Research Paper

Synthesis and Characterization of Homo and Copolymers of N-1-naphthylmaleimide with Methyl methacrylate and Styrene

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Abstract: *The free radical copolymerization of each of methyl methacrylate (MMA) and styrene (ST) with N-1-naphthylmaleimide (NMI), initiated by AIBN, was performed in tetrahydrofuran (THF) solvent at 70°C. A series of copolymersamples of NMI-MMAand NMI-ST were prepared using different feed ratios of comonomers. The polymer samples have been characterized by solubility tests, intrinsic viscosity measurements, FT-IR, and ^{1}H-NMR spectral analysis, and thermo-gravimetric analysis.The values of monomer reactivity ratios r_1 and r_2 determined by Fineman-Ross and Kelen-Tudos methods are 0.85 and 1.06 in NMI/MMA system and 0.80 and 0.15 in NMI/ST system, respectively. Alfrey-Price Q-e values for NMI or Q = 0.84 and e = 0.72 in NMI/MMA system and0.79 and 1.85in NMI/ST system, respectively. It was found that the initial and final decomposition temperatures increased with the increase content of NMI in the copolymer samples.*

Introduction

Polymers are widely used in several technological applications. Thermally stable and heat resistant polymers are in great demand for use as insulators, varnishes, enamels, adhesives etc. [1]. A large percentage of such material is used in modern military and civil aircraft. Reinforced plastics, based on high temperature resistant polymers are light in weight and even many a times stronger than the metals. Reinforced plastics find applications in the building of ships, cars, bridges, etc. Aerospace adhesives are also made from the temperature resistant polymers. Among a few other applications, these polymers have been used in electrical insulation, protective coatings and for various kinds of plastic films etc. For the use of polymers in the instruments and in the aerospace applications, the most important properties are strength and stability at high temperature. Thus, the high demand for new materials requires the preparation of new polymeric materials with enhanced mechanical and thermal properties.

In general, the polymers containing aromatic and/or heterocyclic ring structures are known to have excellent thermal stability because of their minimal number of oxidizable hydrogen atoms and high extent of double bond conjugation. Polyimide related groups of plastics have some outstanding properties for electronic applications, protective coatings and for various kinds of plastic films and laminates. This is due to their combination of high thermal stability up to and beyond 260°C, good electrical and mechanical properties which are also relatively stable from low negative temperature to high positive temperatures, dimensional stability in most environments, excellent resistance to ionization radiation, very low out gassing in vacuum and good optical properties. This provides advantages in many high temperature electronic applications. All these properties also make polyimide excellent material choice in the extreme environment of space and temperature[2-6].

Material and Methods

Maleic anhydride (SRL, extra pure) was first recrystallized from chloroform and then was further purified by sublimation at 54±2°C. 1-Naphthylamine (Mackson chemicals, Ahmadabad, Extra pure) was used as received. Methylmethacrylate (BDH, AR) and styrene (National chemicals) were purified by shaking two to three times with 5% NaOH solution to eliminate hydroquinone inhibitor[7]. They were dried over anhydrous calcium chloride for 6 h and distilled. The head and tail fractions were discarded.2, 2'-Azobisisobutyronitrile (AIBN)

obtained from Wilson Lab was recrystallized from methanol and prior to use. Anhydrous sodium acetate (Polypharm, AR) was used as received. Dimethylformamide (DMF), acetic anhydride, methanol and acetone used in the present work were of laboratory grade of purity better than 99 mol%, and were used as received. Tetrahydrofuran (THF, Qualigen fine Chemicals, AR) was purified by distillation after being refluxed for 4 h in the presence of sodium[7].

Elemental analysis C, H, N% of NMI, PNMI and N% of all copolymer samples was carried out on Perkin Elmer 2400 by using Combustion's method. FT-IR spectra of all polymer samples have been scanned in KBr pellet on Perkin-Elmer RX2,IR spectrometer by KBr pellet technique. The ^{1}H-NMR spectra were taken in CDCl$_3$ solvent on BrukerAvance Spectrometer at 400 MHz (S.A.I.F., Chandigarh) with a sweep time of 10 min. at room temperature. The internal reference used was TMS. The viscosity measurements were carried out in chloroform at 30±0.2^{o}C, using an Ubbelohde suspended-level viscometer. Solubility of the various polymer samples were examined in a number of polar and nonpolar solvents. 30-40 mg samples of finely grounded polymer powder were placed into small test tubes and 1 mL of each type of was added and then stirred at 30°C for some time. A swollen gel during shaking was formed indicating dissolution of polymer in that solvent, which gradually disintegrated into a true solvent. In some cases dissolution took longer time or it was necessary to raise the temperature.

