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Synthesis, Characterization, and Reactivity Ratios of Bis (1-Oxododecyl) Peroxide Initiated Methacrylonitrile Copolymers

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Abstract: ***Copolymer of Methacrylonitrile (MAN) with ethyl methacrylate (EMA) was synthesized by free radical polymerization method using bis (1-oxododecyl) peroxide as initiator in dimethylformamide (DMF) solvent at 60 ± 1^{0}C. The copolymer samples were characterized by Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, and ^{13}C nuclear magnetic resonance (^{13}C-NMR). The monomer reactivity ratios were computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The computed reactivity ratio values confirm the formation of random copolymers. The formation of random copolymer was also supported by azeotropic composition evaluation. The number of MAN units in copolymer increased with increasing concentration of MAN. Hence EMA acts as a retarder in the copolymerization.***

Keywords: Ethyl methacrylate, Co-polymer, Methacrylonitrile, Reactivity ratios

1. Introduction

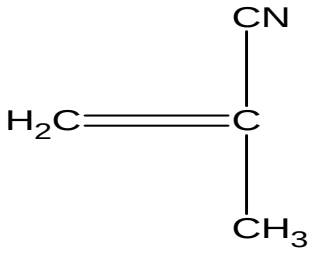
Copolymers are used in a wide range of applications often for their low cost, light weight, and good mechanical properties or for combination of these characteristics. A few of the limitations of poly acrylates have been overcome by the copolymerization with nitriles [1-2]. Nitriles and alkyl acrylic esters are prime candidates for diverse applications. Introduction of ethyl methacrylate into various copolymers appears to modify and improve the properties of several copolymers. The ^{1}H-NMR spectroscopic analysis has been used as a powerful tool for the evaluation of copolymer composition [3-6]. In this article we report the synthesis, structural characterization, reactivity ratios and Azeotropic composition of (MAN–EMA) copolymer.

2. Experimental

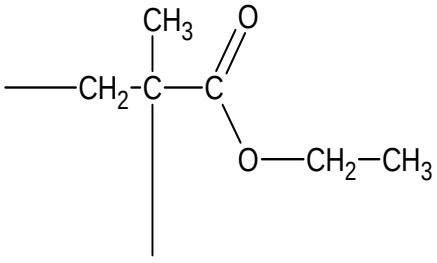
Methacrylonitrile (MAN) (Sigma Aldrich Chemie, Germany) and ethyl methacrylate (EMA) (Sigma Aldrich Chemie, Germany) were purified by washing with 5% solution of sodium hydroxide and distilled water, dried over calcium chloride under reduced pressure. The middle fraction of the distillate was collected 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 ± 1^{0}C and the polymerization continued for 90 min.

The copolymer is isolated by pouring polymerization mixture into large quantity of distilled 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 1.

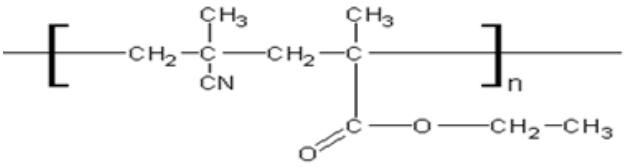
Infrared spectra (IR) of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in the wave number range 4000 to 400 cm^{-1} with KBr pellets. The ^{1}H -NMR spectra of the samples were recorded using $CDCl_3$ as solvent on Avance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by ^{1}H-NMR spectra. 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 Ubbelhode Viscometer in different solvents at 30 ± 0.1^{o}C. The structures of monomer and polymer units are represented as follows:



Methacrylonitrile (MAN)



Ethyl methacrylate (EMA)



MAN-EMA Polymer Repeating Unit

3. Results and Discussion

3.1. IR Spectroscopy

The IR spectrum of the copolymer of MAN – EMA is shown in Figure.1. Appearance of Strong absorption bands at 2853.36, 1736.50, 2243.64, 1453.22 and 2925.32 cm^{-1} correspond to methylene ($-CH_2$) stretching, >C=O stretching in ester, cyano (-CN), ($-OCH_2-$) group and methyl ($-CH_3$) stretching vibrations respectively. The appearance of absorption bands corresponding to ester (>C =O), $-OCH_2$ and –CN group and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-EMA copolymer.

