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Synthesis, Characterization, Thermal, Refractive and Di Electric Studies of BIS (1-Oxododecyl) Peroxide Initiated Copolymers of Methacrylonitrile-Methyl Methacrylate

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Abstract: ***Copolymer of Methacrylonitrile (MAN) with Methyl methacrylate (MMA) was synthesized by free radical polymerization method by using bis (1-oxododecyl) peroxide as initiator in dimethylformamide (DMF) at 60^{0}C. The copolymer samples were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR and dielectric studies. The monomer reactivity ratio was computed both by Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods. The reactivity ratio values revealed the formation of random copolymers. The formation of random copolymer was also supported by azeotropic composition evaluation method. The dielectric constant (ε) of methacrylonitrile-methyl methacrylate (MAN-MMA) copolymers was found to dependent both on temperature and frequency. The increase in dielectric loss (tanδ) with temperature is attributed to formation of more dipoles at higher temperatures. The Refractive index and molar refractivity and Thermo gravimetric analysis (TGA) of the copolymers was also reported. The appearance of absorption bands corresponding to >C=O, -OCH$_3$ and –CN groups and the vanishing of absorption bands corresponding to olefinic bond conforms the formation of MAN-MMA copolymer.***

Keywords: Methacrylonitrile (MAN), Methyl methacrylate (MMA), reactivity ratios, dielectric properties, thermal properties, Refractive index, Molar refractivity.

1. Introduction

Polymers are generally 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 fusion with alkyl nitriles through copolymerization [1-4]. The combination of durability, versatility and the ability to tailor molecules relatively easily has made alkyl acrylates prime candidates for diverse applications. Alkyl nitriles and alkyl acrylic esters copolymers are prime candidates for diverse applications. ^{1}H-NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition [5-9]. In this article we report the synthesis, structural characterization, reactivity ratios, thermal, refractive and dielectric studies of (MAN–MMA) copolymer.

2. Experimental

MAN (Aldrich) and MMA (Aldrich) 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 (Aldrich) initiator was used as such. The copolymerization was carried out in DMF 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 $\underline{+}$ 1^{0}C and the polymerization continued for 90 min. The copolymer is isolated by pouring polymerization mixture into large quantity of 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 Table1.

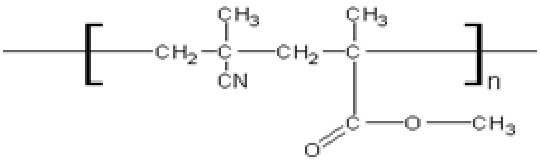
Infrared spectra of the samples were recorded on a Thermo Nicolet Nexus 670 IR spectrophotometer in the wave number range 4000 to 400 cm^{-1} with KBr pellets .^{1}H -NMR spectra of the samples were recorded using CDCl$_3$ as solvent on Avance 300 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by ^{1}H-NMR spectra. The thermogravimetric analysis of the polymers was performed on a Perkin Elmer Diamond thermal analyzer at a heating rate of 15^{0}C/min. Glass transition temperature (T$_g$) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of 15^{o}C/min. T$_g$ values of the copolymers obtained from the DSC curves. 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. A Capacitance bridge model GR 1620 (WG) is used to measure the dielectric constant (ε) and dielectric loss (tanδ) of the copolymers. And To determine the refractive index values of the copolymer Abbe's refractometer is used.

Table 1: Copolymerization data of MAN with MMA

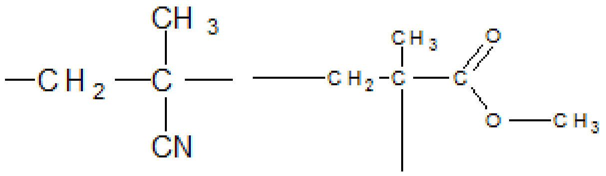
Copolymer system	Mole fraction in the feed		Intensity of methylene protons of MAN (2H)(M_1)	Intensity of (-OCH_3) - protons of MMA (2H) (M_2)	Copolymer composition	
	MAN (M_1)	MMA (M_2)			MAN (m_1)	MMA (m_2)
MAN-MMA-1	0.80	0.70	3.18	2.36	0.574	0.425
MAN-MMA-2	0.90	0.60	3.56	2.16	0.622	0.377
MAN-MMA-3	1.00	0.50	4.03	2.12	0.655	0.344
MAN-MMA-4	1.10	0.40	4.96	1.84	0.729	0.270
MAN-MMA-5	1.20	0.30	5.74	1.60	0.782	0.217