Universal V2.6D TA (TGA Q500 V6.3) was used to obtain the thermograms of the present polymer samples with a constant heating rate of 10°C/min in N$_2$ atmosphere. The average molecular weights and polydispersity of the polymers were obtained by Gel Permiation Chromatography (GPC) with cross-linked styrene divinyl benzene copolymer by differential refractometer (JASCO) with PSS-GPC software. Columns used were SHODEX-KD804 (Garda chemicals Panoli, Ankleshwar, Gujarat, India).

Synthesis
Preparation of N-1-Naphthylmaleimide
NMI was synthesized by condensation of maleic anhydride with a 1-naphthylamine followed by cyclodehydration using acetic anhydride (AcA) and sodium acetate (NaAc)[8,9] as shown in Scheme 1. 1-naphthylamine (14.3g, 100mmol) in acetone was added drop wise to a well stirred acetone solution of maleic anhydride (9.88g, 100mmol) in a round bottom flask. The entire reaction mixture was cooled externally. The orange solids of N-1-naphthylmaleamic acid (NMA) were filtered and then dried at 55±5°C. NMA was purified by recrystallization from methanol. Yield 92%, mp160^{o}C. Cyclodehydration of the NMA to maleimide was carried out by reacting 24.1 g (100mmol) NMA, 16.4 g (200mmol) NaAc and 115 mL AcA in 200 mL DMF were continuously stirred for 3 h at room temperature. The reaction mixture was poured into crushed ice. Yellow solids of NMI were filtered, washed with 10% NaHCO$_3$ solution, and dried at 55±5°C for several hours. NMI was further recrystallized from acetone-water. Yield 79%, mp 124°C. Elemental analysis(C$_{14}$H$_9$O$_2$N) calculated. (C 75.33, H 4.06, N 6.27%), found (C 73.93, H 3.47, N 5.79%).
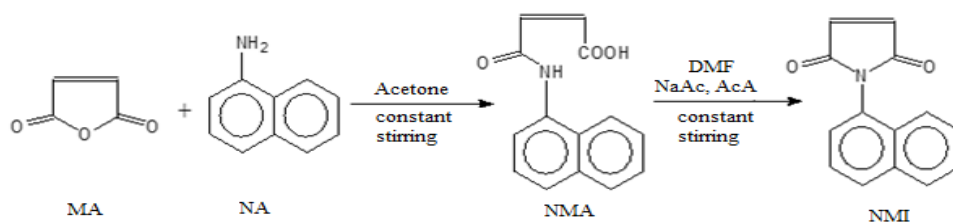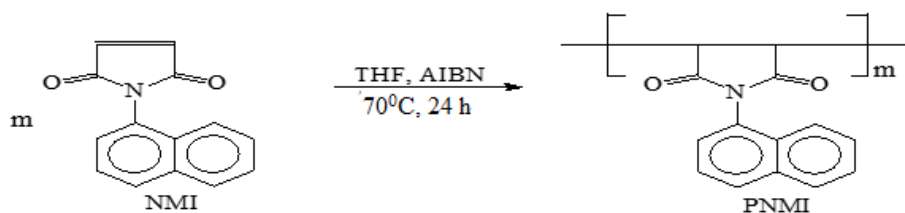

Scheme 1: Preparation of N-1-naphthylmaleimide: maleic anhydride (MA), 1-naphthylamine (NA), N-1-naphthylmaleamic acid (NMA), N-1-naphthylmaleimide (NMI)

MMA   R' = -CH$_3$,   R'' = -COOCH$_3$,   ST   R' = -H,   R'' = -C$_6$H$_5$
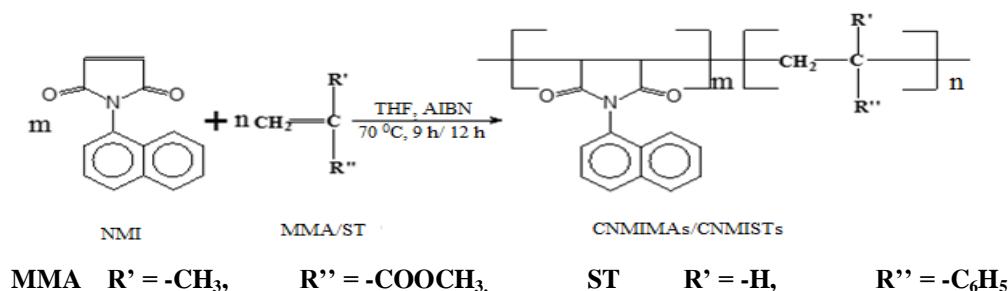
Scheme 2:Preparation of copolymers of N-1-naphthylmaleimide(NMI) with methyl methacrylate (MMA) and styrene (ST)

