for copoly (5-IMA-Co-GMA) is 94.28°C . Actually by the incorporation of GMA unit in the copolymer, there is a visible increase in the 'T_g' value.

3.5. 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

4. Conclusion:

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

References:

- Iqbal, M.S., Jamil, Y., Kausar, T. & Akhtar, M.. Thermal degradation study of glycidyl methacrylate acrylonitrile copolymers. *Journal of Thermal Analysis and Calorimetry*, 2009, 96, 225-233.
- Senkal, B.F., Bildik, F., Yavuz, E. & Sarac, A., Preparation of poly(glycidyl methacrylate) grafted sulfonamide based polystyrene with tertiary amine for the removal of dye from water. *Reactive & Functional Polymers*, 2007, 67, 1471-1477.
- Kenawy E-L, Biologically active polymers. IV: Synthesis and antimicrobial activity of polymers containing 8-hydroxyquinoline moiety, *J Appl Polym Sci*, 2001, 82, 1364-1374.
- Muscatello MMW, Asher SA, Poly(vinyl alcohol) rehydratable photonic crystal sensor materials, *Adv Funct Mater*, 2008, 18, 1186-1193.
- Bandgar BP, Patil AV, Fluoroboric acid adsorbed on silica gel catalyzed regioselective ring opening of epoxides with nitrogen heterocycles, *Tetrahed Lett*, 2007, 48, 173-176.
- Kotsuki H, Hayashida K, Shimanouchi T, Nishizawa H, High pressure organic chemistry. 19: High-pressure-promoted, silica gel-catalyzed reaction of epoxides with nitrogen heterocycles, *J Org Chem*, 1996, 61, 984-990.
- Feit E.D, Wurtz M.E, Kammlott G.W., Sol-gel behavior and image formation in poly(glycidyl methacrylate) and its copolymers with ethyl acrylate, *J. Vac. Sci. Technol.* 1978, 15 (3), 944.
- Kalal .J, Svec . F, Marousek .V, Reactions of epoxide groups of glycidyl methacrylate copolymers, *J. Polym. Sci. Polym. Symp.* 1974, 47, 155.
- Lee.H, Newille.K, Handbook of Epoxy Resins, McGraw-Hill, 1967.
- May C.A, Epoxy Resins, Chemistry and Technology, Marcel Dekker, 1988.
- D.A. Tomalia, in: Yocum R.H, Nuquist (Eds.) E.B, Functional Monomers, vol. 2, Marcel Dekker, 1974, Part 1.
- Iwakura .Y, Kurosaki .T, Ariga.N, T. Ito, Copolymerization of methylmethacrylate with glycidyl methacrylate and the reaction of the copolymer with amines, *Die. Makromol. Chem.* 1966, 97, 128.
- Paul .S, Ranby.B, Studies of methyl methacrylate-glycidyl methacrylate copolymers: copolymerization to low molecular weight and modification by ring-opening reaction of epoxy side groups, *J. Polym. Sci. Polym. Chem. Ed.* 1976, 14 (10), 244.
- Kalal.J, Some synthetic polymers with functional groups for biomedical applications, *Polym. Sci.* 1979, USSR 21 (11), 2703.
- Hradil.J, Svec.F, Frechet J.M, Mechanism of phase-transfer catalysis using glycidyl methacrylate-ethylene dimethacrylate copolymers modified with tributylammonium groups in nucleophilic displacement reactions, *J. Polym.* 1987, 28 (9), 1593.
- Hradil.J, Svec.F, Reactive polymers. XXXIX: changes in the porous structure of macroporous copolymers due to successive effects of solvents and temperature, *Angew. Makromol. Chem.* 1985, 130, 81.

17. Paul.S, Ranby .B, Methyl methacrylate (MMA)-glycidyl methacrylate (GMA) copolymers. A novel method to introduce sulfonic acid groups on the polymeric chains, *Macromolecules*,1976, 92, 337.
18. Migonney.V, Lacroix M.D, Douzon.C, Jozefowicz.M, Chemical modifications of insoluble polystyrene derivatives, *J. Appl. Polym. Sci.* 1992, 46 (7), 1151.
