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Synthesis, Characterization, Solution, Thermal and Dielectric Properties of 1,1′-Azo*bis*(cyclohexanecarbonitrile) Initiated Copolymers of Methacrylonitrile and Vinyl Butyrate

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Copolymer of methacrylonitrile (MAN) with vinyl butyrate (VB) was synthesized 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 suggest the formation of random copolymers which has been supported by the azeotropic composition evaluation. The mean sequence length ($\bar{n}_1$) and probabilities (p) in the formation of various structural units were evaluated. The molecular weights of the polymers were determined by gel permeation chromatography, which increase with the increase of the copolymer of methacrylonitrile content. The solubility parameters were determined with the 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 also studied. The dielectrical property of the copolymer is also studied.

Key Words: Vinyl butyrate, Reactivity ratios, Solution properties, Thermal properties, Di-electrical property.

INTRODUCTION

Introduction of vinyl butyrate (VB) into various copolymers appears to modify and improve the properties of a number of copolymers[1-4]. The estimation of copolymer composition and determination of the reactivity ratios are important for making copolymers with required physico-chemical properties. ^{1}H NMR spectroscopic analysis has been used as a powerful tool for the estimation of copolymer composition. In this work, the synthesis, characterization, reactivity ratios, solution and thermal properties of the copolymers of methacrylonitrile with vinyl butyrate are reported.

EXPERIMENTAL

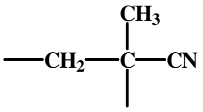
Methacrylonitrile (Aldrich) and vinyl butyrate (Aldrich) were purified by washing with 5 % solution of sodium hydroxide and distilled water, dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate was collected and used for copolymerization. 1,1'-Azo *bis*(cyclohexanecarbonitrile)

(VAZO) (Aldrich) as initiator was recrystallized from methanol. The solvent used in copolymerization was DMF which was a reagent grade chemical. This was dried 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 sealed in an atmosphere of nitrogen and introduced into the thermostat at 60 ± 1 ºC and the polymerization was continued for 1.5 h to get less than 10 % conversion. The polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered, washed thoroughly with water followed by ether and hexane and finally dried under vaccum. Different samples were prepared by changing the initial monomer feed. The initiator was used at 2.5 g/dm^3 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 presented in Table-1.

TABLE-1
COPOLYMERIZATION DATA OF METHACRYLONITRILE-VINYL BUTYRATE (MAN-VB)

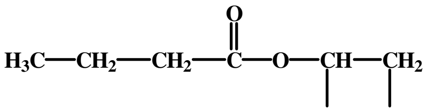
Copolymer system	Mole fraction in the feed		Intensity of methylene protons of MAN (2H) (M_1)	Intensity of propyl protons of VB (7H) (M_2)	Copolymer composition	
	MAN (M_1)	VB (M_2)			MAN (m_1)	VB (m_2)
MAN-VB$_1$	0.80	0.70	6.41	5.11	0.556	0.444
MAN-VB$_2$	0.85	0.65	6.18	4.24	0.593	0.407
MAN-VB$_3$	0.90	0.60	5.94	3.85	0.607	0.393
MAN-VB$_4$	0.95	0.55	5.64	3.37	0.626	0.374
MAN-VB$_5$	1.00	0.50	4.93	2.54	0.660	0.340

The monomer unit structures are represented as follows:



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{|}{C}}-CN$$

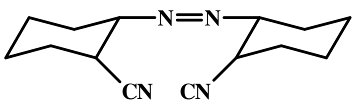
I) methacrylonitrile (MAN)



$$H_3C-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-\underset{|}{CH}-\underset{|}{CH_2}$$

II) vinyl butyrate (VB)

Structure of initiator:



1,1'-Azo *bis*(cyclohexanecarbonitrile) (VAZO)