Table 1: Radical Polymerization of NMI and MMA and Copolymerization NMI with MMA and NMI with ST in THF at 70°C

Polymer code	Feed mol fraction(X_1)	Polymerization time in hrs.	Yield in %	Appearance	[η] dl/g	% N
PMMA	1.0	6	76.0	Wh-S	0.321	0.00
CNMIMA1	0.1	9	47.1	LB-S	0.309	1.05
CNMIMA2	0.2	9	43.8	LB-S	0.288	1.96
CNMIMA3	0.3	9	40.0	LB-S	0.267	2.76
CNMIMA4	0.4	9	37.5	B-S	0.247	3.26
CNMIMA5	0.5	9	35.8	B-S	0.234	3.86
CNMIMA6	0.6	9	33.2	B-S	0.214	4.36
CNMIMA7	0.7	9	31.9	B-S	0.194	4.79
CNMIMA8	0.8	9	29.7	B-S	0.182	5.12
CNMIMA9	0.9	9	27.2	B-S	0.166	5.47
CNMIST1	0.1	14	47.1	Cream-S	0.427	2.97
CNMIST2	0.2	14	49.3	Cream-S	0.414	3.67
CNMIST3	0.3	14	51.8	Cream-S	0.394	3.87
CNMIST4	0.4	14	54.9	Cream-S	0.370	4.09
CNMIST5	0.5	14	57.0	Cream-S	0.352	4.42
CNMIST6	0.6	14	50.0	Cream-S	0.331	4.65
CNMIST7	0.7	14	45.2	Cream-S	0.307	4.95
CNMIST8	0.8	14	42.1	Cream-S	0.289	5.25
CNMIST9	0.9	14	37.5	Cream-S	0.265	5.47
PNMI	1.0	24	26.3	DB-S	0.189	5.79

Scheme 3: Polymerizaton of N-1-naphthylmaleimide, N-1-naphthylmaleimide (NMI), polynaphthyl-maleimide (PNMI)

Polymerization Procedure

N-1-naphthylmaleimide copolymers synthesis: In a round bottom flask, fitted with a reflux condenser, calculated amounts of monomers MMA and NMI in 35 mL THF solvent were refluxed after adding 30 mg AIBN at 70°C for 9 h with occasional shaking (scheme 2). The copolymer samples were isolated in excess quantity of methanol containing 5% water. After dissolving the crude copolymer in THF, it was re-precipitated from an excess quantity of methanol–water mixture. The process was repeated three times to purify the copolymer samples. The precipitated copolymers were washed with methanol

several times and dried at 60°C under vacuum. The series of copolymer samples of each of MMA and ST with NMI (CNMIMA1 to CNMIMA9 and CNMIST1to CNMIST9) listed in Table 1 were synthesized by the same procedure and identical reaction conditions as described in the preceding paragraph except the duration for copolymerization of NMI with ST. Duration of the later reaction was kept 14 h instead of 9 h. Wh-S = White solid,

LB-S = Light brown solid, B-S = Brown solid, DB-S = Dark brown solid

Polynaphthylmaleimide(PNMI)synthesis

PNMI was synthesized by refluxing NMI (2.23 g, 10 mmol) in 35 mL THF with 30mg AIBN at 70°C for 24 h, with occasional shaking (scheme 3). The polymer PNMI was isolated by using an excess quantity of methanol–water. The crude PNMI was purified by dissolving in THF and re precipitating from a methanol–water mixture. It was dried under vacuum at 60°C, obtaining PNMI in 26.3% yield. The yield depends on the duration of polymerization.

Polymethylmethacrylate(PMMA)

MMA was polymerized under identical condition to that employed for the polymerization of NMI, except reducing the reaction to only 6 h. The PMMA was isolated in water containing small amount of methanol.

Results and Discussion
Copolymer Composition

The dependence of copolymer composition on feed ratio shown in Figures 1 and 2 shows that the composition of monomer in copolymers of CNMIMA (Figure 1) is almost same as feed, which suggests formation of an azeotropic copolymer, while in case of CNMIST composition is different than the feed. In case of CNMIST, the curve in Figure 2 is typical curve for copolymerization of the NMI/ST system with a tendency toward alternation [10, 11].

Monomer reactivity ratios

The monomer reactivity ratios were calculated from the knowledge of copolymer composition using Fineman–Ross[12] and Kelen–Tudos[13] methods. The values of r_1 (NMI) and r_2 (MMA or ST) are givenin Table 2. The Q and e values for the NMI monomer, calculated by using the Alfrey and Price equation[14] are shown in Table 2. The average values of r_1 and r_2 are 0.85 and 1.06, and 0.80 and 0.15 in the NMI/MMA, and NMI/ST systems, respectively. Alfrey-Price Q-e values for NMI were calculated as Q =0.84 and e =0.72, and 0.79 and 1.85 in the NMI/MMA and NMI/ST systems respectively.

