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Synthesis and Characterization of Copolymer of Methacrylonitrile with Isobornyl Methacrylate

S. SRIDEVI and P. RAGHUNATH RAO*
Department of Chemistry, Kakatiya University, Warangal-506 009, India
E-mail : raghunath_pemma@yahoo.com

Copolymer of methacrylonitrile (MAN) with isobornyl methacrylate (IBM) has been studied by free radical polymerization using azo-*bis*-isobutyro nitrile (AIBN) as initiator in dimethyl formamide (DMF) at 60 ± 1ºC. The monomer reactivity ratio was computed by both Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The reactivity ratio values suggest the formation of random copolymers which has been supported by the azeotropic composition evaluation. The mean sequence length ($\overline{n}$) 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 the increase of the 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). Thermogravimetric analysis (TGA) of the copolymer was studied. The dielectric properties of the copolymer like the dielectric constant and dielectric loss were studied. The results are compared with methacrylonitrile and isobornyl acrylate (MAN-IBA) system.

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

INTRODUCTION

Introduction of isobornyl methacrylate (IBM) into various copolymers seem to modify and improve the properties of a number of copolymers[1,2]. In our earlier paper[3] we have discussed the copolymers of isobornyl acrylate (IBA) with methacrylonitrile (MAN). In this paper, the synthesis, characterization, reactivity ratios, solution properties, thermal and dielectric properties of the copolymers of IBM with MAN have been reported and compared the results with IBA-MAN system.

EXPERIMENTAL

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

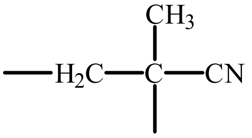
(Fluka) was crystallized from methanol. The solvent used in copolymerization was DMF (reagent grade) and purified by distillation before use.

All experiments were performed in glass tubes with appropriate quantities of dry monomers, solvents and initiator. The tubes are then sealed in an atmosphere of nitrogen. They were introduced into the thermostat at 60 ± 1ºC for 1.5 h 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 dried under vaccum. Different samples were prepared by changing the initial monomer feed. The initiator is used at 2.5 g/L of solvent. The total monomer concentration was maintained at 1.5 M, while the feed ratio is varied. The data of composition of feed and copolymers are given in Table-1.

TABLE-1
COPOLYMERIZATION DATA OF MAN WITH IBM

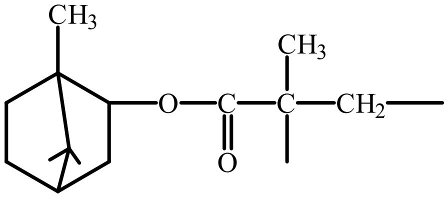
Copolymer system	Mole fraction in the feed		Intensity of methyl protons	Intensity of isobornyl methyl protons	Copolymer composition	
	MAN (M_1)	IBM (M_2)	(3H) (M_1)	(9H) (M_2)	MAN (m_1)	IBM (m_2)
MAN - IBM_1	0.600	0.400	50.73	91.20	0.640	0.360
MAN - IBM_2	0.666	0.333	39.11	86.70	0.689	0.310
MAN - IBM_3	0.734	0.266	30.95	81.20	0.724	0.276
MAN - IBM_4	0.800	0.200	20.50	74.01	0.783	0.217
MAN - IBM_5	0.867	0.133	10.34	69.23	0.870	0.130

The monomer unit structures are represented as follows:



$$-H_2C-\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}-CN$$

Methacrylonitrile (MAN)



Isobornyl methacrylate (IBM)

RESULTS AND DISCUSSION

Infrared spectra of the samples were recorded on a Perkin-Elmer model Bx IR spectrophotometer in 4000-400 cm^{-1} range with KBr pellets. Appearance of infrared strong absorption bands at 2857, 1718, 2244 and 1390 cm^{-1} correspond to methylene (-CH) stretching, >C=O stretching in ester and cyano (-CN) and methyl ($-CH_3$) 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.

Determination of copolymer composition: The proton magnetic resonance spectra of the samples were recorded using acetone-d_6 as solvent for IBM copolymer on Varian Gemini 200 MHz NMR spectrophotometer with TMS as internal reference. The copolymer compositions were determined by ^{1}H-NMR. The distinct peaks due to methyl (CH_3) groups of IBM units appears as a singlet at 0.8-1.0 ppm, (9H), CH_2 protons of IBM units appears as a doublet at 1.9-2.4 ppm and methylene protons of MAN appears as triplet at 2.7-2.9 ppm are considered for the composition analysis. Since the peak area corresponds to the total number of protons of a particular group, the composition of the copolymer was calculated[4].

$$\text{by \% IBM in MAN} = \frac{\text{H} - \text{methyl}/9}{{}^1\text{H} - \text{methyl}/9 + {}^1\text{H} - \text{methyl}/3}$$

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 was used for the evaluation of reactivity ratios of the MAN-IBM copolymer by Fineman-Ross[5] (F-R) (Fig. 1) and Kelen-Tudos[6] (K-T) (Fig. 2) methods. The values of reactivity ratios were summarized in Table-2. In the systems studied the reactivity ratio of MAN are higher than that of IBA and IBM indicates that the copolymer formed is richer in MAN than their comonomers. The product of r_1r_2 value (Table-2), which is less than 1 suggests that the monomers were arranged in a random sequence. This may be attributed due to the steric factor, which enables the molecules to participate in the reaction. This is unlike the case[7-9] where MAN is straight compounds where as acrylate and methacrylate contains fused rings.

