



1, 1' AZOBIS (CYCLOHEXANECARBONITRILE) INITIATED COPOLYMERIZATION OF ACRYLONITRILE COPOLYMERS AND THEIR CHARACTERIZATION

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ABSTRACT

Copolymer of acrylonitrile (AN) with ethylmethacrylate (EMA) was synthesized by free radical polymerization using 1, 1' azo bis (cyclohexanecarbonitrile) (VAZO) as initiator in dimethyl formamide (DMF) at 60 ± 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}_1) and probabilities (ρ) 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 AN 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 studied. The di-electrical property of the copolymer is also studied.

Keywords: Ethylmethacrylate Reactivity ratios , Solution properties , Thermal properties and Di-electrical property.

INTRODUCTION

Introduction of ethylmethacrylate (EMA) into various copolymers appears to modify and improve the properties of a number of copolymers¹⁻⁴. The estimation of copolymer composition and determination of the reactivity ratios are important for making copolymers with required physico-chemical properties. The ¹H-NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition⁵⁻⁸. In this article we reported the synthesis, characterization, reactivity ratios, solution and thermal properties of the copolymers of AN with EMA.

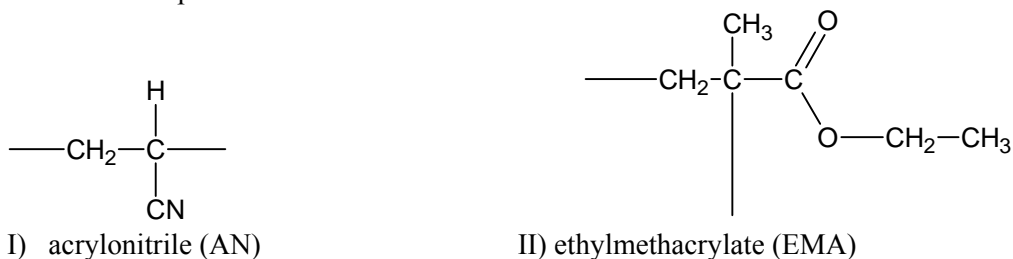
EXPERIMENTAL

AN (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 ± 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^3 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.

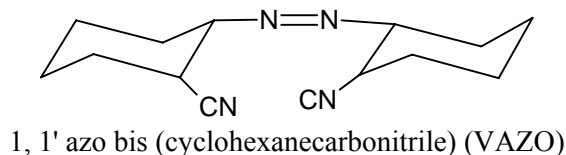
RESULTS AND DISCUSSION

IR Spectroscopy: Infrared spectra of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in 4000 to 400 cm^{-1} range with KBr pellets. The IR spectrum of the copolymer of AN and EMA (AN-co-EMA) is shown in (Fig.1) showing the characteristic bands of both the monomer units.

The monomer unit structures are represented as follows:



Structure of initiator:



Appearance of strong absorption bands at 2864.02, 1734.34, 2240.93, 1448.73 and 2934.94 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 to $>\text{C}=\text{O}$, $-\text{OCH}_2$ and $-\text{CN}$ groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the AN-EMA copolymer.

Determination of copolymer composition: $^1\text{H-NMR}$ spectra of the samples were recorded using DMSO-d_6 as solvent for AN copolymer on a Avance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by $^1\text{H-NMR}$ spectra shown in (Fig.2). The characteristic peaks due to methyl ($-\text{CH}_3$) protons of ethylmethacrylate unit appears at 1.20- 1.25 ppm, methylene ($-\text{CH}_2$) protons of EMA unit appears as singlet at 1.8-1.9 ppm, methylene ($-\text{CH}_2$) protons of AN unit appears at 2.0 ppm, methoxy ($-\text{OCH}_2$) protons of EMA unit appears at 4.0 – 4.1 ppm, ($-\text{CH}-$) protons of AN appears at 2.5 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 calculated⁹ by the relation