The large e value correlates with strong electron acceptor nature of the maleimide monomer due to its carbonyl group

Solubility behavior

Solubility of the various polymer samples PNMI, CNMIMA1, CNMIMA3, CNMIMA5, CNMIMA7, CNMIMA9, CNMIST1, CNMIST3 CNMIST5, CNMIST7, CNMIST9 were examined in a number of polar and nonpolar solvents at 30°C (Table 3). The PNMI was completely soluble in acetone, THF, DMF, DMSO, benzene, nitrobenzene, chlorobenzene, chloroform, 2-butanone, and ethyl acetate. A comparison of solubility of

PNMI with PMMA (as reported in earlier publication[15]) indicated that the solubility pattern of PNMI in some of the solvents was quite different, especially in the case of aniline and carbon tetrachloride.

The PNMI was insoluble in the later solvents whereas the PMMA was soluble. All the investigated copolymers CNMIMA1, CNMIMA3, CNMIMA5, CNMIMA7, CNMIMA9, CNMIST1, CNMIST3 CNMIST5, CNMIST7, and CNMIST9 were soluble in acetone, THF, DMF, DMSO, benzene, nitrobenzene, chlorobenzene, chloroform, 2-butanone, and ethyl acetate. These copolymers were found to be soluble on heating in aniline and carbon tetrachloride. The solubility behavior in carbon tetrachloride and aniline were interesting. PNMI was insoluble whereas its copolymers with each of MMA and ST were soluble on heating. All the copolymer samples were found to be totally insoluble in hexane, cyclohexane, ethanol, methanol, petroleum ether, diethyl ether and water.
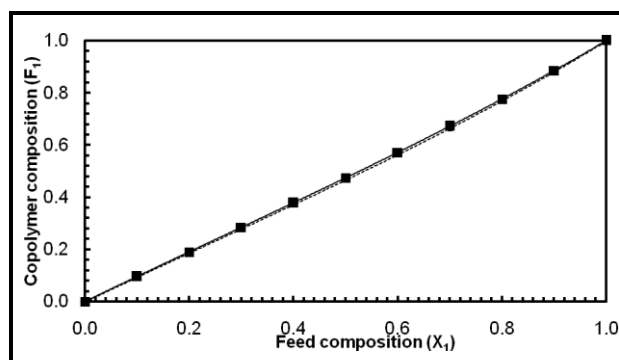

Figure 1: Variation of co-polymer composition as a function of feed composition in CNMIMAs
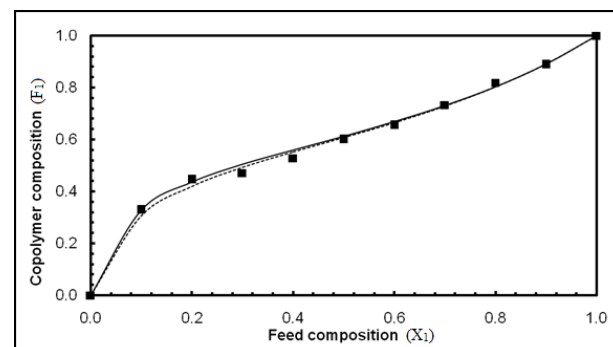

Figure 2: Variation of co-polymer composition as a function of feed composition in CNMISTs

Table 2: Monomer Reactivity Ratios in Copolymers and Alfrey-Price Q-e Parameters of NMI with respect to MMA and ST, respectively

System	Finman-Ross		Kelen-Tudos		Average		Q	e
	r_1	r_2	r_1	r_2	r_1	r_2		
NMI/MMA	0.84	1.04	0.86	1.08	0.85	1.06	0.84	0.72
NMI/ST	0.8	0.14	0.8	0.16	0.8	0.15	0.79	1.85

Table 3: Relative Solubilities of Homo and Copolymers in different Solvents at 30°C

SOLVENT	CNMIMAs					CNMISTs					PNMI
	1	3	5	7	9	1	3	5	7	9	
Acetone	S	S	S	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S	S
Benzene	S	S	S	S	S	S	S	S	S	S	S
Nitrobenzene	S	S	S	S	S	S	S	S	S	S	S
Chlorobenzene	S	S	S	S	S	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S	S	S	S	S	S
2-Butanone	S	S	S	S	S	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S	S	S	S	S	S
Aniline	S	S*	S*	IS	IS	S	S	S	S*	S*	IS
CCl$_4$	S	S*	S*	IS	IS	S*	S*	S*	S*	IS	IS
Hexane	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Cyclohexane	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Petroleum ether	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Water	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS

S= soluble, IS= insoluble, S* Soluble on heating

Intrinsic Viscosity

Intrinsic viscosity [η] is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the polymer coil in a given solution. There are number of methods which have been used to calculate the intrinsic viscosity [η] of polymer solutions. The equations of Huggins[16] and Kraemer[17] are most often used equations for the determination of [η] and found to hold good for low concentration polymer solutions.

