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## Synthesis, characterization, thermal and dielectric properties of bis (1-oxododecyl) peroxide initiated acrylonitrile copolymers

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**Abstract:** Copolymer of acrylonitrile (AN) with ethyl methacrylate (EMA) was synthesized by free radical polymerization method using bis (1-oxododecyl) peroxide as initiator in dimethylformamide (DMF) at 60 °C. The copolymer samples were characterized by Fourier transform infrared spectroscopy (FTIR), in the synthesized copolymer types of carbons and protons are confirmed by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy, <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) and dielectric studies. The possible functional groups of acrylonitrile and their changes after treating with EMA were evaluated by (FTIR). The monomer reactivity ratio was computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The reactivity ratio values revealed the formation of random copolymers. The formation of random copolymer was also supported by azeotropic composition evaluation method. The dielectric constant (ε) of acrylonitrile-ethyl methacrylate (AN-EMA) copolymers was found to dependent both on temperature and frequency. The increase in dielectric loss (tan δ) with temperature is attributed to formation of more dipoles at higher temperatures. Glass transition temperature (T<sub>g</sub>) and Thermo gravimetric analysis (TGA) of the copolymers was also reported. The number of AN units in copolymer increased with increasing concentration of AN. Hence EMA acts as a retarder in the copolymerization. The increased AN content increased intramolecular interaction and thereby polymer segments become less mobile. Hence T<sub>g</sub> occurs at higher temperature with increasing AN content in the polymer.

**Keywords:** Ethyl methacrylate, Co-polymer, AN-EMA, Reactivity ratios, Dielectric properties and Thermal properties.

### 1. Introduction

Polymers are used in a wide range of applications often for their low cost, light weight and good mechanical properties or for combination of these characteristics. A few of the limitations of poly acrylates have been overcome by the fusion with nitriles through copolymerization<sup>[1-2]</sup> Nitriles and alkyl acrylic esters are prime candidates for diverse applications. Introduction of ethyl methacrylate into various copolymers appears to modify and improve the properties of a number of copolymers. The <sup>1</sup>H-NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition.<sup>3-6</sup> In this article we report the synthesis, characterization, reactivity ratios, thermal properties and dielectric properties of (AN-EMA) copolymer.

### 2. Results and Discussion

#### 2.1. IR Spectroscopy

The IR spectrum of the copolymer shows strong absorption bands around 2851.22, 1729.05, 2240.21, 1470.80 and 2917.58 cm<sup>-1</sup> corresponds to methine (-CH) stretching, >C = O stretching in ester, (-CN) stretching in AN, (-OCH<sub>2</sub>-) group and methyl (-CH<sub>3</sub>) stretching vibrations of ester respectively. The appearance of absorption bands corresponding to >C =O, -OCH<sub>2</sub> and -CN groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence to the formation of AN-EMA copolymer.

#### 2.2. Determination of copolymer composition

The <sup>1</sup>H-NMR spectrum of the copolymer shows the characteristic peaks due to methyl (-CH<sub>3</sub>) protons of EMA unit appears at 1.4 ppm, methylene (-CH<sub>2</sub>) protons of EMA and AN unit appears as singlet at 1.7-1.8 ppm, methine (-CH) protons of AN unit appears at 2.1-2.2 ppm, -CH<sub>3</sub> group and (-OCH<sub>2</sub>) group protons of EMA unit appears at 2.0 ppm and 4.0 – 4.1 ppm respectively. These peaks were considered for 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 (1). This equation is based on the fact that the -CH<sub>2</sub> group of AN unit corresponds to two protons, -OCH<sub>2</sub> group of EMA corresponds to two protons.

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

#### 2.3. <sup>13</sup>C- NMR Spectroscopy

The <sup>13</sup>C-NMR spectrum of the polymer indicates the peak at δ 174-176 accounts for carbonyl carbon of EMA. The nitrile carbon at δ 120-123 and methine carbon (-CH) of AN unit appears at δ 28. The peak at δ 40 accounts for the solvent DMSO. The other signals at δ 60 are due to -OCH<sub>2</sub>- carbon of EMA unit. The resonance at δ 34-39 represent quaternary carbon, the resonance at δ 19-24 are due to C-CH<sub>3</sub> methyl group and methylene (-CH<sub>2</sub>) carbon of EMA unit at δ 45. The

end methyl group (-CH<sub>3</sub>) of the EMA signal appears at δ 12. This confirms the formation of copolymer.

