

# 1, 1' AZOBIS CYCLOHEXANECARBONITRILE) INITIATED COPOLYMERIZATION OF METHACRYLONITRILE WITH ALKYL ACRYLATE AND THEIR CHARACTERIZATION

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## ABSTRACT

Copolymer of methacrylonitrile (MAN) with ethylmethacrylate (EMA) was synthesized by free radical polymerization using 1, 1' azo bis (cyclohexanecarbonitrile) (VAZO) as initiator in dimethyl formamide (DMF) at  $60 \pm 1$  °C. The monomer reactivity ratio was computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The reactivity ratio values suggest the formation of random copolymers which has been supported by the azeotropic composition evaluation. The mean sequence length ( $\bar{n}_l$ ) and probabilities ( $p$ ) in the formation of various structural units were evaluated. The molecular weights of the polymers were determined by gel permeation chromatography, which increase with the increase of the MAN content. The solubility parameters were determined with the viscometric method. The glass transition temperature ( $T_g$ ) of the copolymers were determined by differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) of the copolymer was also studied. The di-electrical property of the copolymer is also studied.

**Keywords:** Ethylmethacrylate/ Reactivity ratios/ Solution properties/ Thermal properties and Di-electrical property

## 1. INTRODUCTION

Introduction of ethylmethacrylate (EMA) into various copolymers appears to modify and improve the properties of a number of copolymers (Mihailo, 2007; Kadir Demirelli, 2006; Brar, 2006; Hossein S, 2005). The estimation of copolymer composition and determination of the reactivity ratios are important for making copolymers with required physico-chemical properties. The <sup>1</sup>H-NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition (Tacz, 1998; Ismail Mathakiya, 2003; Balaji, 1998; Balaji, 1999). In this article we reported the synthesis, characterization, reactivity ratios, solution and thermal properties of the copolymers of MAN with EMA.

## 2. MATERIALS AND METHOD

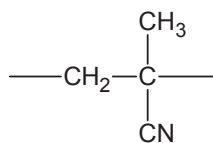
MAN (Aldrich) and EMA (Aldrich) were purified by washing with 5% solution of sodium hydroxide and

distilled water, dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate was collected and used for copolymerization. VAZO (Aldrich) as initiator was recrystallized from methanol. The solvent used in copolymerization was DMF which was a reagent grade chemical. This was dried and purified by distillation before use. All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvents and initiator. The tubes were sealed in an atmosphere of nitrogen and introduced into the thermostat at  $60 \pm 1$ °C and the polymerization was continued for 90 min. to get less than 10% conversion. The polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered, washed thoroughly with water followed by ether and hexane, and finally dried under vacuum. Different samples were prepared by changing the initial monomer feed. The initiator was used at 2.5 g/dm<sup>3</sup> of solvent. The total monomer concentration was maintained at 1.5 M, while the feed ratio was varied. The data of composition of feed and copolymers are presented in Table 1.

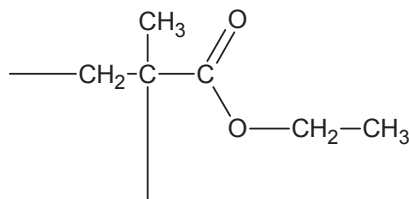
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The monomer unit structures are represented as follows:

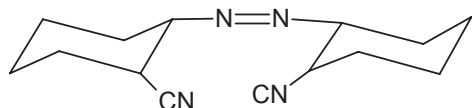


I) methacrylonitrile (AN)



II) ethylmethacrylate (EMA)

**Structure of initiator:**



1, 1'-azo bis (cyclohexanecarbonitrile) (VAZO)