RESULTS AND DISCUSSION

IR Spectroscopy: Infrared spectra of the samples were recorded on a Thermo Electron corporation IR spectrophotometer in 4000 to 400 cm^{-1} range with KBr pellets. IR spectrum of the copolymer of methacrylonitrile and vinyl butyrate (MAN-co-VB) is shown in (Fig. 1) showing the characteristic bands of both the monomer units. Appearance of strong absorption bands at 2865, 1733, 2242 and 2936 cm^{-1} corresponds to methylene ($-CH_2$) stretching, >C=O stretching in ester, cyano (-CN) and methyne (-CH) stretching vibrations, respectively. The appearance of absorption bands corresponding to -CN and >C=O and the disappearance of absorption bands corresponding to olefinic bond is the evidence for the formation of MAN-VB copolymers.

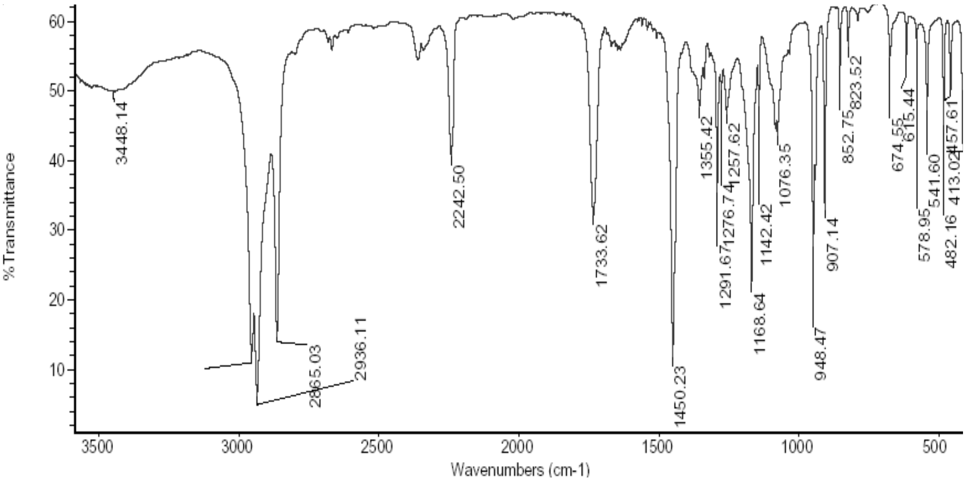


Fig. 1. IR Spectrum of MAN-VB

Determination of copolymer composition: ^1H NMR spectra of the samples were recorded using DMSO-d_6 as solvent for MAN copolymer on a AMX 400 MHz NMR spectrometer with TMS as internal reference. The copolymer compositions were determined by ^1H NMR spectra. The distribution of proton in the two units is an important means to distinguish the monomers in the chain. In the spectrum, methyl ($-CH_3$) protons of vinyl butyrate unit appears at 1.0 to 1.1 ppm, methylene ($-CH_2$) protons of vinyl butyrate unit appears at 1.8 ppm, $-COCH_2-$ protons of vinyl butyrate unit appears at 2.2 ppm, methylene ($-CH_2$) protons of methacrylonitrile unit appears at 2.5 ppm, methyl ($-CH_3$) protons of MAN unit appears at 2.8 ppm and methyne (-CH) protons of vinyl butyrate appears at 5.1 to 5.2 ppm, which were 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[5] by the relation:

$$\%\ \text{VB in MAN} = \frac{{}^1\text{H}-\text{C}_3\text{H}_7/7}{{}^1\text{H}-\text{C}_3\text{H}_7/7+{}^1\text{H}-\text{CH}_2/2} \qquad (1)$$

This equations is based on the fact that the $-CH_2$ group of MAN unit corresponds to two protons, $-C_3H_7$ group of vinyl butyrate corresponds to seven protons.