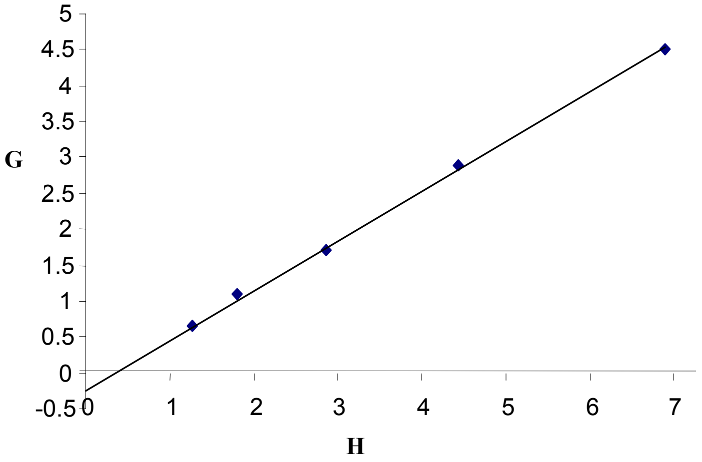


Fig. 1. Reactivity ratios of the MAN-IBM copolymer by Fineman-Ross method

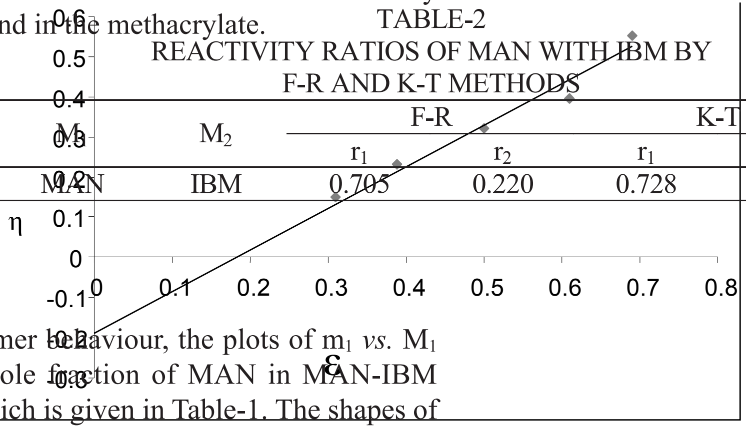


Fig. 2. Reactivity ratios of the MAN-IBM copolymer by Kelen-Tudos method

The rate of polymerization depends on the nature of the methacrylate. This can be understood form 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 is 1.39. This value is compared with the value[4] of MAN-IBA value of 1.22 which shows that acrylate is 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.

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
MAN	IBM	0.705	0.220	0.728	0.1

To ascertain the normal copolymer behaviour, the plots of m_1 *vs.* M_1 were drawn, in which m_1 is the mole fraction of MAN in MAN-IBM system and M_1 is 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[10]:

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

The value of MAN-IBM system is 0.75 indicates that the copolymer is richer in MAN below this point and richer in IBM above this point. This behaviour also 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 has been calculated and given in Table-3. The $\bar{n}_1$ and $\bar{n}_2$ for M_1 and M_2 units are calculated using equations of Expenyong[7]. For MAN-IBM at 86.7% MAN (13.3 % IBM) in the monomer mixture each copolymer segment with M_1 units was approximately six times longer than its adjoining segment with M_2 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 is relatively more than that of MAN-IBA system. This retarding effect of methacrylate is more than that of acrylate[4]. The number of MAN units in copolymer increases 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 theoretically[8] corresponds to the ratio m_1/m_2, where m_1 and m_2 are the corresponding compositions of M_1 and M_2 in the copolymer for each monomer mixture, is given in Table-3.

TABLE-3
MEAN SEQUENCE LENGTH DISTRIBUTION OF MAN-IBM COPOLYMERS $[M_1]$ = MAN

$[M_1]$ mol%	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_1:\bar{n}_2$	Distribution
40.01	2.092	1.126	2:1	2112
33.30	2.456	1.095	3:1	21112
26.60	3.000	1.068	3:1	21112
20.00	3.912	1.047	4:1	211112
13.30	5.745	1.290	6:1	21111112

Solution properties: The molecular weights of the copolymers were determined using KNAUER (WG) GPC with THF as eluent. The $\bar{M}_w$ and $\bar{M}_n$ values of copolymer for different compositions are given in Table-4. These values increase with the increase in the MAN content of the copolymer. This trend is in consonance with variation in intrinsic viscosity.