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

This equations is based on the fact that the $-\text{CH}_2$ group of AN 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 AN-EMA shows resonance at δ 175 for carbonyl carbon of EMA units and the nitrile carbon of AN unit at δ 118-121 (Fig. 3). The triplet at δ 77-80 accounts for the solvent CDCl_3 . The other signals at δ 61.5 are due to methoxy carbon ($-\text{OCH}_2-$) of EMA unit. The resonance at δ 45 represent quarternary carbon, the resonance at δ 24 are due to C-CH_3 and methyl group of EMA unit and methylene($-\text{CH}_2$) group at δ 51. The methyl end ($-\text{CH}_3$) of the EMA unit signal appears at δ 18. This confirms the formation of copolymer.

Reactivity ratios: The copolymer composition data were used for the evaluation of reactivity ratios of the AN-EMA copolymer by Fineman – Ross¹⁰ (F-R) (Fig. 4) and Kelen–Tudos¹¹ (K-T) (Fig.5) methods.

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

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

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

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

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 AN radical. The value of $1/r_1$ for AN-EMA copolymer is 1.49.

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 equation¹²⁻¹⁴

$$N_1 = \frac{(1-r_2)}{(2-r_1-r_2)} \quad \dots\dots\dots (4)$$

The value of AN-EMA is 0.98 indicating that the copolymer is richer in AN below this point than AN and richer in EMA above this point than AN. 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 AN-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.¹⁵

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

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

For example, at 80%AN (20 % EMA) in the monomer mixture each copolymer segment with M_1 units was approximately four times longer than its adjoining segment with M_2 units. The sequence may be expressed as --211112---. This differences between \bar{n}_1 and \bar{n}_2 values are increased from 40.0-46.6% to 80% of AN. Thus, we can say that AN has higher tendencies to form more segments than that of EMA. The number of AN units in copolymer increases with increasing concentration of AN 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 \bar{n}_1/\bar{n}_2 , which theoretically¹⁶ 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 AN-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 AN 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 η_{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 AN 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)^{0.5} have been selected. The solubility parameter value of AN-EMA is 10.1 (cal/cc)^{0.5}.

Table -1:Copolymerization data of AN with EMA

Copolymer system	Mole fraction in the feed		Intensity of methylene protons of AN (2H)(M ₁)	Intensity of ethyl protons of EMA (5H) (M ₂)	Copolymer composition	
	AN (M ₁)	EMA (M ₂)			AN (m ₁)	EMA (m ₂)
AN-EMA ₁	0.80	0.70	5.18	3.26	0.8925	0.1075
AN-EMA ₂	0.93	0.56	3.45	1.76	0.8650	0.1350
AN-EMA ₃	1.08	0.42	2.62	1.14	0.8180	0.1820
AN-EMA ₄	1.12	0.38	1.52	0.42	0.7700	0.2300
AN-EMA ₅	1.20	0.30	0.41	0.14	0.7260	0.2740

Table -2: Parameters of equations (2) and (3) for AN-EM copolymer.

$$\alpha = 2.188$$

S.No.	F=AN/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	1.454	0.356	0.898	0.115	0.290
2	1.50	1.682	0.608	1.337	0.172	0.379
3	2.00	2.03	1.164	2.820	0.322	0.563
4	2.75	2.57	2.101	4.106	0.333	0.652
5	4.00	3.00	2.666	5.333	0.354	0.709

Table – 3:Mean sequence length distribution of AN-EMA copolymers

S.No.	M ₂ (mol%)	\bar{n}_1	\bar{n}_2	\bar{n}_1 / \bar{n}_2	$\bar{n}_1 : \bar{n}_2$	Distribution
1	46.6	1.651	1.175	1.40	2:1	2112
2	40.0	1.855	1.133	1.64	2:1	2112
3	33.3	2.14	1.10	2.01	3:1	21112
4	26.6	2.57	1.07	2.40	3:1	21112
5	20.0	3.28	1.05	3.12	4:1	211112