^{13}C NMR Spectroscopy: ^{13}C NMR spectrum of copolymer of MAN-VB shows resonance at δ 173 for carbonyl carbon of VB units and the nitrile carbon of MAN unit at δ 118. The peak at δ 74 accounts for the solvent $CDCl_3$. The other signals at δ 19 and 27 are due to methylene carbon ($-CH_3$) of VB unit, respectively. The resonance at δ 41 represents the $-CH_2$ and the resonance at δ 33 and 21 are due to quarternary carbon (-C-) and methyne (-CH) groups of MAN and VB units, respectively. The resonance at δ 45 is due to the methyl ($-CH_3$) group of MAN unit and peak at δ 16 is due to methyl group ($-CH_3$) of VB unit. This confirms the formation of copolymer.

Reactivity ratios: The copolymer composition data were used for the evaluation of reactivity ratios of the MAN-VB copolymer by Fineman-Ross[6] (F-R) (Fig. 2) and Kelen-Tudos[7] (K-T) (Fig. 3) methods.

$$G = r_1H - r_2 \tag{2}$$

where $G = \frac{F(f-1)}{f}$ and $H = F^2/f$

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \tag{3}$$

where $\eta = \frac{G}{\alpha + H}$, $\xi = \frac{H}{\alpha + H}$.

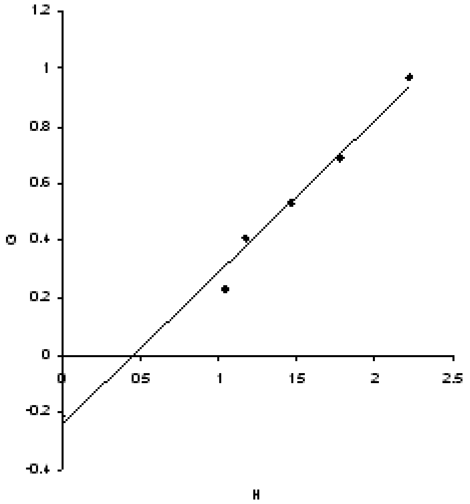


Fig. 2. F-R Plot of copolymer of MAN-VB

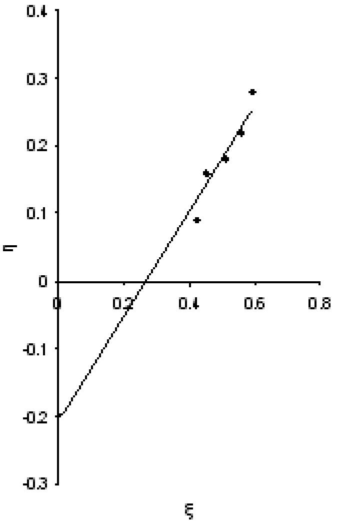


Fig. 3. K-T Plot of copolymer of MAN-VB

The values of reactivity ratios were summarized in Table-2. The product of r_1 and r_2 values, which is less than 1 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-VB copolymer is 1.66.

TABLE-2
PARAMETERS OF EQUATIONS (2) AND (3) VALUES
FOR COPOLYMERS OF MAN-VB

$\alpha = 1.46$

F=MAN/VB	f	$G=\frac{F(f-1)}{f}$	$H=\frac{F^2}{f}$	$\eta=\frac{G}{\alpha+H}$	$\xi=\frac{H}{\alpha+H}$
1.143	1.25	0.23	1.04	0.09	0.42
1.310	1.46	0.41	1.17	0.16	0.45
1.500	1.54	0.53	1.46	0.18	0.50
1.730	1.67	0.69	1.78	0.21	0.55
2.000	1.94	0.97	2.06	0.28	0.59

To ascertain the normal copolymer behaviour, the plots of mole fraction of monomer in the feed (m_1) *versus* that in the copolymer (M_1) were drawn and is given in Table-1. The shapes of the curves (Fig. 4) indicate that the azeotropic compositions of the copolymer systems and the distribution of monomeric units are random. The azeotropic composition was determined by the following equation[8-10]:

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

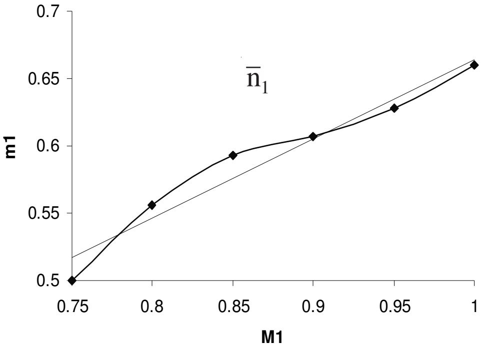


Fig. 4. Azeotropic composition of copolymer of MAN-VB

The value of MAN-VB is 0.91 indicating that the copolymer is richer in MAN below this point than MAN and richer in VB above this point than MAN. This behaviour also suggests the random distribution of monomers in the copolymer.

Sequence length distribution: The mean sequence lengths and $\bar{n}_2$ for MAN-VB copolymer system has been calculated and listed in Table-3. The $\bar{n}_1$ and $\bar{n}_2$ for M_1 and M_2 units are calculated using equations of Expenyong[11]:

$$\bar{n}_1 = \frac{P_{12}}{(1-P_{11})^2} = \frac{1}{P_{12}} = \frac{r_1[M_1]+[M_2]}{[M_2]} \tag{5}$$

$$\bar{n}_2 = \frac{P_{21}}{(1-P_{22})^2} = \frac{1}{P_{21}} = \frac{r_2[M_2]+[M_1]}{[M_1]} \tag{6}$$

TABLE-3
MEAN SEQUENCE LENGTH DISTRIBUTION VALUES OF COPOLYMER OF MAN-VB

M_2 (mol %)	$\bar{n}_1$	$\bar{n}_2$	$\bar{n}_1/\bar{n}_2$	$\bar{n}_1 : \bar{n}_2$	Distribution
46.67	1.68	1.13	1.49	2:1	2112
43.30	1.78	1.11	1.60	2:1	2112
40.00	1.90	1.10	1.72	2:1	2112
36.60	2.03	1.08	1.87	2:1	2112
33.30	2.20	1.07	2.04	2:1	2112

For example, at 80.0 % MAN (20.0 % VB) in the monomer mixture each copolymer segment with M_1 units was approximately two times longer than its adjoining segment with M_2 units. The sequence may be expressed as 2112. This differences between $\bar{n}_1$ and $\bar{n}_2$ values are increased from 40.0-43.3 to 80.0 % of MAN. Thus, we can say that MAN has higher tendencies to form more segments than that of VB. The number of MAN units in copolymer increases with increasing concentration of MAN in the feed, but this is not so for VB. Hence VB acts as a retarder in the copolymerization. The ratio of the mean sequence lengths distribution $\bar{n}_1/\bar{n}_2$, which theoretically[12] 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 of MAN-VB is given in Table-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 ± 0.1 ºC. 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-4. These values increase with the increase in the MAN content of the copolymer. This trend is 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 also be adjusted by selecting proper solvents using this solubility parameter concept to get good film with no defects.

TABLE-4
INTRINSIC VISCOSITY VALUES AT 25 ºC AND MOLECULAR
WEIGHT OF COPOLYMER OF MAN-VB

Copolymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	[η] dl/g
MAN-VB$_1$	2.7760	2.2490	1.35
MAN-VB$_2$	2.7895	2.2572	1.71
MAN-VB$_3$	2.7951	2.2582	1.86

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 MAN content (Table-4). This may be attributed to the greater reactivity of vinyl butyrate content, which facilitates propagation in preference to termination. Solubility parameter values of the copolymer determined in different solvents are presented in 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 copolymer of MAN-VB is 10.6 $(cal/cc)^{0.5}$.

