Solution and Dielectric Properties of BIS (1-Oxododecyl) Peroxide Initiated Copolymers of Acrylonitrile with Methylmethacrylate

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Abstract: Copolymer of acrylonitrile (AN) with Methyl methacrylate (MMA) was synthesized by free radical polymerization method using bis (1-oxododecyl) peroxide as initiator in dimethylformamide (DMF) solvent at $60 \pm 1^{\circ}$ C. The copolymer samples were characterized by Fourier transform infrared spectroscopy (FTIR). 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. And the di-electrical properties of the copolymer were also studied.

Keywords: Methylmethacrylate, acrylonitrile, Solution properties, Di-electrical properties

1. Introduction

Introduction of methylmethacrylate (MMA) into various copolymers appears to modify and improve the properties of several copolymers [1-4]. The solution properties and dielectric properties are important for understating the behavior of copolymers. The NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition [5-8]. In this article we reported the synthesis, characterization, solution, and di-electrical properties of the copolymers AN -MMA copolymers.

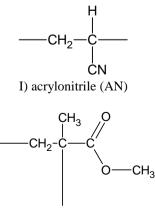
2. Experimental

AN (Aldrich) and MMA (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. Bis (1-oxododecyl) peroxide (Sigma Aldrich Chemie, used as Germany) initiator was 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 $60 \pm 1^{\circ}C$ and the polymerization continued for 90 min. The copolymer is isolated by pouring the 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, the data of composition of feed and copolymers are presented in Table 1.

Con alarman anatom	Mole fraction in the feed	
Copolymer system	$\mathbf{AN}(\mathbf{M}_1)$	MMA (M ₂)
AN-MMA ₁	0.80	0.70
AN-MMA ₂	0.93	0.56
AN-MMA ₃	1.08	0.42
AN-MMA ₄	1.12	0.38
AN-MMA ₅	1.20	0.30

Table 1: Copolymerization data of AN with MMA

The monomer unit structures are represented as follows:



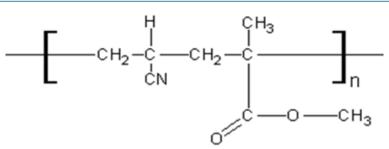
II) methylmethacrylate (MMA) Volume 11 Issue 7, July 2022

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International Journal of Science and Research (IJSR) ISSN: 2319-7064

SJIF (2022): 7.942



AN-MMA Copolymer repeating unit

3. Results and Discussion

3.1. 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 MMA (AN-co-MMA) is shown in Figure-1 showing the characteristic bands of both the monomer units. Appearance of Strong absorption bands at

2854.22, 1731.04, 2242.46, 1452.98 and 2926.60 cm⁻¹ corresponds to methine (-CH) stretching, >C=O stretching in ester, cyano (-CN), methoxy group (-OCH₃), methylene (-CH₂) and methyl (-CH₃) stretching vibrations respectively. The appearance of absorption bands corresponding to >C=O, $-OCH_3$ and -CN groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of AN-MMA copolymers.

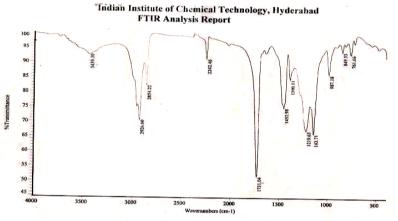


Figure 1: FTIR Spectrum of AN-MMA

3.2.2.¹³ C- NMR Spectroscopy

¹³C-NMR spectrum of AN-MMA copolymer is shown in figure-2. In this spectrum the peak at δ 175-177 accounts for carbonyl carbon of MMA units. The nitrile carbon at δ 122 and methine carbon (-CH) of AN unit appears at δ 30.

The peak at δ 77-79 accounts for the solvent CDCl₃. The other signals at δ 51-54 is due to methoxy carbon (-OCH₃) of MMA unit. The resonance at δ 31 represents quaternary carbon, the resonance at δ 16-25 are due to C-CH₃ carbon and methylene (-CH₂) carbon at δ 44-47 of MMA unit. This confirms the formation of copolymer.

