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## SOLUTION AND THERMAL STUDIES OF ACRYLAMIDE COPOLYMERS INITIATED BY BIS (1-OXODODECYL) PEROXIDE

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### ABSTRACT

Solution properties of low-charge density acrylamide (AA) and ethyl methacrylate (EMA) copolymer was prepared by free radical polymerization using bis (1-oxododecyl) peroxide as initiator in dimethyl formamide (DMF) at  $60 \pm 1^\circ\text{C}$ . The chemical structure is determined by  $^1\text{H-NMR}$  spectroscopy. The molecular weights of the polymers were determined by gel permeation chromatography, which increase with the increase of the AA content. The solubility parameters were determined with the viscometric method. The polymer was characterized thermogravimetric analysis (TGA).

**KEY WORDS:** Acrylamide / gel permeation chromatography and Thermogravimetric analysis.

### 1.INTRODUCTION

Polymers are generally used in a wide range of applications often for their low cost, light weight and mechanical properties or for the three characteristics combined. A few of the limitations of polyacrylamide have been overcome by the fusion with acrylates through copolymerization technique (Ariyamuthu, 2009; Ramesh Babu, 2006; Begam, 2004). The combination of durability and versatility and the ability to tailor molecules relatively easily have made acrylic and methacrylic esters prime candidates for diverse applications. The uses of acrylics in textile finishing and acrylic ester emulsions in leather finishing are well documented. Introduction of ethyl methacrylate into various copolymers appears to modify and improve the properties of a number of copolymers (Mihailo and Danica, 2007; Kadir Demirelli, 2006; Feroz, 2009). In this article, we reported the copolymerization of acrylamide with ethyl methacrylate and characterization by solution and thermal studies.

### 2.MATERIALS AND METHOD

AA (Aldrich), EMA (Aldrich) and bis (1-oxododecyl) peroxide were used as directly for copolymerization. Solvents are used after distillation. 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  $60 \pm 1^\circ\text{C}$  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  $2.5 \text{ g/dm}^3$  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.

### 3.RESULTS AND DISCUSSION

**$^1\text{H-NMR}$  Spectroscopy:**  $^1\text{H-NMR}$  spectra of the samples were recorded using  $\text{DMSO-d}_6$  as solvent for AA copolymer on an Avance 300 MHz NMR spectrometer with TMS as internal reference shown in Figure-1. In the spectrum,  $-\text{OCH}_2$  protons of EMA unit appears at 4.0 ppm, methylene ( $-\text{CH}_2$ ) protons of EMA unit appears at 1.2 ppm, methylene ( $-\text{CH}_2$ ) protons of AA unit appears at 2.5 ppm, methine ( $-\text{CH}$ ) protons of AA unit appears at 1.7-1.8 ppm,  $\alpha\text{-CH}_3$  protons of EMA appears at 0.8-1.0 ppm, end  $-\text{CH}_3$  protons of EMA appears at 2.1 ppm and  $-\text{NH}_2$  protons appears at 6.7-7.2 ppm.

**Molecular weight determination:** Molecular weight of copolymer determined by using gel permeation chromatography with refractive index detector and polystyrene column and 100% THF as eluent. The weight average and number average molecular weights ( $\overline{M}_w$  and  $\overline{M}_n$ ) values of copolymer for different compositions are given in Table-2. The value of polydispersity more than 1 indicates the monomers are polydisperse in solvent.

**Solution properties:** The intrinsic viscosity of copolymers was measured with an Ubbelohde Viscometer in different solvents at  $30 \pm 0.1^\circ\text{C}$ . 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 AA content Table-2. This may be attributed to the greater reactivity of ethylmethacrylate content, which facilitates propagation in preference to termination. Solubility parameter values of the copolymer determined in different solvents are presented in Table-3. Solvents which cover a range of solubility parameter from 8.9 to  $12.1 \text{ (cal/cc)}^{0.5}$  have been selected. The solubility parameter value of AA-EMA is  $10.6 \text{ (cal/cc)}^{0.5}$ .