### 2.4. Reactivity ratios

The copolymer composition data was used for the

evaluation of reactivity ratios of the AN-EMA copolymer by Fineman–Ross<sup>7</sup> and Kelen–Tudos<sup>8</sup> methods. The respectively plots are shown in Figure 1 (a) and (b).

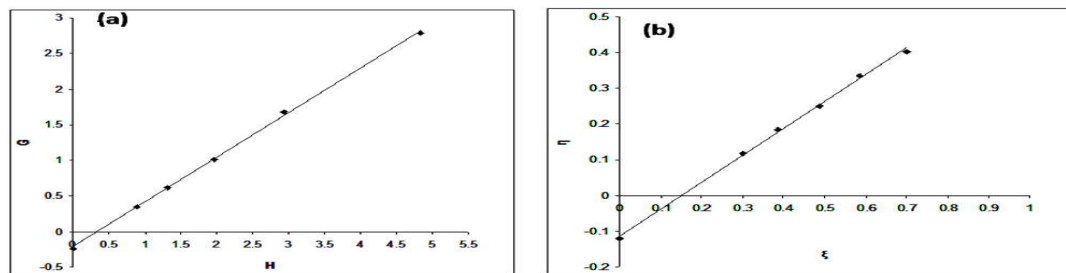


Figure 1. 1(a) F-R Plot and Figure.1 (b) K-T plot.

$$G = r_1 H - r_2 \tag{2}$$

Where

$$G = \frac{F(F-1)}{f} \text{ and } H = \frac{F^2}{f} \tag{3}$$

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}$$

Where

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

The values of reactivity ratios were summarized in Table 1. The product of r<sub>1</sub>r<sub>2</sub> whose value less than unity 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 ethyl methacrylate towards the AN radical. The value of 1/r<sub>1</sub> for AN-EMA copolymer is 1.563.

Table 1. Parameters of equations (2) and (3) for AN-EMA copolymer (α = 2.070)

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	1.45	0.356	0.898	0.118	0.300
2.	1.50	1.71	0.623	1.314	0.183	0.387
3.	2.00	2.03	1.015	1.969	0.250	0.486
4.	2.75	2.57	1.680	2.940	0.335	0.586
5.	4.00	3.30	2.787	4.848	0.402	0.700

### 2.5. Azeotropic Composition

Azeotropic composition of copolymer is determined from the plots of mole fraction of monomer in the copolymer composition (m<sub>1</sub>) versus monomer in the feed (M<sub>1</sub>) as given in Table 5. The plot is shown

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

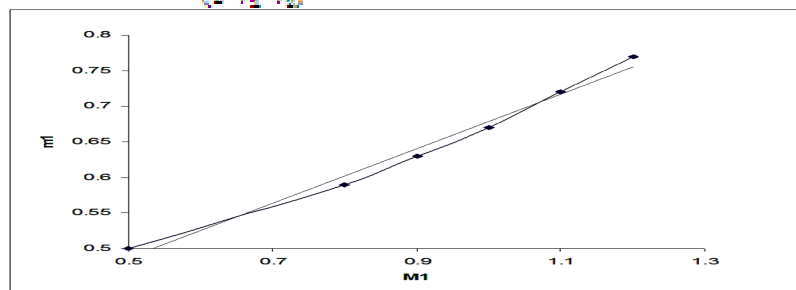


Figure 2. Azeotropic composition of AN-EMA copolymer.

The value of AN-EMA is 1.07 indicating that the copolymer is richer in AN below this point and above this point richer in EMA. This behaviour also suggests the random distribution of monomers in the copolymer.