Table- 4: Intrinsic viscosities at 25⁰C and molecular weight of AN-EMA copolymers

Copolymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$[\eta]$ dl/g
AN-EMA ₁	1.8832	1.201	0.291
AN-EMA ₂	1.8948	1.211	0.298
AN-EMA ₃	1.9122	1.218	0.302

Table-5: Intrinsic viscosities of AN-EMA copolymers and their dependence on solubility parameter of solvents at 30⁰ C

S.NO	Solvent	δ (Cal/cc) ^{0.5}	$[\eta]$ dl/g AN-EMA
1	Toluene	8.9	0.130
2	Benzene	9.2	0.157
3	Chloroform	9.3	0.172
4	Chloro benzene	9.5	0.178
5	Dichloro methane	9.7	0.291
6	Acetic acid	10.1	-
7	Diethyl formamide	10.6	-
8	1,4 Dioxane	10.7	0.210
9	Dichloro acetic acid	11.0	-
10	Dimethyl sulfoxide	12.0	0.151
11	Dimethyl formamide	12.1	0.143

Table- 6:Thermal behavior of AN-EMA copolymers

Copolymer	IDT (°C)	IPDT(°C)	Temperature (°C) at wt. loss			Tg (°C)
			10%	20%	50%	
AN-EMA ₁	125.54	150.62	161.71	260.32	378.46	114.06
AN-EMA ₂	126.42	152.66	162.58	271.79	382.95	116.52
AN-EMA ₃	126.95	152.92	165.36	281.34	390.36	119.78
AN-EMA ₄	128.65	153.52	168.22	298.12	425.47	--
AN-EMA ₅	130.25	155.87	169.54	311.60	482.44	--

Thermal studies: The thermogravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of 15⁰C/min. Glass transition temperature (T_g) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of 15⁰C/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 AN content.. When the AN content increases intramolecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature¹⁷⁻²¹. 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 (ϵ) and dielectric loss ($\tan\delta$) of the AN-EMA copolymers. All samples are annealed prior to use for the measurement. The results of variation of (ϵ) and $\tan\delta$ at constant frequency of 20 KHz against temperature for AN-EMA (Fig-9) are given in Table 7. The results shows that the ϵ and $\tan\delta$ are unaffected by temperatures up to 125°C. Beyond that region, both ϵ and $\tan\delta$ increases. A peak due to relaxation is observed in $\tan\delta$, known as α relaxation, at about 120°C, in the rubbery state of the polymer²²⁻²³. This temperature is higher than T_g for the polymer obtained by a DSC method is 114.06°C. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions^{24,25}. As the temperature is raised, more and more dipole groups are released and the mobility of polymers segment increases.

CONCLUSIONS

The copolymer of AN with EMA has been synthesized using a VAZO as initiator in DMF. The copolymer is characterized by IR and ¹H-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 is also studied to find the electrical stability.

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

Temperature	AN-EMA	
	E	$\tan\delta$
25	2.131	0.036
50	2.166	0.04
75	2.181	0.043
100	2.217	0.047
125	2.238	0.052
150	2.266	0.046