3.2. ^{1}H-NMR Spectroscopy and Determination of copolymer composition

The ^{1}H-NMR Spectrum of MAN-EMA is shown in Figure 2. The distribution of protons in the two units is an important means of distinguishing the monomers in the chain. In this spectrum, methyl ($-CH_3$) protons of EMA unit appears at 1.2-1.4 ppm, methylene ($-CH_2$) protons of EMA unit and MAN unit appears at 2.4 ppm, methyl ($-CH_3$) protons of MAN unit appears at 1.6-1.8 ppm. The ($-CH_3$) group and $-OCH_2-$ group protons of EMA appear at 2.0-2.1 ppm and 4.1 to 4.2 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 that the $-CH_2$ group of AN unit corresponds to two protons, $-OCH_2$ group of EMA corresponds to two protons.

%EMA in MAN = ((^{1}H-OCH_2)/2) / ((^{1}H-OCH_2)/2 +(^{1}H- CH_2)/2)

…….. (1)

3.3. ^{13}C- NMR Spectroscopy

The ^{13}C-NMR spectrum of MAN-EMA is shown in Figure.3. In this spectrum the peak at δ 177 is for carbonyl carbon of EMA units and the nitrile carbon of MAN unit at δ 122. The peak at δ 73 accounts for the solvent $CDCl_3$. The other signal at δ 61 is due to $-OCH_2-$ carbon of EMA unit. The resonance at δ 40 represent quaternary carbon, the resonance at δ 22 and 20 are due to C-CH_3 of MAN, and methyl group of EMA unit respectively and methylene ($-CH_2$) carbon at δ 57. The methyl carbon ($-CH_3$) of EMA unit signal appears at δ 12. This confirms the formation of copolymer.

3.4. Reactivity ratios

The copolymer composition data was used for the evaluation of reactivity ratios of the MAN-EMA copolymer by Fineman–Ross [7] and Kelen–Tudos [8] methods. The respectively plots are shown in figure 4 (a) and (b).

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

Where

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

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

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_1r_2 whose value less than unity suggests the formation of random copolymer. The rate of polymerization depends on the value of 1/r that gives a measure of the reactivity of the ethyl methacrylate towards the MAN radical. The value of $1/r_1$ for MAN-EMA copolymer is 1.600.

3.5. Azeotropic Composition

Azeotropic composition of copolymer is determined from the plots of mole fraction of monomer in the copolymer composition (m_1) versus monomer in the feed (M_1) as given in Table 1. The plot is shown Figure-5 indicate that the azeotropic compositions of the copolymer system and conveys the distribution of monomeric units are random. The azeotropic composition was determined by the following equation [9-11].

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

The value of MAN-EMA is 0.970 indicating that the copolymer is richer in MAN below this point and above this point richer in EMA. This behaviour also suggests the random distribution of monomers in the copolymer.

4. Conclusion

In the present work the copolymer of MAN with EMA has been synthesized using a bis (1-oxododecyl) peroxide as initiator in DMF. The co polymer structure elucidate by FTIR, ^{1}H-NMR and ^{13}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. The number of MAN units in copolymer increased with increasing concentration of MAN. Hence EMA acts as a retarder in the copolymerization.

Acknowledgement

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Table 1: Copolymerization data of MAN with EMA

Copolymer system	Mole fraction in the feed		Intensity of methyl protons of MAN (2H)(M_1)	Intensity of (-OCH_2) - protons of EMA (2H) (M_2)	Copolymer composition	
	MAN (M_1)	EMA (M_2)			MAN (m_1)	EMA (m_2)
MAN-EMA-1	0.80	0.70	2.51	1.40	0.641	0.358
MAN-EMA-2	0.90	0.60	2.30	1.12	0.672	0.327
MAN-EMA-3	1.00	0.50	2.40	1.08	0.689	0.310
MAN-EMA-4	1.10	0.40	1.58	0.50	0.759	0.240
MAN-EMA-5	1.20	0.30	3.19	0.71	0.817	0.182

Table 2: Parameters of equations (2) and (3) for MAN-EMA copolymer (α = 1.600)

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	1.792	0.505	0.728	0.215	0.310
2.	1.50	2.053	0.769	1.095	0.286	0.405
3.	2.00	2.222	1.100	1.800	0.323	0.529
4.	2.75	3.160	1.879	2.393	0.471	0.598
5.	4.00	4.492	3.109	3.561	0.600	0.689

Table 3: Intrinsic viscosities molecular weight of MAN-EMA copolymers

Copolymer	$\overline{M}_w$ x 10^4	$\overline{M}_n$ x 10^4	[η] dl/g
$MAN\text{-}EMA_1$	1.88	1.17	0.156
$MAN\text{-}EMA_3$	1.90	1.21	0.172
$MAN\text{-}EMA_5$	1.94	1.23	0.203