TABLE-5
INTRINSIC VISCOSITY VALUES OF MAN-VB AND THEIR DEPENDANCE ON SOLUBILITY PARAMETER OF SOLVENTS AT 30 ºC

Solvent	δ $(cal/cc)^{0.5}$	[η] dl/g MAN-VB
Toluene	8.9	0.46
Benzene	9.2	0.56
Chloroform	9.3	0.80
Chloro benzene	9.5	-
Dichloro methane	9.7	-
Acetic acid	10.1	1.15
Diethyl formamide	10.6	1.35
1,4-Dioxane	10.7	1.32
Dichloro acetic acid	11.0	0.95
Dimethyl sulfoxide	12.0	0.82
Dimethyl formamide	12.1	0.64

Thermal studies: Thermogravimetric analysis of the polymers was performed on a Perkin-Elmer Diamond thermal analyzer at a heating rate of 15 ºC/min. Glass transition temperature (T_g) of the copolymers was determined using a Mettler Toledo 822E thermal analyzer at a heating rate of 15 ºC/min. T_g values of the copolymers obtained from the DSC curves. T_g of the copolymer increases with increase in the MAN content. When the MAN content increases intramolecular interaction increase and the polymer segments become less mobile and T_g occurs at higher temperature[13,14]. 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 shown in (Fig. 5). To obtain a comparative picture of relative thermal stability of the copolymer their IDT, IPDT and DT values are given in Table-6.

TABLE-6
THERMAL BEHAVIOUR OF COPOLYMERS OF MAN-VB

Copolymer	IDT (ºC)	IPDT (ºC)	Temperature (ºC) at wt. loss			T_g (ºC)
			10 %	20 %	50 %	
MAN-VB_1	114.78	160.87	148.26	157.18	184.35	110.88
MAN-VB_2	115.52	162.35	150.62	159.32	191.85	114.84
MAN-VB_3	116.35	163.85	151.84	164.62	195.75	119.78
MAN-VB_4	117.95	164.27	152.96	168.64	198.22	–
MAN-VB_5	118.72	165.18	154.21	169.71	201.15	–

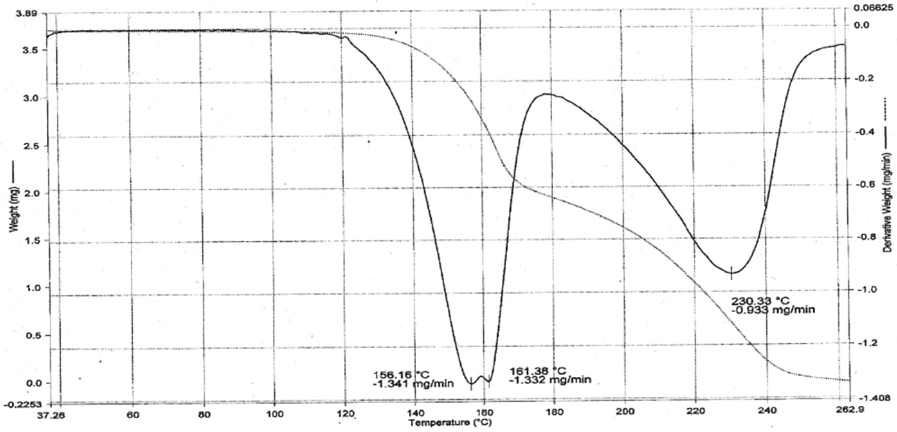


Fig. 5. TGA/DTG Curve of MAN-VB copolymer

Dielectric properties: A capacitance bridge model GR 1620(WG) is used to measure the dielectric constant (ε) and dielectric loss (tan δ) of the MAN-VB 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 MAN-VB (Fig. 6) are given in Table-7. The results show 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 a relaxation, at *ca.* 120 °C, in the rubbery state of the polymer[15,16]. This temperature is higher than T_g for the polymer obtained by a DSC method is 110.88 °C At lower temperature, molecular chains are not only immobile but also tightly bound at some points because of dipole-dipole interactions[17,18]. As the temperature is raised, more and more dipole groups are released and the mobility of polymers segment increases.