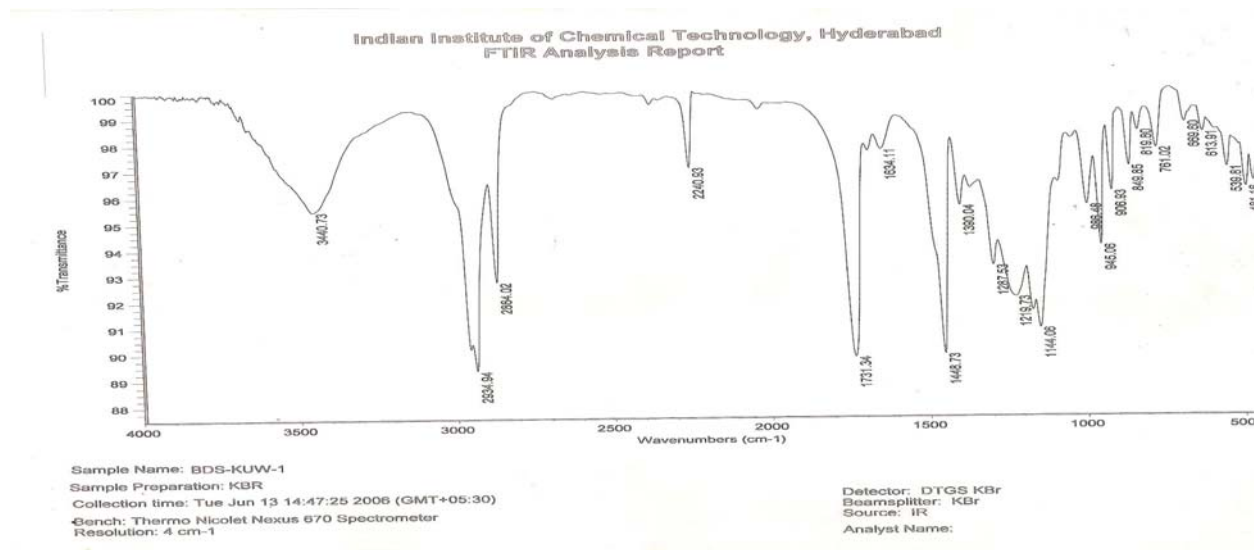


Fig.-1: IR Spectrum of AN-EMA

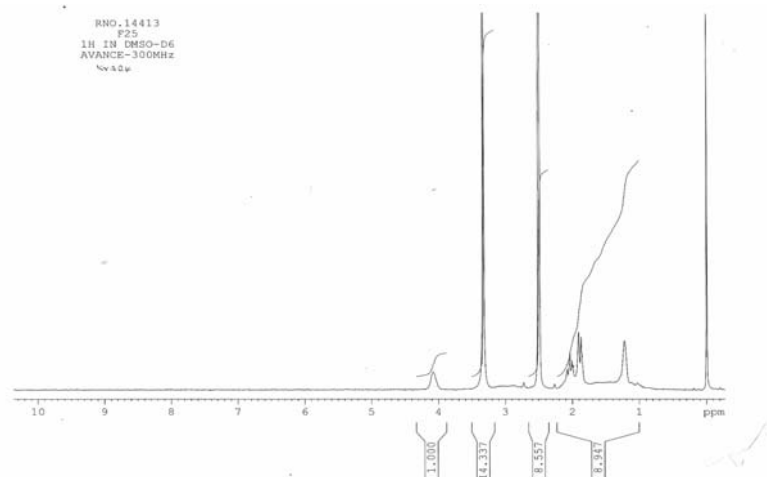


Fig.-2: ¹H-NMR Spectrum of AN-EMA