Huggins[16]

$$\eta_{rel} /C = [\eta] + K_H [\eta]^2 C \qquad [1]$$

Kraemer[17]

$$\ln \eta_{rel}/C = [\eta] - K_K [\eta]2 C \qquad [2]$$

where, K_H and K_K represent, respectively Huggins and Kraemer constants for the given polymer / solvent / temperature system. The values of [η] and constants K_H and K_K of Eqs. (1)-(2) in chloroform solvent at 30°C were obtained. The [η] of present polymer samples determined in chloroform at 30°C of Eqs.(1) and (2) by applying the method of least-squares are given Table 4 along with Huggins K_H and Kraemer K_K constants. For the present polymer samples, the values of K_H+K_K are in the range 0.49 to 0.54, with an average value of 0.51.

This average value of K_H+K_K is in excellent agreement with the theoretically predicted value of 0.5[18]. Further, generally the values of K_H (hydrodynamic constant) are > 0.30, indicating chloroform to be a good solvent for these polymers.

The Huggins and Kraemer equations require measurements at different concentrations of polymer solutions to determine the intrinsic viscosity [η], which is definitely time consuming and may need large quantity of solvents.

To overcome the problem, number of equations has been proposed by Solomon and Ciuta[19], Deb and Chatterjee[20], Rudin and Wagner[21], Ram Mohan Rao and Yaseen[22], Khan et al.[23] and Raju and Yaseen[24], where only single viscosity measurement is sufficient for the determination of the intrinsic viscosity [η].

Table 4: Intrinsic Viscosity and Parameters of Homo- and Copolymers in Chloroform at 30°C derived from Huggins and Kraemer Equations

Polymer code	Huggins eq.(1)		Kraemer eq.(2)		$K_H + K_K$
	[η] dl/g	K_H	[η] dl/g	K_K	
PNMI	0.162	0.34	0.163	0.15	0.49
PMMA	0.321	0.33	0.321	0.17	0.50
CNMIMA1	0.305	0.39	0.305	0.12	0.51
CNMIMA2	0.284	0.40	0.285	0.12	0.52
CNMIMA3	0.267	0.28	0.267	0.21	0.49
CNMIMA4	0.246	0.34	0.246	0.16	0.50
CNMIMA5	0.232	0.41	0.232	0.11	0.52
CNMIMA6	0.213	0.34	0.213	0.16	0.50
CNMIMA7	0.193	0.29	0.193	0.20	0.49
CNMIMA8	0.181	0.32	0.181	0.18	0.50
CNMIMA9	0.165	0.37	0.165	0.14	0.51
CNMIST1	0.425	0.31	0.425	0.18	0.49
CNMIST2	0.409	0.35	0.409	0.15	0.50
CNMIST3	0.386	0.43	0.387	0.10	0.53
CNMIST4	0.363	0.44	0.364	0.10	0.54
CNMIST5	0.344	0.44	0.345	0.09	0.53
CNMIST6	0.326	0.38	0.326	0.13	0.51
CNMIST7	0.305	0.36	0.305	0.15	0.51
CNMIST8	0.286	0.38	0.286	0.13	0.51
CNMIST9	0.262	0.38	0.262	0.13	0.51

Solomon and Ciuta (SC)[19] equation is
$$[\eta] = (\sqrt{2}/C)(\eta_{sp} - \ln\eta_{rel})^{1/2} \qquad [3]$$

Deb and Chatterjee (DC)[20] proposed the equation
$$[\eta] = (1/C)\{3\ln\eta_{rel} + (3/2)\eta_{rel}^2 - 3\eta_{sp}\} \qquad [4]$$

Rudin and Wagner (RW)[21] equation is of the form
$$[\eta] = (\eta_{sp}/C)(1.0 + 0.24\eta_{sp})^{-1} \qquad [5]$$

Ram Mohan Rao and Yaseen (RMY)[22] gave the equation
$$[\eta] = (1/2C)(\eta_{sp} + \ln\eta_{rel}) \qquad [6]$$

Single parameter Khan, Gupta and Bhargava (KGB)[23] equation is
$$[\eta] = (\eta_{sp}/C)(1 + 0.28\eta_{sp})/(1 + (K_H + 0.28)\eta_{sp}) \qquad [7]$$

where K_H = Huggins constant

Raju and Yaseen (RY)[24] develop the equation
$$\log[\eta] = \log(\eta_{sp}/C) - 0.14\eta_{sp} \qquad [8]$$