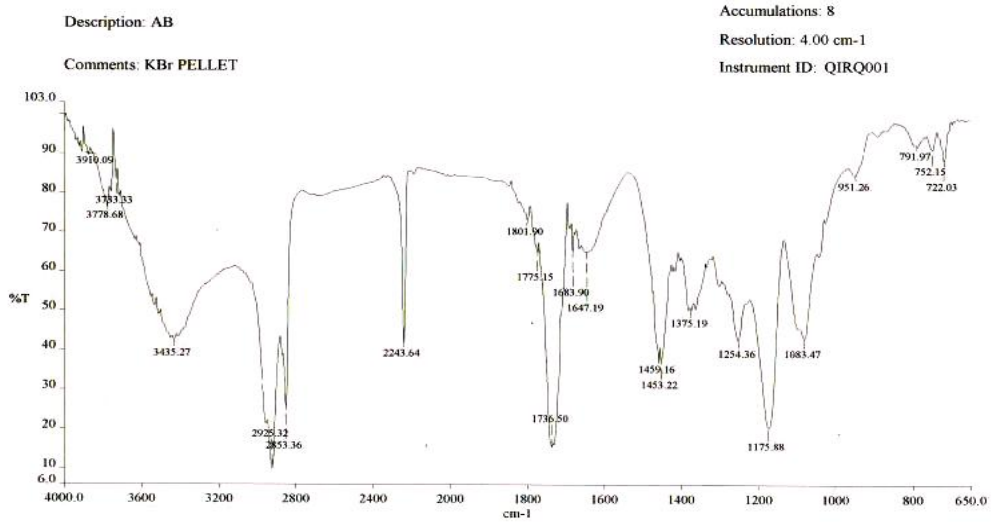


Figure 1: IR Spectrum of MAN-EMA copolymer

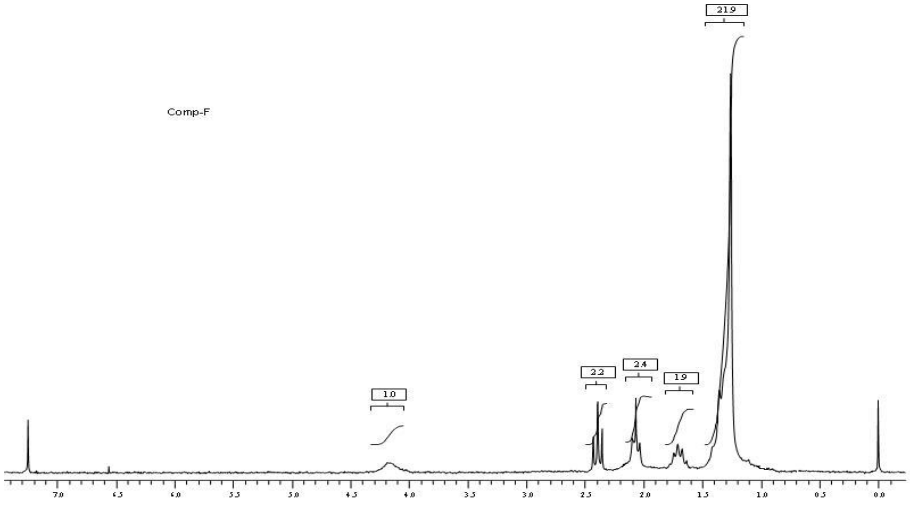


Figure 2: ^{1}H-NMR Spectrum of MAN-EMA

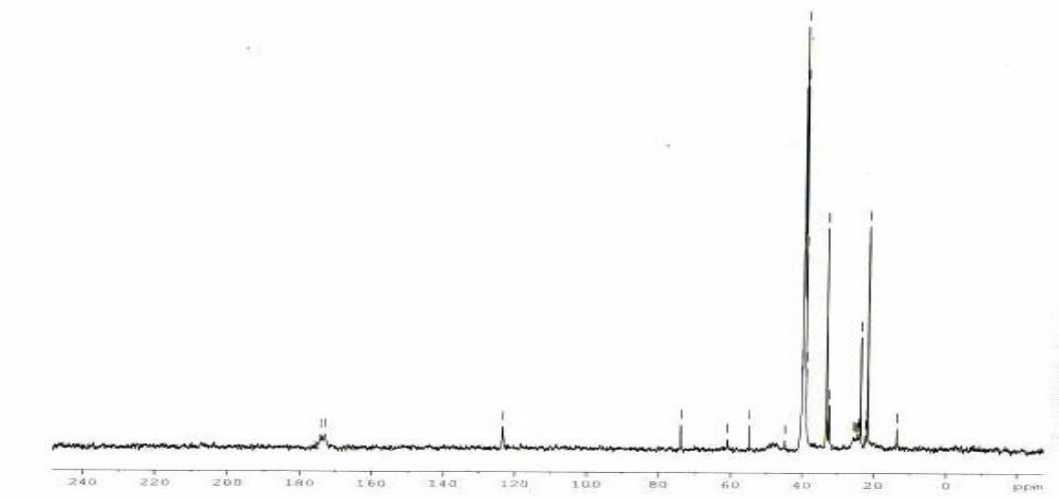
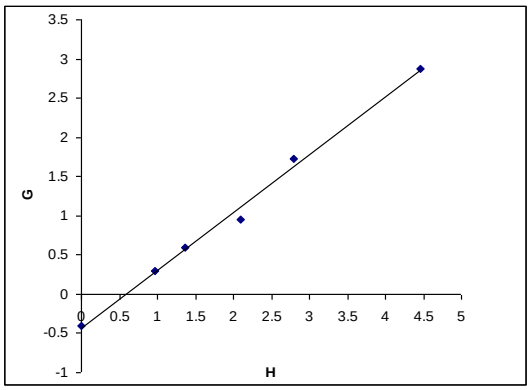