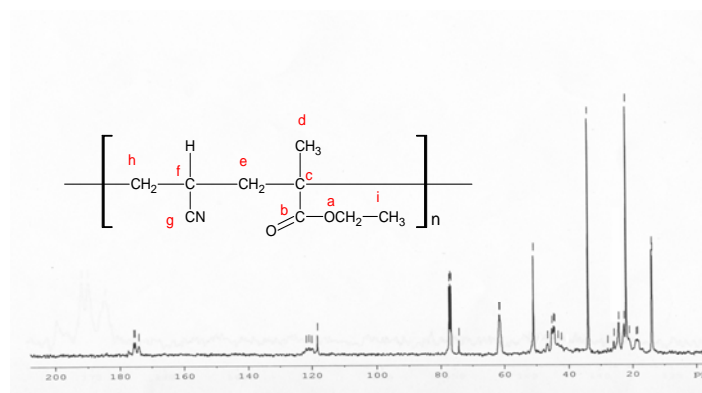


Fig.-3: ¹³C-NMR of AN-EMA copolymer

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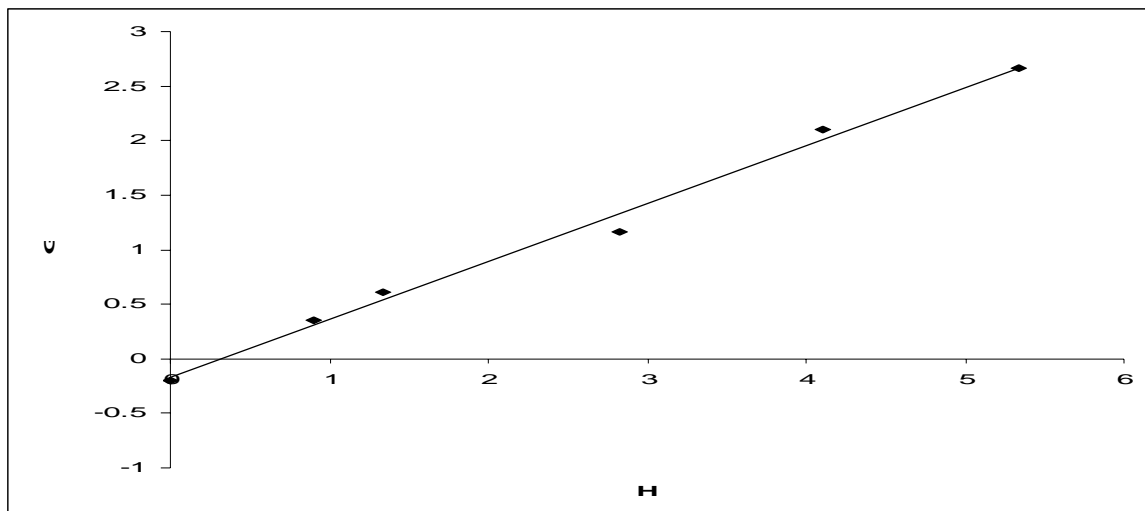