In -Eqs. (3) to (8), η_{rel} and η_{sp} represent real viscosity and specific viscosity[14,16] at concentration C g/dl. In order to check their accuracy in predicting [η], the values of [η] obtained from these equations are compared with most commonly used Huggins and Kraemer equations. The values of [η] obtained in chloroform at 30°C using the equations (3) to (8) due to Solomon and Ciuta (SC), Deb and Chatterjee (DC), Rudin and Wagner (RW), Ram Mohan Rao and Yaseen (RMY), Khan, Gupta and Bhargava (KGB), and Raju and Yaseen (RY) are listed in Table 4 along with the average value of [η] in last column of the Table 5. A comparison of the values of [η] obtained by various Eqs. (3) to (8) with the equations due to Huggins and Kraemer shows that there is a good agreement with

each other within the ±1.0% of average values. The value of [η] of individual polymers depends on the composition of copolymers and decreases in all copolymer samples of CNMIMAs and CNMISTs as the content of NMI in the copolymer is increased.

Spectral Characterization

*NMA:*FT-IR (in cm^{-1}) at 3282, 1557 (amide N-H), 3052 (aromatic and alkene C-H), 1711 (carboxylic acid and amide), 1278 (carboxylic acid C-O), 1637 alkene (C=C), 909 (CH=CH), 848 (2,3-disubstituted benzene), 764 (mono-substituted benzene), 687 (cis- CH=CH) and 625 (C-H bending).

*NMI:*FT-IR (in cm^{-1}, Figure 3), 1772 and 1711 (C=O symmetric and asymmetric stretch in a five-member imide ring [25–28]), 1596, 1509, 1463 (C=C, aromatic), 1403 (C-H bending), 1309 (C-N stretching [29]), 952 (CH=CH), 772 (mono-substituted benzene), and 694 (cis -CH=CH-). The peak at 3465 cm^{-1} is for N-H of residual NMA.

^{1}H-NMR spectrum (400MHz, TMS, CDCl$_3$, δ ppm, Figure 4) confirms the structure of NMI as follows: two olefinic protons (CH=CH) (a) at δ6.89(S), four aromatic protons (b) in the range δ 7.54 to 7.58(m) ppm, two aromatic protons (c) in the range δ 7.37 to 7.39(d) ppm and one aromatic proton (d) at δ 7.94 to 7.98(m).

PNMI: The absence of a sharp band at 952 cm^{-1} (in FT-IR, Figure 5) and chemical shifted δ at 6.89 ppm (in ^{1}H-NMR, 400MHz in CDCl$_3$, Figure 6) in PNMI due to -CH=CH- in NMI monomer, indicates the formation of polymer via vinyl group polymerization[28, 30,31].
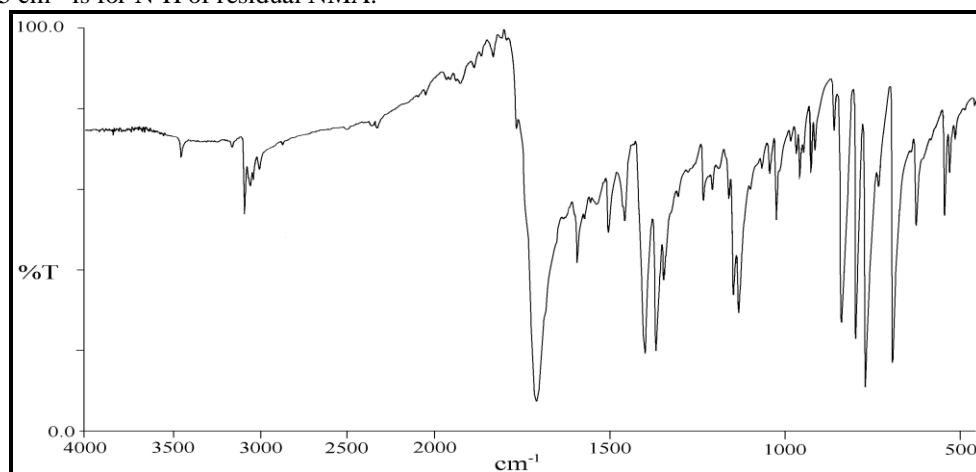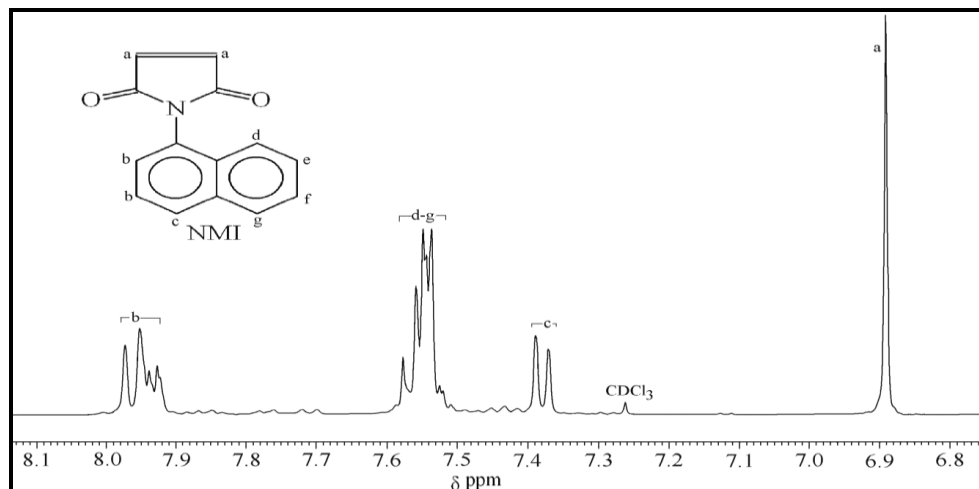

