

Reactivity ratios determination of methacrylonitrile with isobornyl methacrylate by ¹H NMR spectroscopy

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Accepted : March, 2009

ABSTRACT

Copolymer of Methacrylonitrile (MAN) with Isobornyl methacrylate (IBM) has been studied by free radical polymerization using 1,1' azo bis (cyclohexanecarbonitrile) (VAZO) as initiator in Dimethyl formamide (DMF) at 60±1^oC. The monomer reactivity ratio was computed by both Fineman–Ross (F-R) and Kelen–Tudos (K-T) methods. The reactivity ratio values suggested the formation of random copolymers which has been supported by the azeotropic composition evaluation. The mean sequence length (\bar{n}) and probabilities (p) in the formation of various structurally units were evaluated. The molecular weights of the polymers were determined by gel permeation chromatography and they increase with increasing MAN content. The solubility parameters were determined with viscometric method. The glass transition temperature (T_g) of the copolymers were determined by differential scanning calorimetry (DSC). Thermo gravimetric analysis (TGA) of the copolymer was studied. The dielectric properties of the copolymer like the dielectric constant and dielectric loss were studied. The results have been compared with methacrylonitrile and isobornyl acrylate (MAN-IBA) system.

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Key words : Methacrylonitrile, Isobornyl methacrylate, Copolymerization, Reactivity ratios, Thermal and Dielectric properties

Introduction of IBM into various copolymers seem to modify and improve the properties of a number of copolymers^{1,2}. The estimation of copolymer composition and determination of the reactivity ratios are important for making copolymer with required-physico chemical properties. The H NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition³⁻⁶. In this paper, the synthesis, characterization, reactivity ratios, solution properties, thermal and dielectric properties of the copolymers of IBM with MAN have been described.

MATERIALS AND METHODS

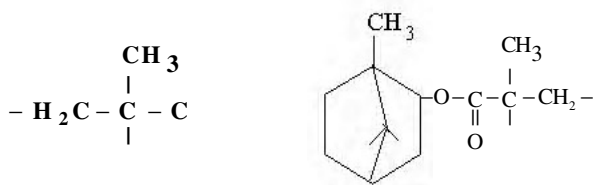
MAN (Aldrich) and IBM (Lancaster) were purified by washing with 5% solution of sodium hydroxide and distilled water. Then they were dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate was collected and used for

copolymerization. VAZO was crystallized from methanol. The solvent used in copolymerization was DMF (reagent grade) and purified by distillation before use. All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvents and initiator. The tubes were then sealed in an atmosphere of nitrogen and then they were introduced into the thermostat at 60 ± 1^oC for 90 minutes to get less than 10% conversion. After that the polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered and washed thoroughly with water followed by ether and hexane. Pure sample was then dried under vacuum. Different samples were prepared by changing the initial monomer feed. The initiator was used at 2.5 gr/ lit 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 given in Table 1.

Table 1 : Copolymerization data of MAN with IBM

Copolymer system	Mole fraction in the feed		Intensity of Methyl protons (3H)(M ₁)	Intensity of isobornyl methyl protons (9H) (M ₂)	Copolymer composition	
	MAN (M ₁)	IBM (M ₂)			MAN (m ₁)	IBM (m ₂)
MAN-IBM ₁	0.600	0.400	35.84	62.63	0.636	0.364
MAN-IBM ₂	0.666	0.333	37.45	79.23	0.679	0.321
MAN-IBM ₃	0.734	0.266	33.88	81.50	0.723	0.277
MAN-IBM ₄	0.800	0.200	26.14	96.60	0.787	0.215
MANIBM ₅	0.867	0.133	17.02	98.78	0.853	0.147

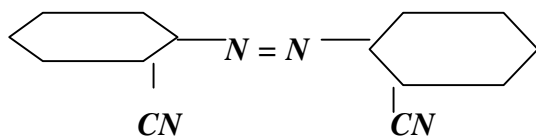
The monomer unit structures are represented as follows :



Methacrylonitrile (MAN)

Isobornylmethacrylate (IBM)

Structure of initiator:



1, 1' azo bis (cyclohexanecarbonitrile) (VAZO)