### 3. RESULTS AND DISCUSSION

**FTIR Spectroscopy:** Infrared spectra of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in 4000 to 400  $\text{cm}^{-1}$  range with KBr pellets. The IR spectrum of the copolymer of MAN and EMA (MAN-co-EMA) is shown in (Fig.1) showing the characteristic bands of both the monomer units. Appearance of strong absorption bands at 2864.33, 1726.40, 2236.26, 1448.74 and 2951.49  $\text{cm}^{-1}$  corresponds to methylene ( $-\text{CH}_2$ ) stretching,  $>\text{C}=\text{O}$  stretching in ester, cyano ( $-\text{CN}$ ), methoxy group ( $-\text{OCH}_2-$ ) and methyl ( $-\text{CH}_3$ ) stretching vibrations respectively. The appearance of absorption bands corresponding due to ester ( $>\text{C}=\text{O}$ ),  $-\text{OCH}_2$  and  $-\text{CN}$  group and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-EMA copolymer.

**Determination of copolymer composition:**  $^1\text{H-NMR}$  spectra of the samples were recorded using  $\text{DMSO-d}_6$  as solvent for MAN copolymer on a Avance 300 MHz

$^1\text{H-NMR}$  spectrometer with TMS as internal reference. The copolymer compositions were determined by  $^1\text{H-NMR}$  spectra shown in (Fig.2). The distribution of proton in the two units is an important means of distinguishing the monomers in the chain. In the spectrum, methyl ( $-\text{CH}_3$ ) protons of EMA unit appears at 1.20 to 1.25 ppm, methyl ( $-\text{CH}_3$ ) protons of EMA unit appears at 1.6 ppm, methylene ( $-\text{CH}_2$ ) protons of methacrylonitrile unit appears at 2.0 ppm, methyl ( $-\text{CH}_3$ ) protons of MAN unit appears at 1.4 ppm and methoxy ( $-\text{OCH}_2-$ ) protons of EMA appears at 4.1 to 4.2 ppm, which were considered for the composition analysis. Since the peak area corresponds to the total number of protons of a particular group, the composition of the copolymer was calculated by the relation (Brar, 2006)

$$\% \text{ EMA in MAN} = \frac{{}^1\text{H-OCH}_2 / 2}{{}^1\text{H-OCH}_2 / 2 + {}^1\text{H-CH}_2 / 2} \dots\dots (1)$$

This equations is based on the fact that the  $-\text{CH}_2$  group of MAN unit corresponds to two protons,  $-\text{OCH}_2$  group of EMA corresponds to two protons.

**$^{13}\text{C-NMR}$  Spectroscopy:**  $^{13}\text{C-NMR}$  spectrum of MAN-EMA shows resonance at  $\delta$  176 for carbonyl carbon of EMA units and the nitrile carbon of MAN unit at  $\delta$  123 (Fig. 3). The peak at  $\delta$  77-80 accounts for the solvent  $\text{CDCl}_3$ . The other signals at  $\delta$  61 are due to methoxy carbon ( $-\text{OCH}_2-$ ) of EMA unit. The resonance at  $\delta$  45 represent quaternary carbon, the resonance at  $\delta$  20 are due to  $\text{C-CH}_3$  and methyl group of EMA unit and methylene ( $-\text{CH}_2$ ) group at  $\delta$  52. The methyl group of MAN unit signal appears at 22 and methyl end group ( $-\text{CH}_3$ ) of EMA unit signal appears at  $\delta$  18. This confirms the formation of copolymer.

**Reactivity ratios:** The copolymer composition data were used for the evaluation of reactivity ratios of the MAN-EMA copolymer by Fineman – Ross (Morton Fineman, 1950) (F-R) (Fig. 4) and Kelen–Tudos (Kelen, 1975) (K-T) (Fig.5) methods

$$G = r_1 H - r_2 \dots\dots\dots (2)$$

$$\text{where } G = \frac{F(f-1)}{f} \text{ and } H = F^2 / f$$

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \dots\dots\dots (3)$$

$$\text{where } \eta = \frac{G}{\alpha + H} \quad \xi = \frac{H}{\alpha + H}$$

The values of reactivity ratios were summarized in Table 2. The product of  $r_1 r_2$  values, which is less than 1 suggests that the monomers were arranged in a random sequence. The rate of polymerization depends on the value of  $1/r$  that gives a measure of the reactivity of the methyl methacrylate towards the MAN radical. The value of  $1/r_1$  for MAN-EMA copolymer is 0.86.