**2.6. Solution properties** The weight average and number average molecular weight ( $\bar{M}_w$  and  $\bar{M}_n$ ) values of copolymer for different compositions are given in Table 2. These values increased with the increase in 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.

**Table 2.** Intrinsic viscosities at 25 °C and molecular weight of AN-EMA copolymers.

Copolymer	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	$[\eta]$ dl/g
AN-EMA <sub>1</sub>	1.88	1.20	0.241
AN-EMA <sub>3</sub>	1.91	1.21	0.267
AN-EMA <sub>5</sub>	1.95	1.23	0.291

The 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 molecular weight increased with increase in the AN content Table 2. This may be attributed to the greater reactivity of nitrile, which facilitates propagation in preference to

termination. Solubility parameter values of copolymer determined in different solvents are given in Table 3. 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 AN-EMA is 10.1 (cal/cc)<sup>0.5</sup>.

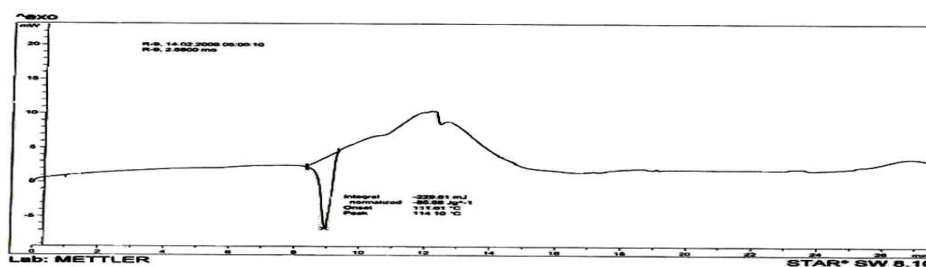
**Table 3.** Intrinsic viscosities of AN-EMA copolymers and their dependence on solubility parameter of solvents at 30 °C.

Solvent	$\delta$ (Cal/cc) <sup>0.5</sup>	$[\eta]$ dl/g AN-EMA	Solvent	$\delta$ (Cal/cc) <sup>0.5</sup>	$[\eta]$ dl/g AN-EMA
Toluene	8.9	0.140	Acetic acid	10.1	0.287
Benzene	9.2	0.164	1,4 Dioxane	10.7	0.221
Chloroform	9.3	0.181	Dichloro acetic acid	11.0	-----
Chloro benzene	9.5	0.213	Dimethyl sulfoxide	12.0	0.151
Dichloro methane	9.7	0.241	Dimethyl formamide	12.1	0.103

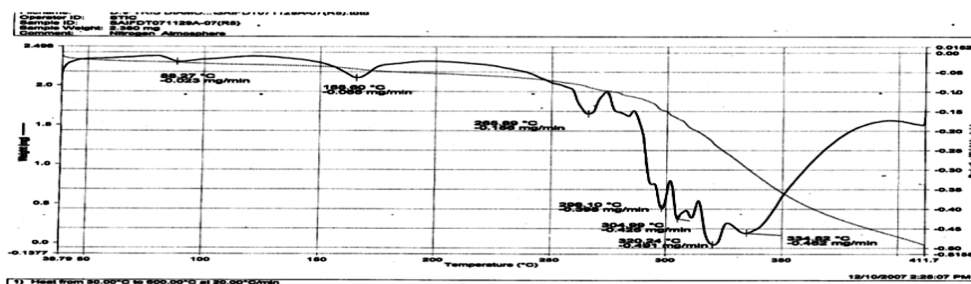
**2.7. Thermal studies**

The differential Scanning Calorimetry thermogram (DSC) is shown in Figure.3. The glass transition temperature (T<sub>g</sub>) values of the copolymers were evaluated from DSC curves. It is observed that T<sub>g</sub> of the copolymer increased with increase in the AN content. When the AN content increases intramolecular interaction increases and the polymer segments become less mobile and thereby T<sub>g</sub> occurs at higher

temperatu re.<sup>12-15</sup> The relative thermal stabilities are evaluated by TGA/DTG thermogram is shown in Figure.4. The comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss of different compositions of AN-EMA are shown in Table.4.