Fig.-4: F-R Plot of AN-EMA copolymer

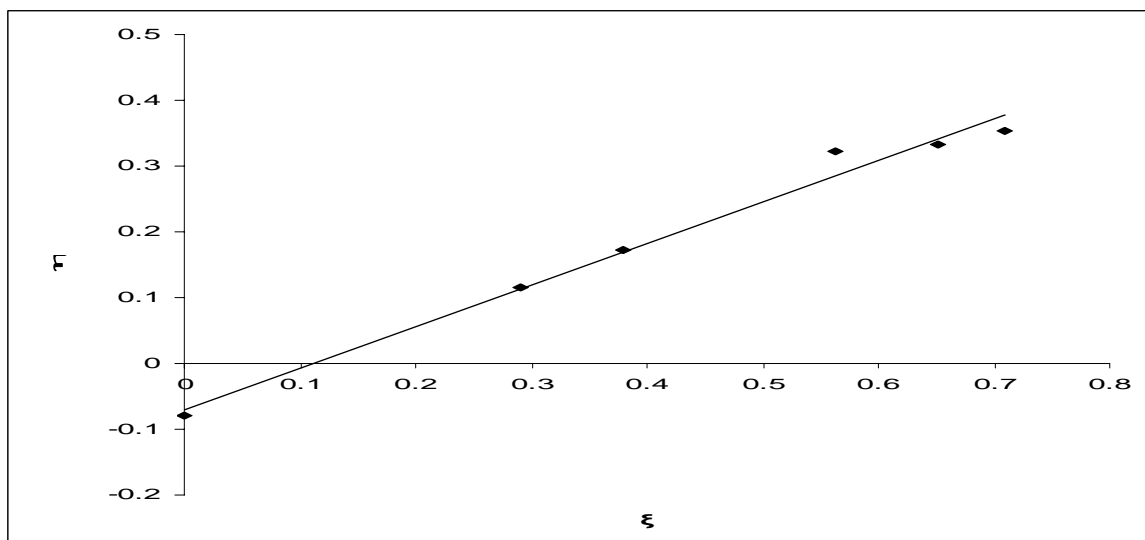


Fig.-5: K-T Plot of AN-EMA copolymer

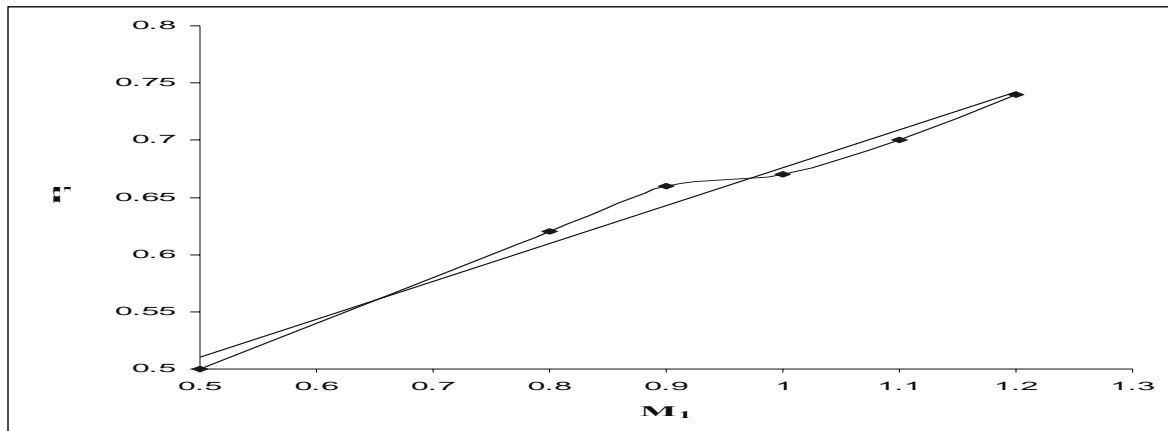


Fig-6: Azeotropic composition of AN-EMA copolymer

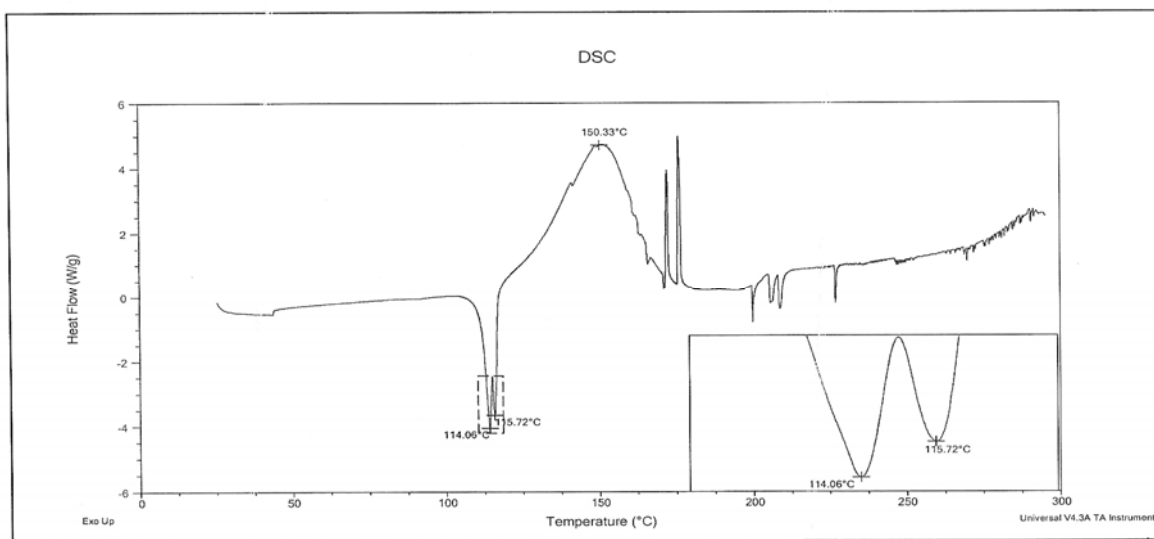


Fig-7; DSC curve of AN-EMA copolymer