To ascertain the normal copolymer behavior, the plots of mole fraction of monomer in the feed ( $m_1$ ) vs that in the copolymer ( $M_1$ ) were drawn and is given in Table 1. The shapes of the curves (Fig. 6) indicate that the azeotropic compositions of the copolymer systems and the distribution of monomeric units are random. The azeotropic composition was determined by the following equation (Gowrikar, 1996; Billmeyer, 1982; Odian, 1981).

$$M_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \dots\dots\dots(4)$$

The value of MAN-EMA is 1.04 indicating that the copolymer is richer in MAN below this point than MAN and richer in EMA above this point than MAN. This behaviour also suggests the random distribution of monomers in the copolymer.

**Sequence length distribution:** The mean sequence lengths  $\bar{n}_1$  and  $\bar{n}_2$  for MAN-EMA copolymer system has been calculated and listed in Table 3. The  $\bar{n}_1$  and  $\bar{n}_2$  for  $M_1$  and  $M_2$  units are calculated using equations of Expenyong (Kieran, 1985).

$$\bar{n}_1 = \frac{P_{12}}{(1 - P_{11})^2} = \frac{1}{P_{12}} = \frac{r_1 [M_1] + [M_2]}{[M_2]} \text{-----}(5)$$

$$\bar{n}_2 = \frac{P_{21}}{(1 - P_{22})^2} = \frac{1}{P_{21}} = \frac{r_2 [M_2] + [M_1]}{[M_1]} \text{-----}(6)$$

For example, at 80.0%AN (20.0% EMA) in the monomer mixture each copolymer segment with  $M_1$  units was approximately six times longer than its adjoining segment with  $M_2$  units. The sequence may be expressed as —2111112—. This differences between  $\bar{n}_1$  and  $\bar{n}_2$  values are increased from 40.0-46.6% to 80.0% of MAN. Thus, we can say that MAN has higher tendencies to form more segments than that of EMA. The number of MAN units in copolymer increases with increasing concentration of MAN in the feed, but this is

not so for EMA. Hence EMA acts as a retarder in the copolymerization. The ratio of the mean sequence lengths distribution, which theoretically (Mitsuru Ueda, 1986) correspond to the ratio  $[M_1]/[M_2]$ , where  $[M_1]$  and  $[M_2]$  are the corresponding compositions of  $M_1$  and  $M_2$  in the copolymer for each monomer mixture of MAN-EMA is given in Table 3.

**Solution properties:** The molecular weights of the copolymers were determined with a KNAUER (WG) GPC with THF as eluent. The intrinsic viscosity of the copolymers was measured with an Ubbelohde Viscometer in toluene at  $30 \pm 0.1^\circ\text{C}$ . The weight average and number average molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) values of copolymer for different compositions are given in Table 4. These values increase with the increase in the MAN content of the copolymer. This trend is in consonance with variation in intrinsic viscosity. The solubility parameter helps in explaining the viscosity behavior of solution, polymer-polymer compatibility, dispersion and tolerance for dilution with non-solvents. Proper solvents can be selected to control the viscosity of polymer solution by using these values. The evaporation of solvent can also be adjusted by selecting proper solvents using this solubility parameter concept to get good film with no defects.

Plots of  $\eta_{sp}/c$  against concentration are found to be linear and the intrinsic viscosity values are obtained by extrapolating it to zero concentration. In all the copolymers intrinsic viscosity and hence molecular weight increases with increase in the MAN content Table 4. This may be attributed to the greater reactivity of vinyl propionate content, which facilitates propagation in preference to termination. Solubility parameter values of the copolymer determined in different solvents are presented in Table 5. Solvents which cover a range of solubility parameter from 8.9 to 12.1 (cal/cc)<sup>0.5</sup> have been selected. The solubility parameter value of MAN-EMA is 9.7 (cal/cc)<sup>0.5</sup>.