IR Spectroscopy:

Infrared spectra of the samples were recorded on a Perkin-Elmer model Bx IR spectrophotometer in 4000 to 400 cm⁻¹ range with KBr pellets. The IR spectrum of copolymer of MAN and IBM (MAN-Co-IBM) is given in Fig. 1 showing the characteristic bands of the both the monomer units. Appearance of strong absorption bands at 2950, 1716, 2241 and 1392 cm⁻¹ correspond to methylene (-CH) stretching, >C=O stretching in ester and cyano (-CN) and methyl (-CH₃) stretching vibrations, respectively. The appearance of absorption bands corresponding to >C=O and -CN groups and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-IBM copolymer.

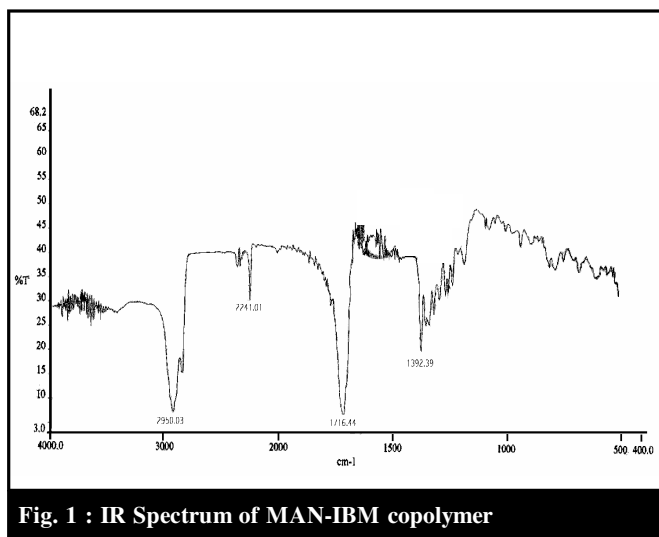
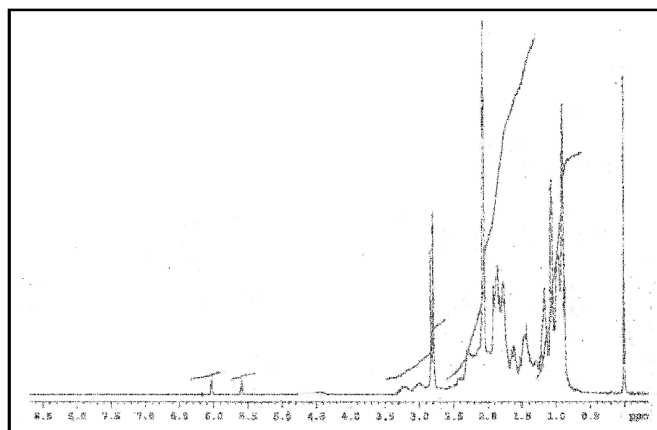


Fig. 1 : IR Spectrum of MAN-IBM copolymer

Determination of copolymer composition:

The proton magnetic resonance spectra of the samples were recorded using acetone-d₆ as solvent for IBM copolymer on Varian Gemini 200 MHz NMR spectrophotometer with TMS as internal reference. The copolymer compositions were determined by ¹H-NMR spectra Fig. 2. The distinct peaks due to methyl (CH₃) groups of IBM units appeared as a singlet at 0.9 to 1.0 ppm, (9H), CH₂ protons of IBM units appeared as a doublet at 1.8 to 2.4 ppm and methylene protons of MAN appeared as triplet at 2.7 to 2.8 ppm and were considered

Fig. 2 : ¹H-NMR Spectrum of MAN-IBM copolymer

for the composition analysis. Since the peak area corresponded to the total number of protons of a particular group, the composition of the copolymer was calculated as follows:

$$\text{by \% IBM in MAN} = \frac{\text{H - methyl}/9}{\text{H - methyl}/9 + \text{H - methyl}/3}$$

This equation is based on the fact that the methyl group of isobornyl unit corresponds to nine protons and -C-methyl group of MAN unit to three protons.