Figure 3: ^{13}C-NMR Spectrum of MAN-EMA copolymer



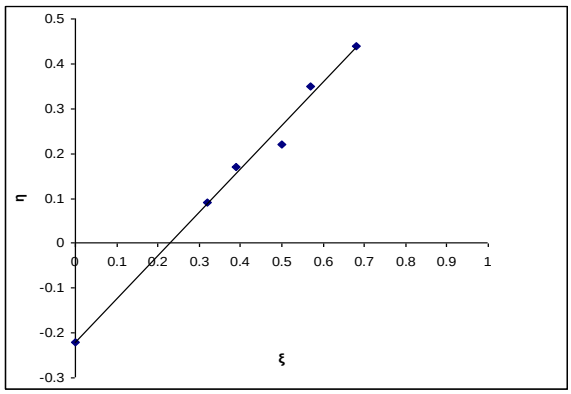


Figure 4: 4(a) F-R Plot and Figure.4 (b) K-T plot

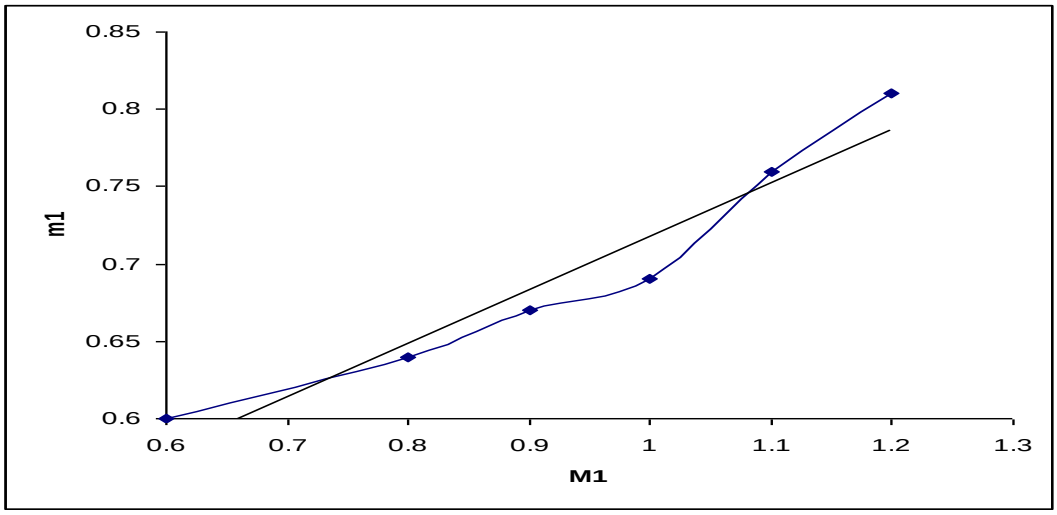


Figure 5: Azeotropic composition of MAN-EMA copolymer