**Thermal studies:** The thermogravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of  $15^\circ\text{C}/\text{min}$ . Glass transition temperature ( $T_g$ ) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of  $15^\circ\text{C}/\text{min}$  and shown in (Fig-7).  $T_g$  values of the copolymers obtained from the DSC curves.  $T_g$  of the copolymer increases with

increase in the MAN content.. When the MAN content increases intramolecular interaction increase and the polymer segments become less mobile and  $T_g$  occurs at higher temperature (Raghunath Rao, 2007; Ewing, 2003; Julio San Roman, 2003; Raghunath Rao, 1992; Salem, 2003). The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss shown in (Fig.8). To obtain a comparative picture of relative thermal stability of the copolymer their IDT, IPDT and DT values are given in Table 6.

**Di-electric properties:** A Capacitance bridge model GR 1620(WG) is used to measure the dielectric constant ( $\hat{\epsilon}$ ) and dielectric loss ( $\tan\delta$ ) of the MAN-EMA copolymers. All samples are annealed prior to use for the measurement. The results of variation of ( $\hat{\epsilon}$ ) and  $\tan\delta$  at constant frequency of 20 KHz against temperature for MAN-EMA (Fig-9) are given in Table 7. The results shows that the  $\hat{\epsilon}$  and  $\tan\delta$  are unaffected by temperatures up to 125°C. Beyond that region, both  $\hat{\epsilon}$  and  $\tan\delta$  increases. A peak due to relaxation is observed in  $\tan\delta$ , known as  $\alpha$  relaxation, at about 120°C, in the rubbery state of the polymer (Adam, 1962; Tanaka, 1962). This temperature is higher than  $T_g$  for the polymer obtained by a DSC method is 114.52°C. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions (Gupta, 1981; Srilatha, 2003). As the temperature is raised, more and more dipole groups are released and the mobility of polymers segment increases.

#### 4. CONCLUSION

The copolymer of MAN with EMA has been synthesized using a VAZO as initiator in DMF. The copolymer is characterized by IR and  $^1\text{H-NMR}$ . Reactivity ratio of the copolymer was determined using the F-R and K-T methods which suggest that random copolymers were formed. Intrinsic viscosities and solubility parameter was determined to establish interactions in polymer solutions. Thermal properties like  $T_g$ , IDT and IPDT have been evaluated to find the thermal stability of the polymer. Di-electric properties of co-polymer are also studied to find the electrical stability.

**Table - 1 Copolymerization data of MAN with EMA**

Copolymer system	Mole fraction in the feed		Intensity of methylene protons of MAN (2H)(M <sub>1</sub> )	Intensity of ethyl protons of EMA (5H)(M <sub>2</sub> )	Copolymer composition	
	MAN (M <sub>1</sub> )	EMA (M <sub>2</sub> )			MAN (m <sub>1</sub> )	EMA (m <sub>2</sub> )
MAN-EMA <sub>1</sub>	0.8	0.7	2.85	1.30	0.686	0.314
MAN-EMA <sub>2</sub>	0.9	0.6	2.51	0.96	0.723	0.277
MAN-EMA <sub>3</sub>	1.0	0.5	2.37	1.167	0.759	0.241
MAN-EMA <sub>4</sub>	1.1	0.4	1.26	0.49	0.800	0.200
MAN-EMA <sub>5</sub>	1.2	0.3	3.19	0.71	0.818	0.182