3. Results and Discussion

The structures of monomers and copolymer unit can be represented as follows:



Repeating unit in MAN-MMA



Methacrylonitrile (MAN) Methyl methacrylate (MMA)

3.1 IR Spectroscopy

The infrared spectrum of methacrylonitrile and methyl methacrylate (MAN-MMA) is shown in figure-1. The characteristic absorption bands appeared at 2851.10, 1730.67, 2234.45, 1470.66 and 2922.46 cm^{-1} corresponds to methylene (-CH_2) stretching, >C=O stretching in ester, cyano (-CN), methoxy group (-OCH_3) and methyl (-CH_3) stretching vibrations respectively. The appearance of absorption bands corresponding due to ester >C=O, -OCH_3 and –CN group and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-MMA copolymer.

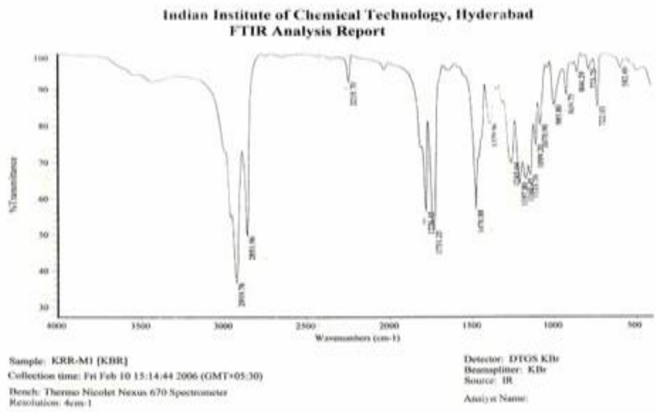


Figure 1: IR Spectrum of MAN-MMA copolymer

3.2 Determination of copolymer composition

Figure-2 shows ^{1}H-NMR spectrum of MAN-MMA copolymer. In the spectrum methyl (-CH_3) protons of MMA unit appears at 1.4 ppm, methylene (-CH_2) protons of MMA unit and MAN unit appears at 2.1 ppm, methyl (-CH_3) protons of MAN unit appears at 1.6-1.8 ppm and methoxy (-OCH_3) protons of MMA appears at 3.5 ppm respectively.

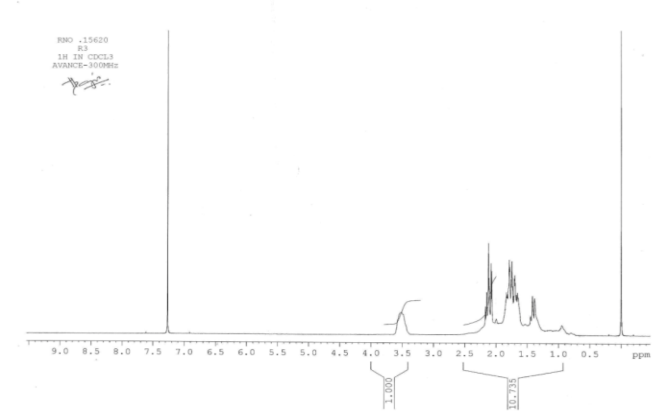


Figure 2: ^{1}H-NMR Spectrum of MAN-MMA copolymer

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 equations is based on the fact that the –CH_2 group of MAN unit corresponds to two protons, -OCH_3 group of MMA corresponds to three protons.

$$\%\text{MMA in MAN} = \frac{(^1\text{H}-\text{OCH}_3)/3}{(^1\text{H}-\text{OCH}_3)/3+(^1\text{H}-\text{CH}_2/2)} \qquad (1)$$