Reactivity ratios:

The copolymer composition data were used for the evaluation of reactivity ratios of the MAN-IBM copolymer by Fineman - Ross⁹ (F-R) (Fig. 3) and Kelen-Tudos¹⁰ (K-T) (Fig. 4) methods. The values of reactivity ratios were summarized in Table 2. In the systems studied, the reactivity ratio of MAN were higher than that of IBA and IBM indicated that the copolymer formed is richer in MAN than their comonomers. The product of r₁r₂ value (Table 2), which was less than 1 suggested that the monomers were arranged in a random sequence. This may be attributed due to the steric factor, which enables

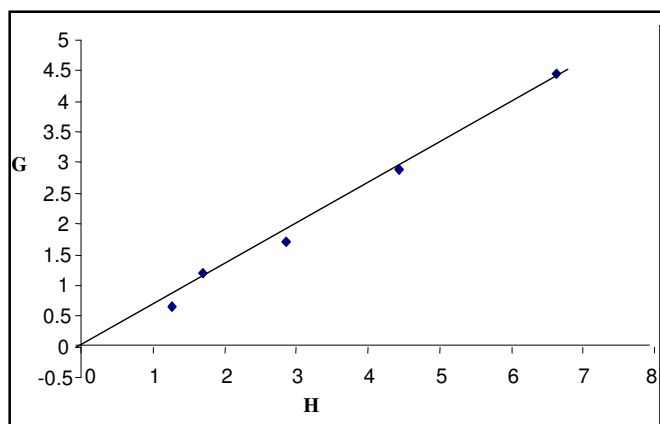


Fig. 3 : Reactivity ratios of the MAN-IBM copolymer by Fineman-Ross method

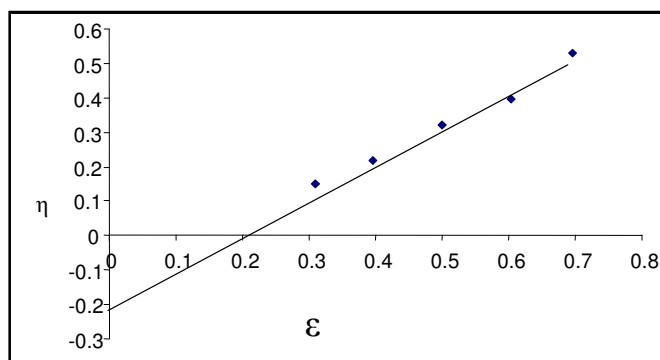


Fig. 4 : Reactivity ratios of the MAN-IBM copolymer by Kelen - Tudos method

Table 2 : Reactivity ratios of MAN with IBM by F-R and K-T methods

M ₁	M ₂	F-R		K-T	
		r ₁	r ₂	r ₁	r ₂
MAN	IBM	0.641	0.202	0.632	0.191

the molecules to participate in the reaction. This is unlike the case¹¹⁻¹³ where MAN is straight compounds where as acrylate and methacrylate contains fused rings.

The rate of polymerization depends on the nature of the methacrylate. This can be understood from the value of $1/r$ that gives a measure of the reactivity of the

methacrylate towards MAN radical. The value of $1/r_1$ for MAN-IBM copolymer was 1.58. This value was compared with the value⁴ of MAN-IBA value of 1.39 which showed that acrylate was more reactive than methacrylate towards MAN; it may be due to the hindrance caused by $-CH_3$ group present at the double bond in the methacrylate. To ascertain the normal copolymer behaviour, the plots of m_1 vs M_1 were drawn, in which m_1 was the mole fraction of MAN in MAN-IBM system and M_1 was that of the feed which is given in Table 1. The shapes of the curves indicate that the azeotropic compositions of the copolymer systems and the distribution of monomeric units are random. The azeotropic composition for the system is determined by the following equation^{14, 15}:

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

The value of MAN-IBM system was 0.79 which indicated that the copolymer was richer in MAN below this point and richer in IBM above this point. This behaviour suggests the random distribution of monomers in the copolymer.