Figure 3: FT-IR spectrum of NMI

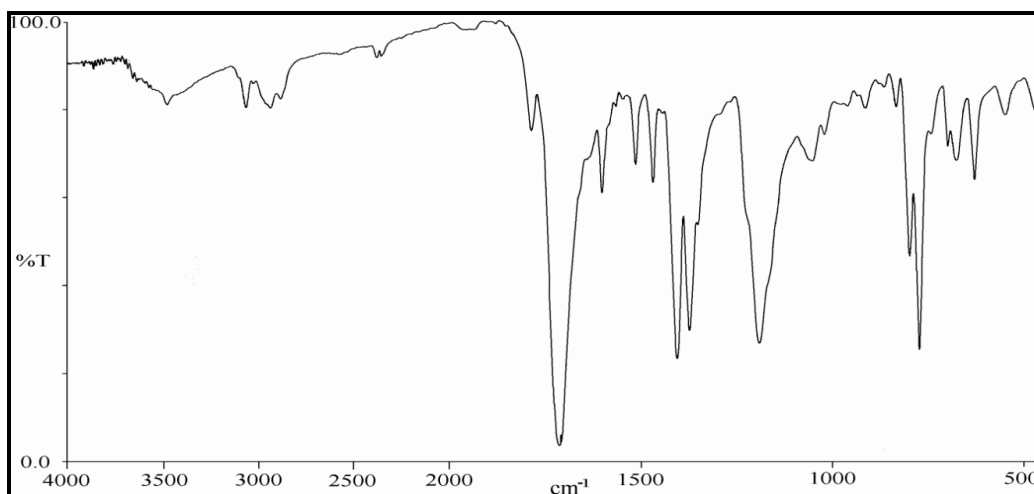**Figure 4: ^{1}H-NMR spectrum of NMI at 400 MHzin CDCl$_3$**

Figure 5: FT-IR spectrum of PNMI
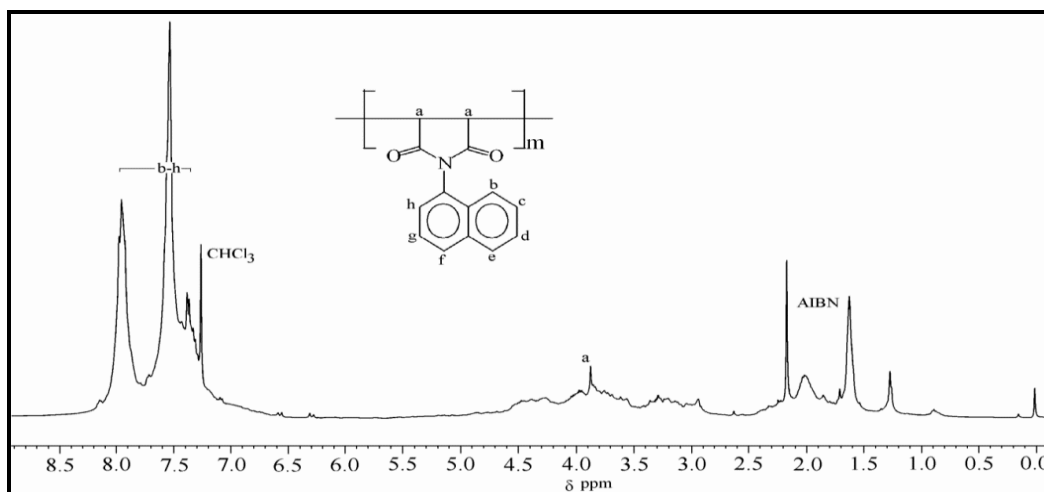
Figure 6: ¹H-NMR spectrum of PNMI at 400 MHz in CDCl₃

The δ observed at 6.89 ppm due to -CH=CH- in monomer NMI (Figure 2) has shifted to very small peak at 3.6–4.0 ppm in PNMI as a result of the formation of semi-flexible poly(substituted methine) -[CH-CH]ₙ- group [27, 29].