3.3 ^{13}C- NMR Spectroscopy

^{13}C-NMR spectrum of MAN-MMA copolymer is shown in figure-3. In this spectrum the peak at δ 178 for carbonyl carbon of MMA units and the peak of nitrile carbon of MAN unit appear at δ 122. The peak at δ 74-77 accounts for the solvent $CDCl_3$. The other signals at δ 64 is due to methoxy carbon (-OCH_3) of MMA unit. The resonance at δ 45 represents quaternary carbon , the resonance at δ 18-23 are due to C-CH_3 and methyl group of MMA unit and methylene (-CH_2) group at δ 52. The methyl (-CH_3) group of MAN unit appears at δ 29-32. This confirms the formation of copolymer.

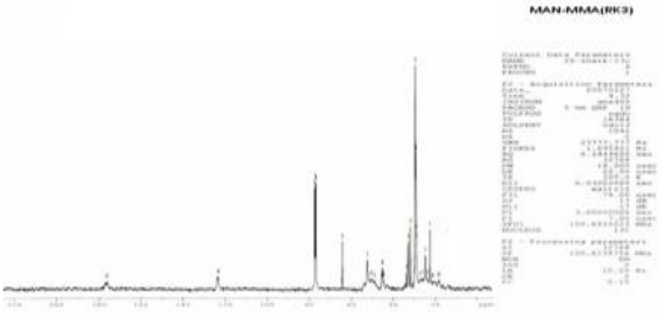


Figure 3: ^{13}C-NMR of MAN-MMA copolymer

3.4 Reactivity Ratios

The copolymer composition data was used for the evaluation of reactivity ratios of the MAN-MMA copolymer by

Fineman–Ross [10] and Kelen–Tudos [11] methods. The respectively plots are shown in figure 4 (a) and (b).

$G = r_1 H - r_2$ (2) Where $G = \frac{F(f-1)}{f}$ and $H = \frac{F^2}{f}$

$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$ (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 $r_1 r_2$ whose value less than unity suggests that the monomers were arranged in a random sequence. The rate of polymerization depends on the value of 1/r that gives a measure of the reactivity of the methyl methacrylate towards the MAN radical. The value of $1/r_1$ for MAN-MMA copolymer is 1.31.

Table 2: Parameters of equations (2) and (3) for MAN-MMA copolymer (α = 2.079)

S.No.	F=AN/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	1.347	0.294	0.969	0.095	0.318
2	1.50	1.648	0.589	1.365	0.171	0.395
3	2.00	1.900	0.947	2.104	0.227	0.502
4	2.75	2.695	1.729	2.805	0.354	0.573
5	4.00	3.587	2.885	4.459	0.440	0.682

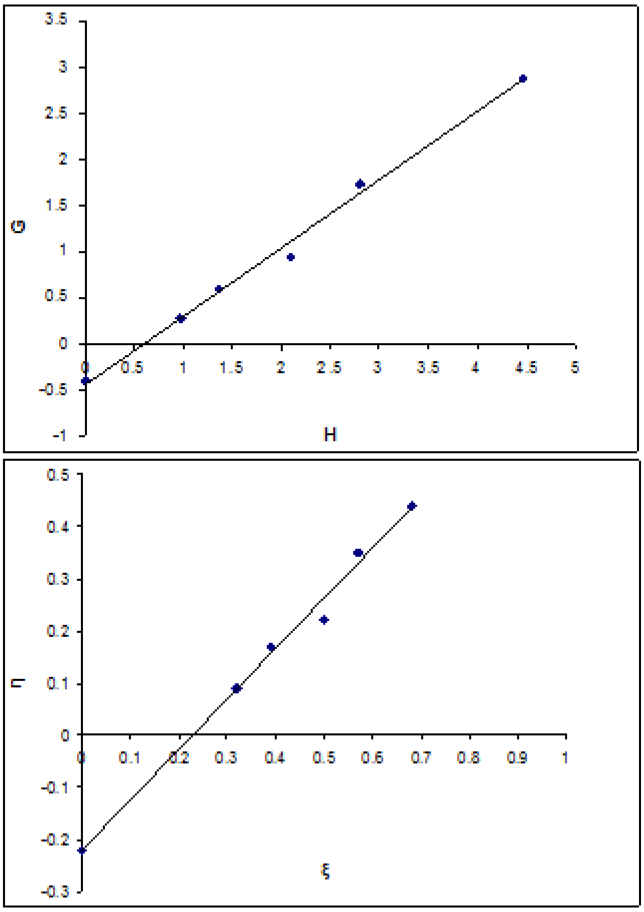


Figure 4: (a) F-R Plot Figure.4 (b) K-T plot

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 also conveys the distribution of monomeric units are random. The azeotropic composition was determined by the following equation.