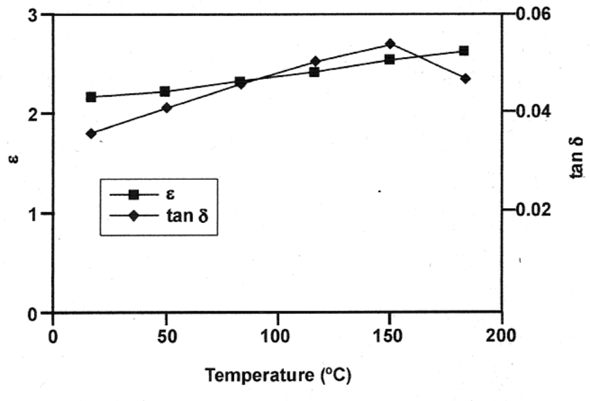


Fig. 6. Typical plot of ε and tand against temperature for copolymer of MAN-VB

TABLE-7
VARIATION OF DI-ELECTRIC CONSTANT AND DI-ELECTRIC LOSS VALUES WITH TEMPERATURE FOR COPOLYMER OF MAN-VB AT 20 KHz

Temperature	MAN-VB	
	ε	tan δ
25	2.154	0.036
50	2.192	0.041
75	2.317	0.046
100	2.409	0.05
125	2.535	0.054
150	2.593	0.047

Conclusion

The copolymer of methacrylonitrile with vinyl butyrate has been synthesized using a 1,1'-azo *bis*(cyclohexanecarbonitrile) as initiator in DMF. The copolymer is characterized by IR and ^{1}H NMR. Reactivity ratio of the copolymer was determined using the F-R and K-T methods which suggest that random copolymers were formed. Intrinsic viscosities and solubility parameter was determined to establish interactions in polymer solutions. Thermal properties like T_g, IDT and IPDT have been evaluated to find the thermal stability of the polymer. Di-electric properties of co-polymer is also studied to find the electrical stability.

REFERENCES

1. M.S. Jacovic and D. Milosevic, *J. Polym. Sci.: Polym. Symposia*, **42**, 1443 (2007).
2. T. Hirai, *Angew. Makromol. Chem.*, **43**, 93 (2003).
3 M. Inoki, F. Akutsu, H. Yamaguchi, K. Naruchi and M. Miurra, *Macromol. Chem. Phys.*, **195**, 2799 (2003).
4. H.S. Hosseini and A. Ghavami, *Iran. Polym. J.*, **14**, 617 (2005).
5. A.S. Brar and T. Saini, *J. Polym. Sci. A: Polym. Chem.*, **44**, 2955 (2006).
6. M. Fineman and S.D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
7. T. Kelen and F. Tudos, *J. Macromol. Sci. Chem.*, **9A**, 1 (1975).
8. V.R. Gowrikar, N.V. Viswanathan and Sreedhar, Poly. Science, New Age International Limited, New Delhi, India, p. 206 (1996).
9. F.W. Billmeyer, Textbook of Polymer Science, John Wiley & Sons, Inc, Tokyo, Japan, edn. 2 (1982).
10. G. Odian, Principles of Polymerization, Wiley Interscience, New York, edn. 2, p. 81 (1981).
11. K.I. Ekpenyong, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 125 (1985).
12. M. Ueda, T. Suzuki, M. Takahashi, Z.B. Li and K. Koyamat, *Macromolecules*, **19**, 558 (1986).
13. R. Khesareh, N.T.A. McManus and A. Penlidis, *J. Macromol. Sci.*, **43A**, 23 (2006).
14. Y. Ohta, Y. Inoue, R. Chujo, M. Kishimoto and I. Seo, *Polymer*, **31**, 1581 (1990).
15. A. Adam, *Kolloid Zeitschrift Zeitshrift Polym.*, **180**, 11 (1962).
16. A. Tanaka and Y. Ishida, *J. Phys. Soc. (Japan)*, **15**, 6 (1962).
17. A.K. Gupta, R.P. Singhal and A.K. Agarwal, *Polymer*, **22**, 285 (1981).
18. T. Srilatha and P.R. Rao, *Asian J. Chem.*, **15**, 241 (2003).

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