**Table - 2 Parameters of equations (2) and (3) for MAN-EMA copolymer.**

$$\alpha = 1.461$$

S.No.	F=MAN/EMA	F	$G = \frac{F(f-1)}{f}$	$H = \frac{F^2}{f}$	$\eta = \frac{G}{\alpha+H}$	$\xi = \frac{H}{\alpha+H}$
1	1.143	2.19	0.621	0.60	0.301	0.291
2	1.50	2.61	0.925	0.862	0.398	0.371
3	2.00	3.16	1.367	1.265	0.501	0.464
4	2.75	4.04	2.06	1.890	0.614	0.564
5	4.00	4.494	3.109	3.560	0.621	0.709

**Table - 3 Mean sequence length distribution of MAN-EMA copolymers**

S.No.	M <sub>2</sub> (mol%)	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_1 / \bar{n}_2$	$\bar{n}_1 : \bar{n}_2$	Distribution
1	46.6	2.32	1.175	1.97	2:1	2112
2	40.0	2.74	1.133	2.41	3:1	21112
3	33.3	3.32	1.104	3.02	4:1	211112
4	26.6	4.19	1.072	4.01	5:1	2111112
5	20.0	5.64	1.054	5.37	6:1	21111112

**Table- 4 Intrinsic viscosities at 25°C and molecular weight of MAN-EMA copolymers**

Copolymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$[\eta]$ dl/g
MAN-EMA <sub>1</sub>	1.8801	1.1721	0.203
MAN-EMA <sub>2</sub>	1.8865	1.1952	0.258
MAN-EMA <sub>3</sub>	1.9025	1.2154	0.294

**Table- 5 Intrinsic viscosities of MAN-EMA copolymers and their dependence on solubility parameter of solvents at 30 °C**

S.NO	Solvent	$\delta$ (Cal/cc) <sup>0.5</sup>	$[\eta]$ dl/g MAN-EMA
1	Toluene	8.9	0.122
2	Benzene	9.2	0.143
3	Chloroform	9.3	0.159
4	Chloro benzene	9.5	0.173
5	Dichloro methane	9.7	0.203
6	Acetic acid	10.1	-
7	Diethyl formamide	10.6	-
8	1,4 Dioxane	10.7	0.131
9	Dichloro acetic acid	11.0	-
10	Dimethyl sulfoxide	12.0	0.160
11	Dimethyl formamide	12.1	0.112

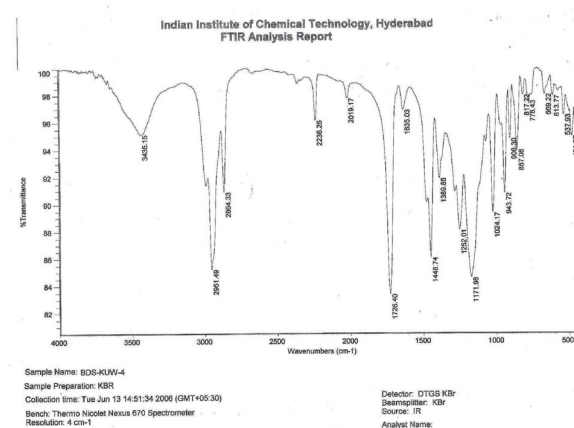
**Table- 6 Thermal behavior of MAN-EMA copolymers**

Copolymer	IDT (°C)	IPDT(°C)	Temperature (°C) at wt. loss			Tg (°C)
			10%	20%	50%	
MAN-EMA <sub>1</sub>	124.25	165.36	154.95	175.65	293.62	114.52
MAN-EMA <sub>2</sub>	125.96	166.59	155.26	179.35	299.36	115.85
MAN-EMA <sub>3</sub>	127.36	167.36	156.95	186.79	302.74	119.32
MAN-EMA <sub>4</sub>	129.32	167.98	158.36	192.95	306.21	--
MAN-EMA <sub>5</sub>	130.58	169.25	159.75	197.56	308.95	--