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

The value of MAN-MMA is 1.06 indicating that the copolymer is richer in MAN below this point and above this point richer in MMA. This behavior also suggests the random distribution of monomers in the copolymer.

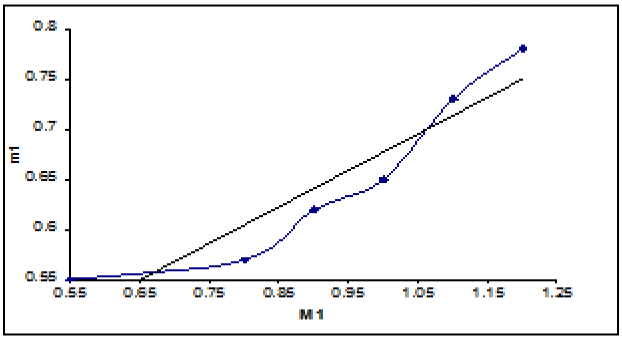


Figure.-5 Azeotropic composition of MAN-MMA copolymer

3.6 Solution properties

The weight average and number average molecular weight ($\overline{M}_w$ and $\overline{M}_n$) values of copolymer for different compositions are given in Table 3. These values increased with the increase in MAN 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 [12-14].the evaporation of solvent can also be adjusted by selecting proper solvents using this solubility parameter concept to get good film with no defects.

Table 3: intrinsic viscosities at 25^0C and molecular weight of MAN-MMA copolymer

Copolymer	$\overline{M}_w$ x 10^4	$\overline{M}_n$ x 10^4	[η] dl/g
MAN-MMA$_1$	1.875	1.184	0.148
MAN-MMA$_3$	1.894	1.256	0.162
MAN-MMA$_5$	1.935	1.268	0.185

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 molecular weight increased with increase in the MAN content Table 4. This may be attributed to the greater reactivity of nitrile, which facilitates propagation in preference to termination. Solubility parameter values of copolymer determined in different solvents are given in Table 4. 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-MMA is 10.1 $(cal/cc).^{0.5}$

Table 4: Intrinsic viscosities of MAN-MMA copolymer and their dependence on solubility parameter of solvents at 30 ^{0} C

Solvent	δ $(Cal/cc)^{0.5}$	[η] dl/g MAN-MMA	Solvent	δ $(Cal/cc)^{0.5}$	[η] dl/g MAN-MMA
Toluene	8.9	0.092	Acetic acid	10.1	0.216
Benzene	9.2	0.151	1,4 Dioxane	10.7	0.165
Chloroform	9.3	0.214	Dichloro acetic acid	11.0	-
Chloro benzene	9.5	0.254	Dimethyl sulfoxide	12.0	0.114
Dichloro methane	9.7	0.284	Dimethyl formamide	12.1	0.102

3.7 Thermal Studies

The differential Scanning Calorimetry thermogram (DSC) is shown in Figure.6. The glass transition temperature (T_g) values of the copolymers were determined from DSC curves. It is observed that T_g of the copolymer increased with increase in the MAN content. When the MAN content increases intramolecular interaction increases and the polymer segments become less mobile and thereby T_g occurs at higher temperature [15-19]. The relative thermal stabilities are evaluated by TGA/DTG thermogram is shown in Figure.7. The comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature (DT) at 50% weight loss of different compositions of MAN-MMA are shown in Table.5.