**Thermogravimetric analysis:** Thermogravimetric analysis is found to be a very useful method to assess the thermal stability of a copolymer (Singru, 2008). The thermogram recorded shown in Figure-2. The relative thermal stabilities

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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. To obtain a comparative picture of relative thermal stability of the copolymer their IDT, IPDT and DT values are presented in Table-4.

## 4. CONCLUSION

The copolymer of AA with EMA has been synthesized using bis (1-oxododecyl) peroxide as initiator in DMF. The copolymer is characterized by <sup>1</sup>H-NMR. Intrinsic viscosities and solubility parameter was determined to establish interactions in polymer solutions. Polydispersity value is less indicates the polymer shows high mechanical strength. Thermal properties like IDT and IPDT have been evaluated to find the thermal stability of the polymer.

**Table 1: Molar ratio of monomers taken for synthesis of copolymer**

Copolymer system	Mole fraction in the feed	
	AA	EMA
AA-EMA <sub>1</sub>	0.80	0.70
AA-EMA <sub>2</sub>	0.85	0.65
AA-EMA <sub>3</sub>	0.90	0.60
AA-EMA <sub>4</sub>	0.95	0.55
AA-EMA <sub>5</sub>	1.00	0.50

**Table- 2 Molecular weights of the AA-EMA copolymers for various feed ratios**

Copolymer	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	$\bar{M}_w / \bar{M}_n$	$[\eta]$ dl/g
AA-EMA <sub>1</sub>	3.216	2.178	1.4765	0.328
AA-EMA <sub>2</sub>	3.221	2.181	1.4768	0.335
AA-EMA <sub>3</sub>	3.228	2.184	1.4780	0.339

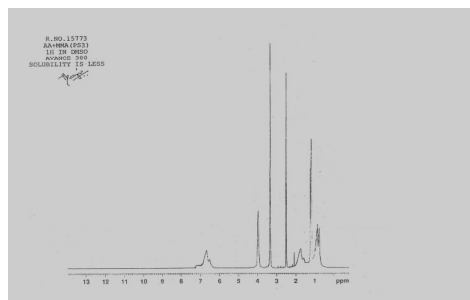
**Table- 3 Intrinsic viscosities of AA-EMA copolymers and their dependence on solubility parameter of solvents at 30° C**

S.No	Solvent	$\delta$ (Cal/cc) <sup>0.5</sup>	$[\eta]$ dl/g
1	Toluene	8.9	0.164
2	THF	9.1	0.201
3	Chloro benzene	9.5	0.292
4	Acetic acid	10.1	0.311
5	Diethyl formamide	10.6	0.402
6	Dichloro acetic acid	11.0	0.199
7	Dimethyl sulfoxide	12.0	0.165
8	Dimethyl formamide	12.1	0.132

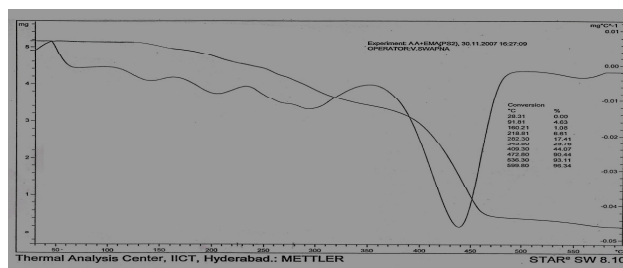
**Table 4: Thermal behavior of AA-EMA copolymers**

Copolymer	IDT (°C)	IPDT(°C)	Temperature (°C) at wt. loss		
			10%	20%	50%
AA-EMA <sub>1</sub>	160.21	378.62	235.71	304.32	419.46
AA-EMA <sub>2</sub>	161.42	380.66	236.58	305.79	420.95
AA-EMA <sub>3</sub>	162.95	384.92	237.36	306.34	421.36
AA-EMA <sub>4</sub>	163.65	385.52	237.95	307.12	423.47
AA-EMA <sub>5</sub>	164.25	385.87	238.12	308.60	425.44

**Figure- 1: <sup>1</sup>H-NMR Spectrum of AA-EMA**



**Figure- 2: TGA/DTG curve of AA-EMA**



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