Sequence length distribution:

The mean sequence lengths \bar{n}_1 and \bar{n}_2 for MAN-IBM copolymer system was calculated and has been given in Table 3. The \bar{n}_1 and \bar{n}_2 M₁ and M₂ units were calculated using equations of Expenyong.¹¹ For MAN-IBM at 86.7% MAN (13.3 % IBM) in the monomer mixture each copolymer segment with M₁ units was approximately seven times longer than its adjoining segment with M₂ units. The sequence may be expressed as —21111112. The increase in number of MAN units in the copolymer with increase in MAN in the feed was relatively more than that of MAN-IBA system. This retarding effect of methacrylate was more than that of acrylate. The number of MAN units in copolymer increased with increasing in (MAN) in the feed, but not so for IBM. Thus IBM acts as a retarder in the copolymerization. The ratio of the mean sequence lengths distribution \bar{n}_1/\bar{n}_2 , which

Table 3 : Mean sequence length distribution of MAN-IBM Copolymers [M₁]=MAN

Sr. No.	M ₂ (mol%)	\bar{n}_1	\bar{n}_2	\bar{n}_1 / \bar{n}_2	$\bar{n}_1 : \bar{n}_2$	Distribution
1.	40.0	2.23	1.18	1.88	2:1	2112
2.	33.3	2.64	1.13	2.43	3:1	21112
3.	26.6	3.26	1.09	2.99	3:1	21112
4.	20.0	4.28	1.06	4.01	4:1	211112
5.	13.3	6.99	1.04	6.71	7:1	21111112

theoretically¹²⁻¹⁵ corresponded to the ratio m_1/m_2 , where m_1 and m_2 were the corresponding compositions of M_1 and M_2 in the copolymer for each monomer mixture, as given in Table 3.

Solution properties:

The molecular weights of the copolymers were determined using KNAUER (WG) GPC with THF as eluent. The \overline{M}_w and \overline{M}_n values of copolymer for different compositions are given in Table 4. These values increased with the increase in the MAN content of the copolymer. This trend was in consonance with variation in intrinsic viscosity. The solubility parameter helps in explaining the viscosity behaviour 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 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 were found to be linear and the intrinsic viscosity values were obtained by extrapolating it to zero concentration. In all the copolymers intrinsic viscosity increased with increase in the MAN content (Table 4). This may be attributed to the greater reactivity of nitrile radical, which facilitates propagation in preference to termination. Thus it can be

Table 4 : Intrinsic viscosities at 25°C and molecular weights of MAN – IBM copolymers

Copolymer	$[\eta]$ dl/g	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$
MAN – IBM ₁	0.42	3.982	2.521
MAN – IBM ₂	0.46	4.209	2.696
MAN – IBM ₃	0.65	4.353	2.721
MAN – IBM ₄	0.73	4.526	2.759
MAN – IBM ₅	0.79	4.621	4.791

inferred that with increase in the content of MAN the molecular weight of the copolymer increases. Solubility parameter values were determined from the plot of intrinsic viscosity against solubility parameter of solvents. Solubility parameter value of MAN-IBM as determined in different solvents are given in the Table 5. Solvents which covered a range of solubility parameter from 8.9 to 12.1 (cal/cc)^{0.5} were selected. The solubility parameter value of MAN-IBM was 10.6 (cal/cc)^{0.5}. This value was less than acrylate value (12cal/cc)^{0.5}, which suggests that the acrylate copolymer is more than that of methacrylate copolymers.

Table 5 : Intrinsic viscosities of the copolymer in different solvents along with solubility parameter values

Sr. No.	Solvent	δ (cal/cc) ^{0.5}	$\frac{\eta_{sp}/c - \text{Values}}{\text{MAN – IBM}_3}$
1.	Toluene	8.9	0.36
2.	THF	9.1	0.72
3.	Chloroform	9.3	--
4.	Chlorobenzene	9.5	1.20
5.	Diethyl Formamide	10.6	1.61
6.	Dichloro acetic acid	11	0.60
7.	Dimethyl Formamide	12.1	0.71

Thermal studies:

Glass transition temperature (T_g) of the copolymer MAN-IBM was determined using Mettler Toledo 851E thermal analyzer at a heating rate of 15°C/min. The T_g values of the copolymers are summarized in Table 6. The values showed that the acrylate copolymer as lower T_g than the methacrylate copolymers. This increasing trend of T_g from acrylate to methacrylate may be due to α -