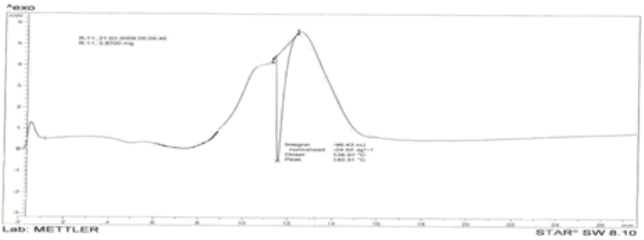


Figure 6: DSC thermogram of MAN-MMA copolymer

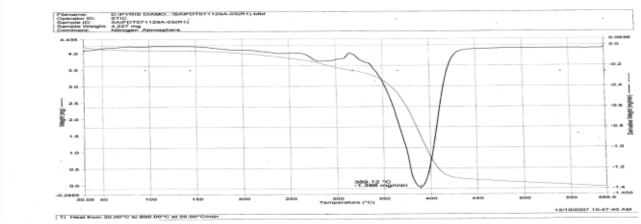


Figure 7: TGA/DTG curve of MAN-MMA copolymer

Table 5: Thermal behavior of MAN-MMA copolymer

Copolymer	IDT (°C)	IPDT (°C)	Temperature (°C) at wt. loss			T_g (°C)
			10%	20%	50%	
MAN-MMA-1	245	380	260	335	385	140.31
MAN-MMA-2	247	382	261	337	386	--
MAN-MMA-3	248	383	263	338	388	--
MAN-MMA-4	249	385	265	340	391	--
MAN-MMA-5	251	386	267	343	393	145.58

3.8 Dielectric Studies

Figures 8 and 9 shows the variations of dielectric constant (ε) with frequency and variation of dielectric loss (tan δ), dielectric constant (ε) with temperature respectively for MAN-MMA samples.

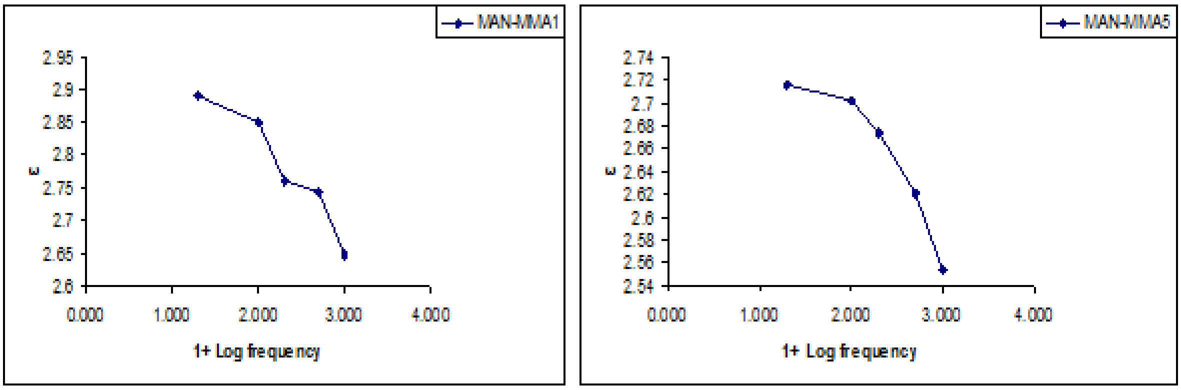


Figure 8: Frequency dependence of tanδ for MAN-MMA-1 and dielectric constant (ε) for MAN-MMA-5.