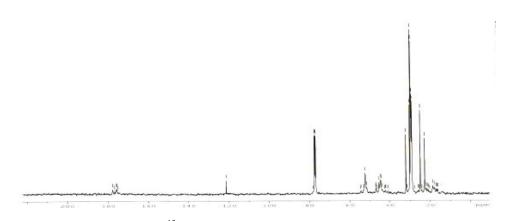


Figure 2: ¹³C-NMR spectrum of AN-EMA copolymer

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3.3. 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 Ubbelhode Viscometer in toluene at $30 \pm 0.1^{\circ}$ C. 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. 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 2. This may be attributed to the greater reactivity of nitrile radical which facilitates propagation in preference to termination. Thus, it can be inferred that with increasing in the content of AN molecular weight of the copolymer increases. 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 (cal/cc)^{0.5} have been selected. The solubility parameter value of AN-MMA is 9.7 (cal/cc).^{0.5}

Copolymer	$\overline{\mathrm{M}}$ w x 10 ⁻⁵	$\overline{M}_{n} \ge 10^{-5}$	[η] dl/g
AN-MMA ₁	1.8712	1.1978	0.226
AN-MMA ₂	1.8872	1.2061	0.233
AN-MMA ₃	1.9327	1.2288	0.248

S.NO Solvent		$\delta (Cal/cc)^{0.5}$	[η]dl/g
5.10	Sorvent	0 (Cal/cc)	AN-MMA
1	Toluene	8.9	0.120
2	Benzene	9.2	0.162
3	Chloroform	9.3	0.184
4	Chloro benzene	9.5	0.199
5	Dichloro methane	9.7	0.254
6	Acetic acid	10.1	0.221
7	Diethyl formamide	10.6	-
8	1,4 Dioxane	10.7	0.195
9	Dichloro acetic acid	11.0	-
10	Dimethyl sulfoxide	12.0	0.131
11	Dimethyl formamide	12.1	0.104

Table 3: Intrinsic viscosities of AN-MMA copolymers and their dependence on solubility parameter of solvents at 30 °C

3.4. Di-electric properties

A Capacitance bridge model GR 1620(WG) is used to measure the dielectric constant (ϵ) and dielectric loss (tan δ) of the AN-MMA copolymers. All samples are annealed prior to use for the measurement. The results of variation of (ϵ) and tan δ at constant frequency of 20 KHz against temperature for AN-MMA are given in Table 4-6. The results shows that the ϵ and tan δ are unaffected by temperatures up to 125°C. Beyond that region, both ϵ and

tan δ increases. A peak due to relaxation is observed in tan δ , known as α relaxation, at about 120°C, in the rubbery state of the polymer [11-12] This temperature is higher than T_g for the polymer obtained by a DSC method is 114.16°C At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions [13-14]. As the temperature is raised, more and more dipole groups are released and the mobility of polymers segment increases.

DOI: 10.21275/SR22701005040

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International Journal of Science and Research (IJSR) ISSN: 2319-7064 SJIF (2022): 7.942

Table 4: Variation of di-electric constant with frequency for AN-MMA Copolymer				
Frequency (f) (KHz)	1+Log frequency	di-electric constant (ɛ)		
		AN-MMA ₁	AN-MMA ₅	
100	3.000	2.458	2.156	
50	2.699	2.511	2.195	
20	2.301	2.634	2.264	
10	2.000	2.681	2.544	
2	1.301	2.715	2.647	

Table 5: Variation of di-electric loss (tan δ) with frequency for AN-MMA Copolymer

Frequency 1 - Log free	1 Log frequency	di-electri	ric loss (tan δ)	
(f) (KHz)	1+Log frequency	AN-MMA ₁	AN-MMA ₅	
100	3.000	0.031	0.032	
50	2.699	0.034	0.035	
20	2.301	0.035	0.036	
10	2.000	0.039	0.044	
2	1.301	0.042	0.047	

Table 6: Variation of dielectric constant and dielectric loss with temperature for AN-MMA copolymer at 20 KHz

Tomporatura	AN-MMA	
Temperature	di-electric constant (ɛ)	di-electric loss (tan δ)
25	1.841	0.028
50	1.912	0.029
75	1.954	0.031
100	2.054	0.036
125	2.116	0.042
150	2.227	0.035

4. Conclusion

In the present work the copolymer of AN with MMA has been synthesized using a bis (1-oxododecyl) peroxide as initiator in DMF. The co polymer structure elucidate by FTIR, and ¹³C-NMR spectroscopy. 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. Di-electric properties of copolymer are studied to find the electrical stability.

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Volume 11 Issue 7, July 2022

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