TABLE-4
INTRINSIC VISCOSITIES AT 25ºC AND MOLECULAR WEIGHTS OF MAN - IBM COPOLYMERS

Copolymer	[η] dL/g	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$
MAN - IBM_1	0.35	5.126	3.417
MAN - IBM_2	0.52	5.626	3.701
MAN - IBM_3	0.61	6.152	4.080
MAN - IBM_4	0.72	6.562	4.374
MAN - IBM_5	0.74	7.123	4.783

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 are found to be linear and the intrinsic viscosity values are obtained by extrapolating it to zero concentration. In all the copolymers intrinsic viscosity increases 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 inferred that with increase in the content of MAN the molecular weight of the copolymer increases. Solubility parameter values are determined from the plot of intrinsic viscosity against solubility parameter of solvents. Solubility parameter value of MAN-IBM has been determined in different solvents are given in the Table-5. 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 MAN-IBM is 9.3 $(cal/cc)^{0.5}$. This value is less than acrylate value (10.6 $(cal/cc)^{0.5}$), which suggests that the acrylate copolymer is more than that of methacrylate copolymers.

TABLE-5
INTRINSIC VISCOSITIES OF THE COPOLYMER IN DIFFERENT SOLVENTS ALONGWITH SOLUBILITY PARAMETER VALUES

Solvent	δ $(cal/cc)^{0.5}$	η_{sp}/c-values
		$MAN\text{-}IBM_3$
Toluene	8.9	0.42
THF	9.1	1.02
Chloroform	9.3	1.41
Chlorobenzene	9.5	–
Diethyl formamide	10.6	1.20
Dichloro acetic acid	11.0	0.80
Dimethyl formamide	12.1	1.30

Thermal studies: Glass transition temperature (T_g) of the copolymer MAN-IBM is determined using Mettler Toledo 851E thermal analyzer at a heating rate of 15ºC/min. The T_g values of the copolymers are summarized in Table-6. The values show 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-methyl group in methacrylate increasing the steric hindrance. T_g copolymer is increasing 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[9,11,12].

Thermal stability of the copolymer MAN-IBM is determined using V5IA Dupont 2000 at a heating rate of 10ºC/min. The relative thermal stabilities 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. In these copolymers, the factors that influence thermal stability are (a) backbone structure (b) nature of the acrylate and (c) nitrile content.

TABLE-6
VARIATION OF T_g WITH COMPOSITION OF
MAN - IBM COPOLYMERS

Copolymer	T_g (ºC)
MAN - IBM_1	167.49
MAN - IBM_2	172.59
MAN - IBM_4	174.16

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 are found to be more than that of acrylate copolymers. This may be attributed to the stability of the radicals formed by the decomposition process.

TABLE-7
THERMAL BEHAVIOUR OF MAN-IBM COPOLYMERS

Copolymer	IDT (ºC)	IPDT (ºC)	Temperature (ºC) at 50% wt. loss
MAN - IBM_1	241.12	315.50	410.12
MAN - IBM_2	281.42	316.82	450.62
MAN - IBM_3	291.62	332.82	472.54

Dielectrical studies: The typical plot of ε′ and tan δ against temperature for MAN-IBM_2 composition shows that ε′ and tan δ are unaffected by temperatures upto 130ºC. Beyond that region both ε′ and tan δ values increase (Fig. 3). A peak due to relaxation is observed in tan δ, known as α relaxation at about 160ºC in the rubbery state of the polymer[13-15]. At lower temperature molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions[16]. As the temperature is raised, more and more dipole groups are released and the mobility of polymer segments increases. The α-relaxation temperature for IBA copolymer is 140ºC. The IBM temperature is more than IBA temperature. This might be due to the presence of relatively bulkier group present in IBM unit than in IBA unit.

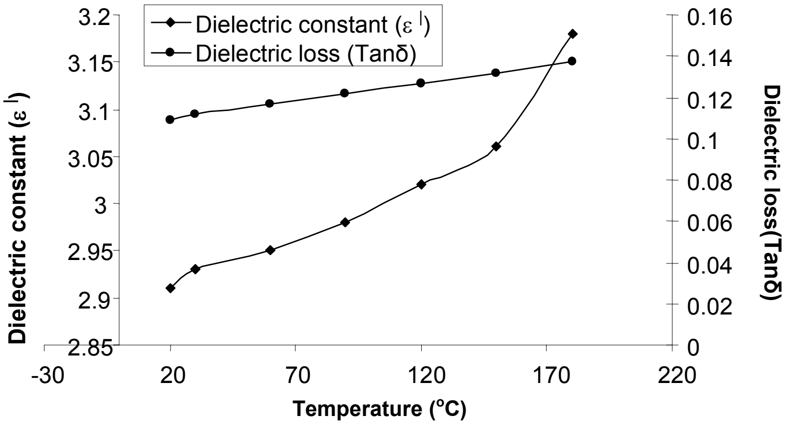


Fig. 3. Typical plot of ε| and tan δ against temperature for MAN-IBM copolymer

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