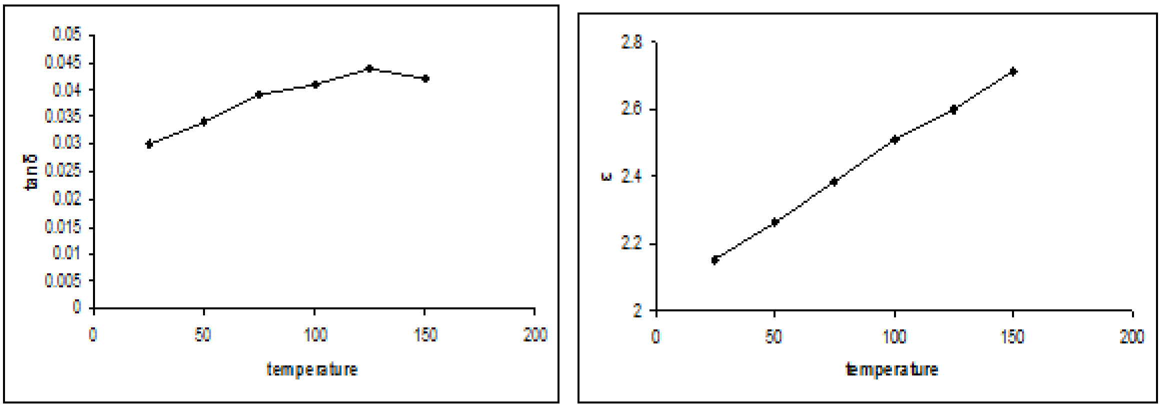


Figure 9: Temperature dependence of tan δ and dielectric constant (ε) for MAN-MMA copolymer

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

Temperature	MAN-MMA	
	ε	tan δ
25	2.152	0.03
50	2.264	0.034
75	2.384	0.039
100	2.511	0.041
125	2.602	0.044
150	2.713	0.042

Dielectric loss (tan δ) and dielectric constant (ε) increases continuously with increasing temperature. Whereas tan δ decreases when temperature reaches near to the glass temperature (Tg) value. The higher values of dielectric constant at lower frequency are due to larger contribution of space charge polarization which results in higher value of ε. The increase of dielectric constant and loss with temperature is not rapid initially, but it is more pronounced above 100°C (near to the Tg of the co polymer).

The mobility of polymer molecular chains is limited at lower temperatures and due to dipole-dipole interactions their mobility is restricted [20]. With increasing temperature around glass transition temperature, increase in ε can be attributed to increased mobility of polymer segments [21].

3.9 Refractive Index Study

Lorentz, assuming that a material is made up of spherical molecules through which light travels slower than in the vacuum, in which they are situated. Lorentz proceeding logically from Maxwell's electromagnetic theory and simultaneously derived famous Lorentz-Lorentz equation[22-23]

$$r_D = [n^2-1/n^2+2]\ (1/\rho) \qquad \ldots\ldots\ldots\ldots\ldots(5)$$

where 'r_D' is the specific refraction (cm^3/g)
'ρ' is the density and
'n' is the refractive index of the polymer solution.

The molar refraction R_M is given by Clausius Mosotti relation[24]

$$R_M = [n^2-1/n^2+2]\ (M/\rho) \qquad \ldots\ldots\ldots (6)$$

The space-filling factor (r) which is the fraction of molar volume actually occupied by molecules[25-26] is given by

$$r = [n^2-1/n^2+2] \qquad \ldots\ldots\ldots\ldots\ldots\ (7)$$

The calculated refractive index, molar refraction and space filling values of different polymer solutions are given in Table 7.

From the tabular values it is evident that refractive index varies linearly for different compositions[27] of MAN-MMA copolymer.

Table 7: Refractive index data for MAN-MMA copolymer at 35^0C

% Of solution	Density (ρ)	Refractive index (n)	Filling factor(r)	Molar refractivity (r_m)
1%	0.85	1.311	0.193	37.39
2%	0.86	1.316	0.196	37.72
5%	0.87	1.324	0.200	38.23
10%	0.88	1.328	0.203	38.22

4. Conclusions

The copolymer of MAN with MMA has been synthesized using 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 co polymer – solvent and the polymer-polymer interactions are established by intrinsic viscosities, solubility parameter and refractive index. Thermal stability of the polymer has been evaluated through thermal properties like T_g, IDT and IPDT. The number of MAN units in copolymer increased with increasing concentration of MAN. Hence MMA acts as a retarder in the copolymerization. The increased MAN content increased intramolecular interaction and thereby polymer segments become less mobile. Hence T_g occurs at higher temperature with increasing MAN content in the polymer. Dielectric properties of co-polymer are studied to find the electrical stability and also to know α-relaxation that is observed near to T_g value of the copolymer. The refractive index & solution studies study of the copolymer is useful to understand polymer-solvent interactions.

5. Acknowledgements

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