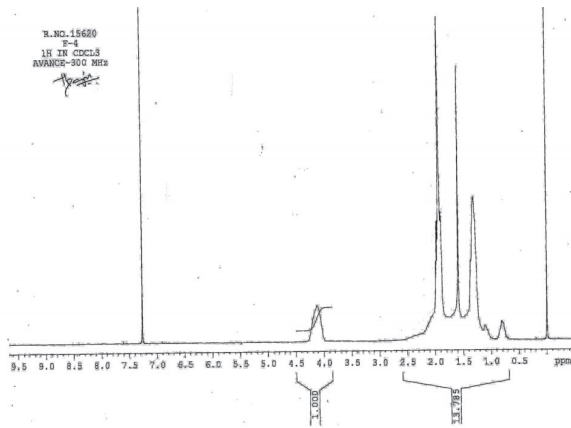
**Table-7 Variation of dielectric constant and dielectric loss with temperature for MAN-EMA copolymer at 20 KHz**

Temperature	MAN-EMA	
	$\epsilon$	$\tan\delta$
25	2.904	0.022
50	2.972	0.027
75	3.077	0.033
100	3.143	0.039
125	3.222	0.043
150	3.309	0.038

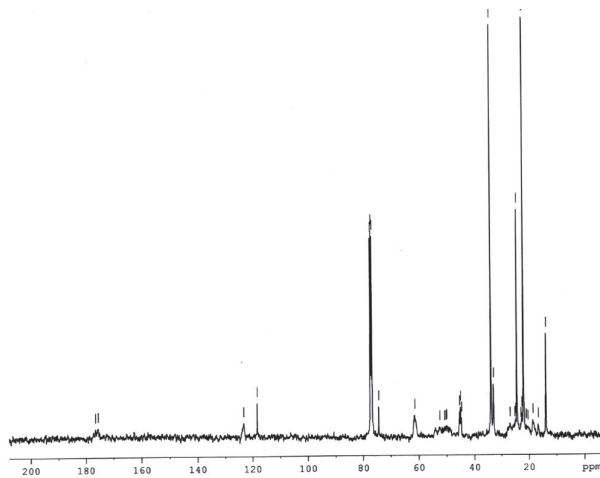
**FIGURES**



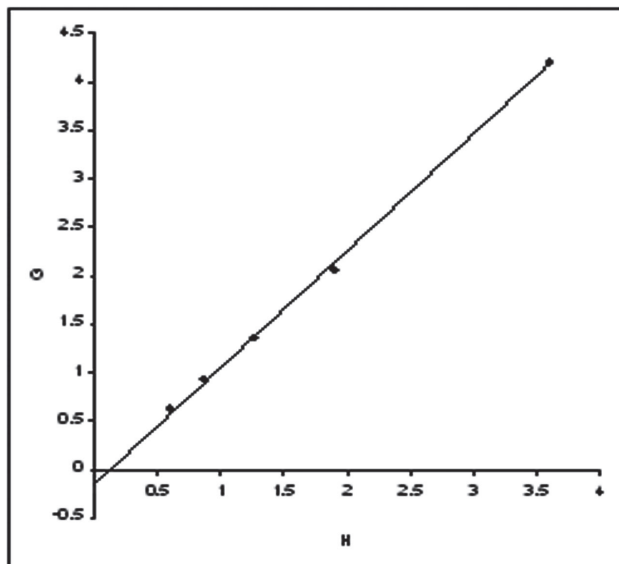
**Fig-1 FTIR Spectrum of MAN-EMA**



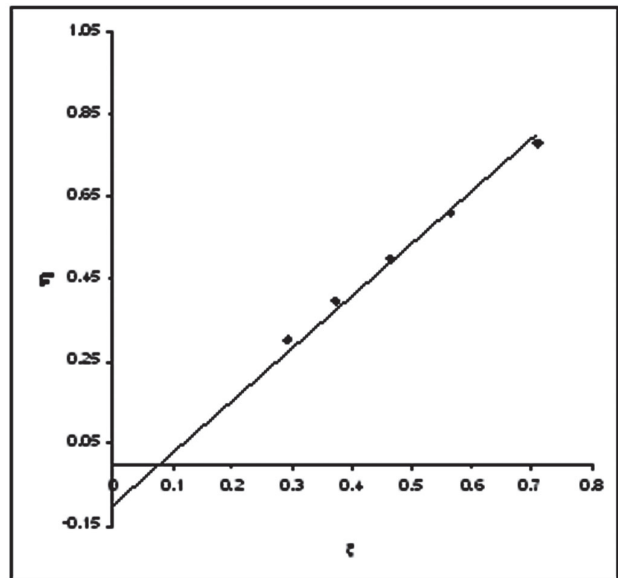
**Fig-2 <sup>1</sup>H-NMR Spectrum of MAN-EMA**