**Figure 3.** DSC thermogram of AN-EMA copolymer.

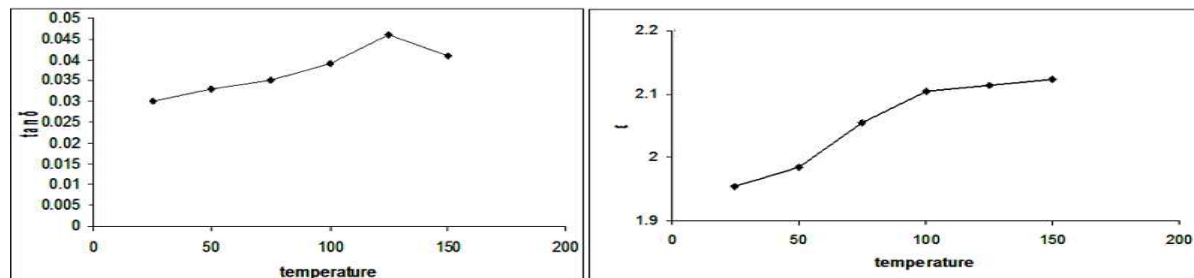


**Figure 4.** TGA/DTG thermogram of AN-EMA copolymer.

**Table 4.** Thermal behavior of AN-EMA copolymers

Copolymer	IDT (°C)	IPDT(°C)	Temperature (°C) at wt. loss			T <sub>g</sub> (°C)
			10%	20%	50%	
AN-EMA-1	225	333	206	281	325	114.10
AN-EMA-2	226	334	207	282	327	-----
AN-EMA-3	228	337	208	284	329	-----
AN-EMA-4	229	338	209	285	331	-----
AN-EMA-5	231	339	210	287	332	115.25

## 2.8. Dielectric Studies

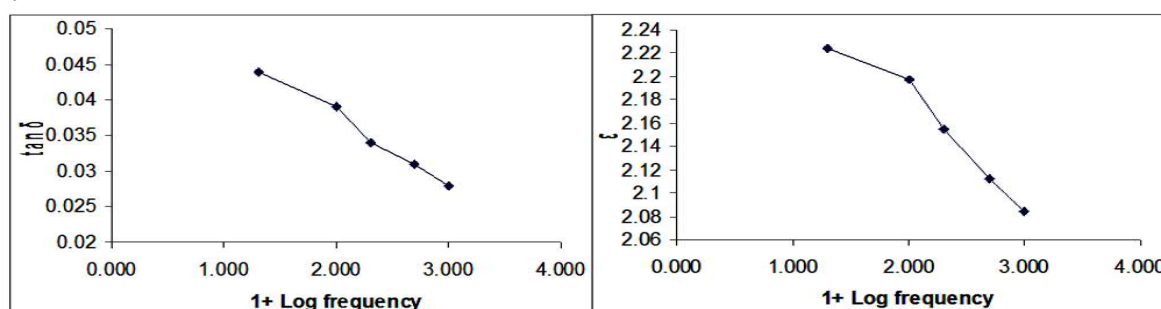


**Figure 5.** The variations of dielectric loss ( $\tan \delta$ ) and dielectric constant ( $\epsilon$ ) with frequency of AN-EMA-1 copolymer.

The variations of dielectric loss ( $\tan \delta$ ) and dielectric constant ( $\epsilon$ ) with frequency and temperature respectively for AN-EMA samples are shown in Figure 5 & 6. Both the dielectric loss ( $\tan \delta$ ) and dielectric constant ( $\epsilon$ ) decreased continuously with increasing frequency. Whereas  $\tan \delta$  and  $\epsilon$  increased with increased temperature. The higher values of dielectric constant at lower frequency are due to larger contribution of space charge polarization which results

in higher value of  $\epsilon$ . The increase of dielectric constant and dielectric loss with temperature is not rapid initially, but it is more pronounced above 100°C (near to the T<sub>g</sub> of the co polymer). The mobility of polymer molecular chains is limited at lower temperatures and due to dipole-dipole interactions their mobility is restricted with increasing temperature around glass transition temperature, increase in  $\epsilon$  can be attributed to increased mobility of polymer segments.<sup>[16-19]</sup>

**Figure 6.** The variations of dielectric loss ( $\tan \delta$ ) and dielectric constant ( $\epsilon$ ) with temperature of AN-EMA-1 copolymer.