Table 6 : Variation of T_g with composition of MAN – IBM copolymers

Copolymer	T_g (°C)
MAN – IBM ₁	124.62
MAN – IBM ₂	129.32
MAN – IBM ₄	134.32

methyl group in methacrylate increasing the steric hindrance. T_g copolymer is increased with increase in the MAN content. Inter and intramolecular interaction influence T_g . When nitrile content increases intra and inter molecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature.¹⁶⁻²¹ Thermal stability of the copolymer MAN-IBM was determined using V5IA Dupont 2000 at a heating rate of 10°C/min as shown in Fig. 5. The relative thermal stabilities were evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss. In these copolymers, the factors that influence thermal stability are (a) backbone structure (b) nature of the acrylate and (c) nitrile content.

To obtain a comparative picture of relative thermal stability IDT, IPDT and DT, values are given in Table 7. Thus, stabilities of MAN-IBM copolymers were found to be more than that of acrylate copolymers. This may be attributed to the stability of the radicals formed by the decomposition process.

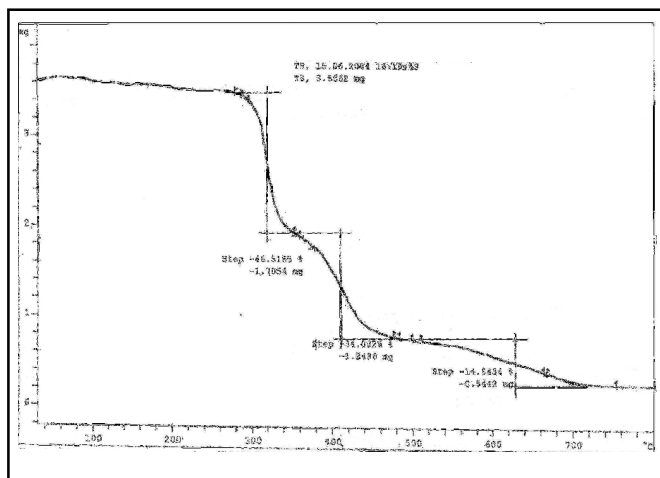


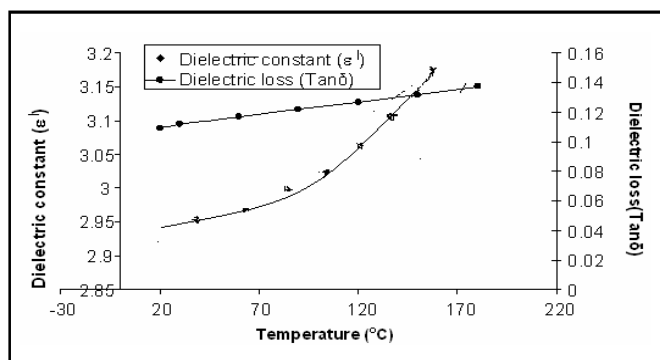
Fig. 5 : TGA Curves of MAN-IBM copolymer

Table 7 : Thermal behaviour of MAN-IBM copolymers

Copolymer	IDT (°C)	IPDT (°C)	Temperature (°C) at 50% wt. loss
MAN – IBM ₁	151.62	270.65	372.42
MAN – IBM ₂	159.72	278.65	384.58
MAN – IBM ₃	162.32	286.36	389.24

Dielectrical studies:

The typical plot of ϵ' and $\tan\delta$ against temperature for MAN-IBM₂ composition showed that ϵ' and $\tan\delta$ are unaffected by temperatures upto 120°C. Beyond that region both ϵ' and $\tan\delta$ values increase (Fig. 6). A peak


 Fig. 6 : Typical plot of ϵ' and $\tan\delta$ against temperature for MAN-IBM copolymer

due to relaxation was observed in $\tan\delta$, known as α relaxation at about 150°C in the rubbery state of the polymer²²⁻²⁴. At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions.²⁵ As the temperature is raised, more and more dipole groups are released and the mobility of polymer segments increases.

Acknowledgement:

One of the authors, S. Sridevi thanks the Principal, Aurora Degree College for encouragement and Head, Department of Chemistry, K.U., Warangal, A.P. for providing facilities.

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