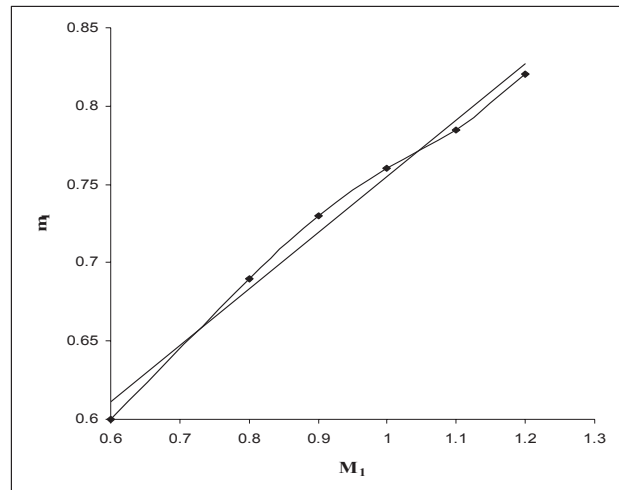
**FIG-3 <sup>13</sup>C-NMR Spectrum of MAN-EMA**



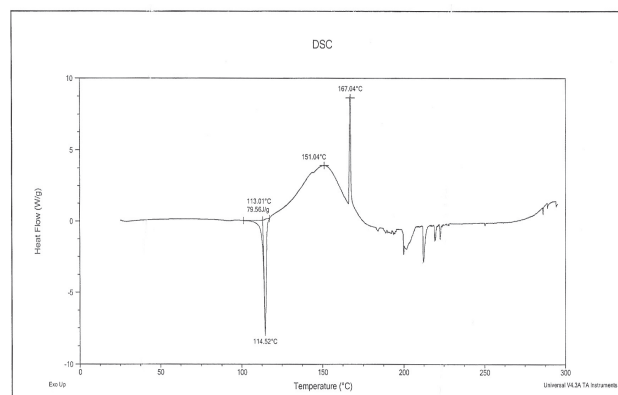
**FIG-4. F-R Plot of MAN-EMA**



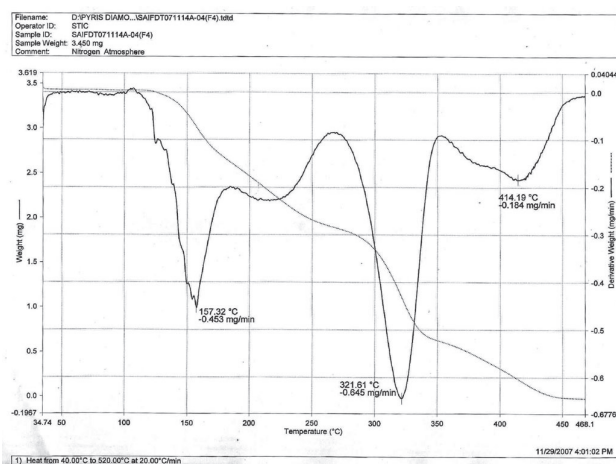
**FIG-5. K-T Plot of MAN-EMA**



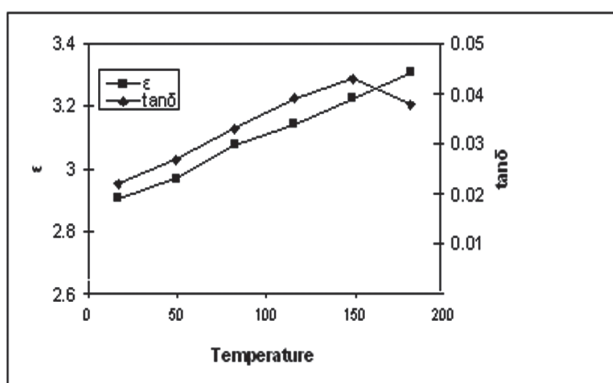
**FIG-6 Azeotropic composition of MAN-EMA**



**FIG-7 DSC Curve of MAN-EMA**



**FIG- 8 TGA/DTG Curve of MAN-EMA**



## REFERENCES

- Adam A, Kolloid Zeitschrift Zeitshrift, Polym, 180, 1962, 11.
- Balaji R, Nanjundan S, J Macromol Sci Chem, A 35(9), 1998, 1527.
- Balaji R, Nanjundan S, Eur Polym J, 35, 1999, 1133.
- Billmeyer FW, Textbook of Polymer Science, Edn 2, John Wiley & Sons, Inc, Tokyo, Japan, 1982.
- Brar AS, Tripta Saini, J Polym Sci Part A: Polym Chem, 44, 2006, 2955-2971.
- Brar A.S, Tripta Saini, J Polym Sci Part A: Polym Chem, 44, 2006, 1975-1984.
- Ewing K, Ken Busfield W, Lan D. Jenkins, Polym. Int, 52, 2003, 1671.
- Gowrikar VR, Viswanathan NV, Sreedhar, Poly Science, New Age International Limited, New Delhi, 1996, 206.

Gupta AK, Singhal RP, Agarwal AK, Polymer, 22, 1981, 285.

Hossein S. Hosseini and Anouchiravan Ghavami, Iranian Polymer Journal, 14(7), 2005, 617-626.

Ismail Mathakiya, Rakshit AK, Rao PVC, International Journal of Polymer Analysis and Characterization, 8(5), 2003, 339 – 358.