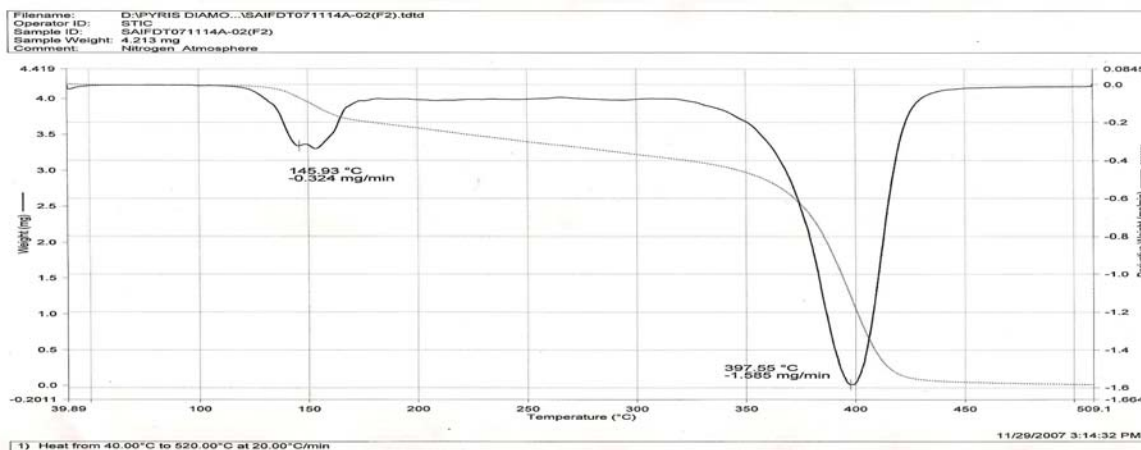


Fig-8: TGA/DTG curve of AN-EMA copolymer

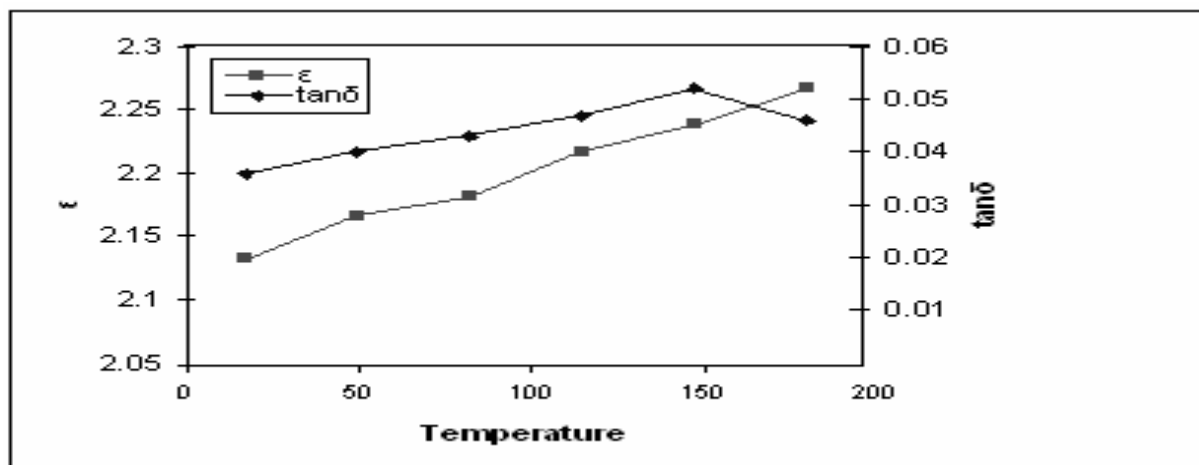


Fig.-9: Typical Plot of ϵ and $\tan\delta$ against temperature for AN-EMA copolymer

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