3.

## Experimental Section

The chemicals acrylonitrile (AN) (Sigma Aldrich Chemie, Germany) and ethyl methacrylate (EMA) (Sigma Aldrich Chemie, Germany) were purified by washing with 5% solution of sodium hydroxide and distilled water, dried over calcium chloride under reduced pressure. The middle fraction of the distillate was collected and used for copolymerization. Bis (1-oxododecyl) peroxide (Sigma Aldrich Chemie, Germany) initiator was used as such. The copolymerization was carried out in DMF (S.D. Fine Chem. Mumbai, India) solvent. All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvent and initiator. The tubes were sealed in an atmosphere of nitrogen and introduced into

the thermostat at  $60 \pm 1^\circ\text{C}$  and the polymerization continued for 90 min. The copolymer is isolated by pouring polymerization mixture into large quantity of water. Subsequently it 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 total monomers concentration was maintained as 1.5 M, while the feed ratio was varied. The data of composition of feed and copolymers are presented in Table 5. The Infrared spectra (IR) of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in the wave number range 4000 to  $400\text{ cm}^{-1}$  with KBr pellets. The  $^1\text{H}$ -NMR spectra of the

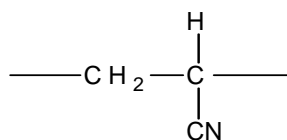
**Table 5.** Copolymerization data of AN with EMA.

Copolymer system	Mole fraction in the feed		Intensity of methyl protons of AN (2H)(M <sub>1</sub> )	Intensity of (-OCH <sub>2</sub> ) - protons of EMA (2H) (M <sub>2</sub> )	Copolymer composition	
	AN (M <sub>1</sub> )	EMA (M <sub>2</sub> )			AN (m <sub>1</sub> )	EMA (m <sub>2</sub> )
AN-EMA-1	0.80	0.70	5.26	3.62	0.592	0.407
AN-EMA-2	0.90	0.60	3.15	1.84	0.631	0.368
AN-EMA-3	1.00	0.50	2.37	1.16	0.670	0.329
AN-EMA-4	1.10	0.40	1.26	0.49	0.720	0.280
AN-EMA-5	1.20	0.30	0.33	0.10	0.767	0.232

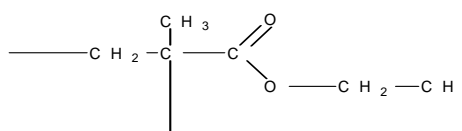
samples were recorded using CDCl<sub>3</sub> as solvent on Avance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by <sup>1</sup>H-NMR spectra. The thermo gravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of 15 °C/min. Glass Transition temperature (T<sub>g</sub>) of the copolymers was determined using a Mettler Toledo

822E thermal analyzer at a heating rate of 15 °C/min. T<sub>g</sub> values of the copolymers obtained from the DSC curves. 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 different solvents at 30 ± 0.1°C.

The structures of monomer unit can be represented as follows:



Acrylonitrile (AN)



Ethyl methacrylate (EMA)

#### 4. Conclusion

In the present work the copolymer of AN with EMA has been synthesized using a bis (1-oxododecyl) peroxide as initiator in DMF. The copolymer structure elucidate by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The Reactivity ratio of the copolymer suggested the formation of random copolymers. The copolymer – solvent interactions are established by intrinsic viscosities and solubility parameter. Thermal stability of the polymer has been evaluated through thermal properties like T<sub>g</sub>, IDT and IPDT. The number of AN units in copolymer increased with increasing concentration of AN. Hence EMA acts as a retarder in the copolymerization. The increased AN content increased intramolecular interaction and thereby polymer segments become less mobile. Hence T<sub>g</sub> occurs at higher temperature with increasing AN content in the polymer.

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