

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, $>\text{C}=\text{O}$ stretching in ester, cyano (-CN), methoxy group (-OCH₃), methylene (-CH₂) and methyl (-CH₃) stretching vibrations respectively. The appearance of absorption bands corresponding to $>\text{C}=\text{O}$, -OCH₃ and -CN groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of AN-MMA copolymers.

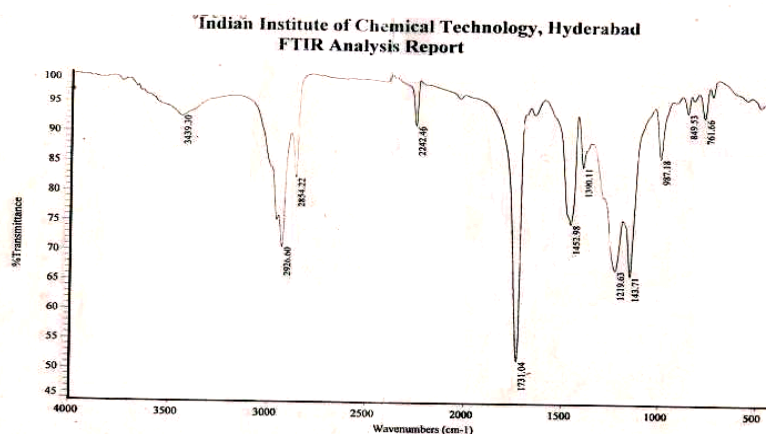
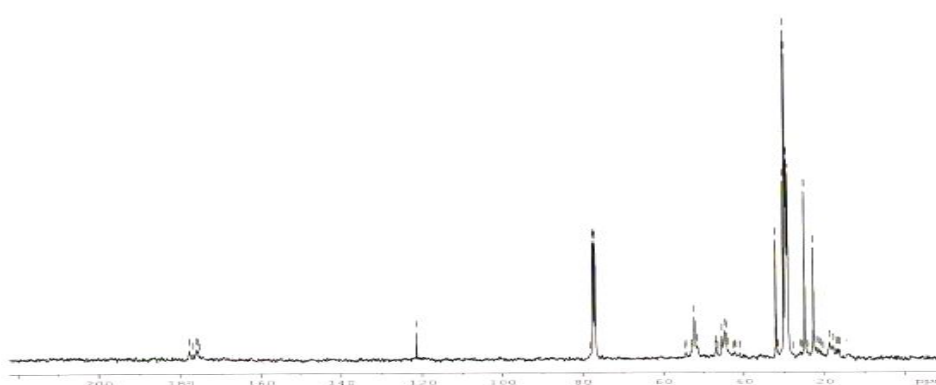


Figure 1: FTIR Spectrum of AN-MMA

3.2.2. ¹³C- 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

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 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 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 $12.1 \text{ (cal/cc)}^{0.5}$ have been selected. The solubility parameter value of AN-MMA is $9.7 \text{ (cal/cc)}^{0.5}$.

Table 2: Intrinsic viscosities at 25°C and molecular weight of AN-MMA copolymers

Copolymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$[\eta] \text{ dl/g}$
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

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

S.NO	Solvent	$\delta \text{ (Cal/cc)}^{0.5}$	$[\eta] \text{ dl/g}$ 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

3.4. 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-MMA 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-MMA are given in Table 4-6. 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 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.

Table 4: Variation of di-electric constant with frequency for AN-MMA Copolymer

Frequency (f) (KHz)	1+Log frequency	di-electric constant (ϵ)	
		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 ($\tan \delta$) with frequency for AN-MMA Copolymer

Frequency (f) (KHz)	1+Log frequency	di-electric loss ($\tan \delta$)	
		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

Temperature	AN-MMA	
	di-electric constant (ϵ)	di-electric loss ($\tan \delta$)
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.

References

- [1] Mihailo S. Jacovic, Danica Milosevic, Journal of Polymer Science: Polymer Symposia, 2007; 42: 1443.
- [2] Kadir Demirelli, Adnan Kurt, M. Fatih Coskun and Mehmet Coskun, Journal of Macromolecular Science, Part A, 2006; 43(3): 573.
- [3] Brar A.S. and Tripta Saini, J Polym Sci Part A: Polym Chem 2006; 44: 1975.
- [4] Hossein S. Hosseini and Anouchiravan Ghavami, Iranian polymer journal 2005; 14 (7): 617.
- [5] Tacx JCJF, Vander Velden GPM and German AL, Polymer 1998; 29:1675.
- [6] Ismail Mathakiya, Rakshit AK, Rao PVC, International Journal of Polymer Analysis and Characterization, 2003; 8 (5): 339.
- [7] Balaji R and Nanjundan S, J. Macromol. Sci. Chem 1998; A 35 (9):1527.
- [8] Balaji R and Nanjundan S, Eur. Polym. J 1999; 35: 1133.
- [9] Billmeyer FW, Textbook of polymer science, 2nd ed, John Wiley & Sons, Inc, Tokyo, Japan, 1982.

- [10] Odian, George, Principles of Polymerization, Wiley Interscience, 2nd ed, New York. 1981: 81.
- [11] Adam A, Kolloid Zeitschrift Zeitschrift Polym 1962; 180: 11.
- [12] Tanaka A and Ishida Y, J. Phys. Soc. Japan 1962; 15: 6.
- [13] Gupta A K, Singhal RP and Agarwal AK, Polymer 1981; 22: 285.
- [14] Srilatha T and Raghunath Rao P, Asian J.Chem 2003; 15: 241