Julio San Roman, Blanca Vázquez, Miguel Valero, Gonzalo Martin Guzman, Die Makromolekulare Chemie, 193(6), 2003, 1321 – 1329.

Kadir Demirelli, Adnan Kurt, Fatih Coskun M, Mehmet Coskun, Journal of Macromolecular Science, 43 (3), 2006, 573.

Kieran I, Ekpenyong, J Polym Sci Polym Chem Edu, 23, 1985, 125.

Kelen T, Tudos F, J. Macromol. Sci. Chem, A(9), 1975, 1.

Mihailo S, Jacovic, Danica Milosevic, Journal of Polymer Science, Polymer Symposia, 42(3), 2007, 1443 – 1454.

Morton Fineman, Sidney D, Ross, J. Polym. Sci, 5(2), 1950, 259.

Mitsuru Ueda, Toshiyuki Suzuki, Masami Takahashi, Zao Bang Li, Kiyohito Koyamat, Macromolecules, 19, 1986, 558.

Odian, George, Principles of Polymerization, Wiley Interscience, Edn 2, New York. 1981, 81.

Raghunath Rao P, Sridevi S, Asian Journal of Chemistry, 19(5), 2007, 3663-3670.

Raghunath Rao P, Bixamaiah B, Sundaram E.V, Macromolecular reports, A30 (1), 1992, 71-86.

Salem SS, Al-Diab, Hwan-Kyu Suh, James E, Mark, Hans Zimmer, Journal of Polymer Science Part A: Polymer Chemistry, 28(2), 2003, 299 – 314.

Srilatha T, Raghunath Rao P, Asian J Chem, 15, 2003, 241.

Tacx JCJF, Vander Velden GPM, German AL, Polymer, 29, 1998, 1675.

Tanaka A, Ishida Y, J Phys Soc Japan, 15, 1962, 6.