The presence of absorption bands at 1775 and 1711 cm⁻¹ due to symmetric and asymmetric stretching of C=O in the five-member imide ring [10, 25, 29] indicates that the imide ring remained intact in the polymerization. δ at 1.26–2.17 ppm are due to terminal methyl protons of AIBN moiety [-(CN)-C-(CH₃)₂] and δ 7.26 ppm for CDCl₃. FT-IR spectra of copolymer samples CNMIMAs in Figure 7(a) and 7(b) shows major characteristic absorption bands at 1778±2, 1720±10 (C=O symmetric and asymmetric stretch in a five-member imide ring and C=O stretch of ester), 1598, 1510 (C=C aromatic), 1404 (due to over lapping of –CN stretch and –CH bend of CH₃ group), 1243 to 1015 (asymmetric and symmetric C-O-C stretch), 987

(out-of-plane C-H bend). These characteristic bands confirm that the monomer NMI copolymerized with MMA. The spectral pattern around frequencies 1778±2,

1720, 1597-1404, 1245-1015 and 688 cm⁻¹ has undergone a change as the copolymer composition is varied. The carbonyl absorption of NMI at 1720 cm⁻¹ merged with that of MMA at 1734 cm⁻¹ to form single peak from 1734 to 1715 cm⁻¹. Its exact position depends on the relative contribution from NMI and vinyl acrylate. Further, with the increase of imide content in the copolymer the peak intensities at 1781 and 1598-1500 and at 688 cm⁻¹ have also gradually increased for CNMIMAs while for CNMISTs the peak intensities remain almost same which indicates that CNMIMAs are random copolymers and CNMISTs are alternate copolymers. The ¹H-NMR of CNMIMAs [400 MHz, TMS, CDCl₃, ppm, Figure 8(a) and 8(b)] has the same absorption pattern with the variation in the peak intensities as a result of the variation in the contents of the copolymer. For the present copolymer CNMIMAs samples,

for Ar-H, -CH-CH- and -OCH$_3$ of imide unit is observed at 7.36-7.98, 3.69, and 3.88 ppm, respectively. Protons for -OCH$_3$, -CH$_2$-, -CH$_3$ in MMA unit appear at 3.59, 2.17, and 0.84-1.43 ppm, respectively. The peak intensity of imide protons is increased whereas that of MMA protons decreased in going from samples.
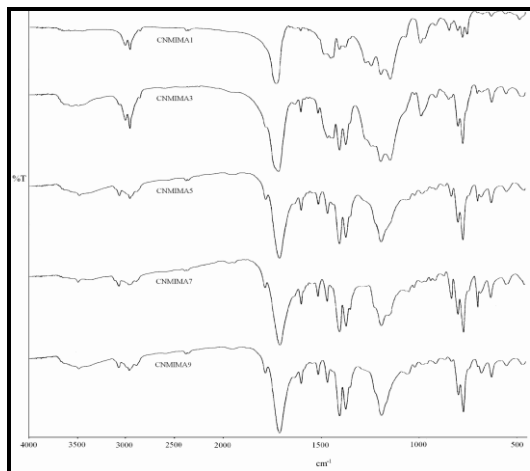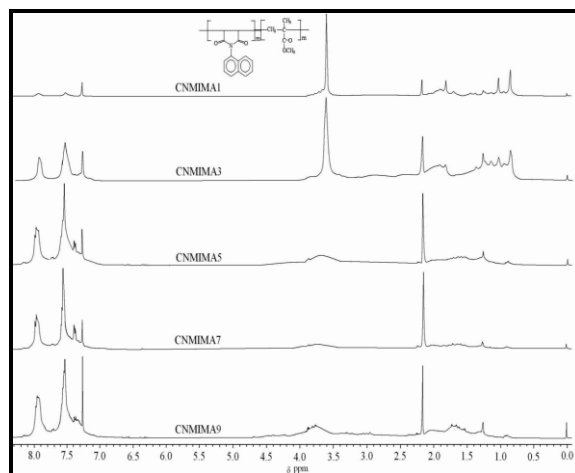

Figure 7 (a): FT-IR spectrum of CNMIMA1, CNMIMA3, CNMIMA5, CNMIMA7 and CNMIMA9
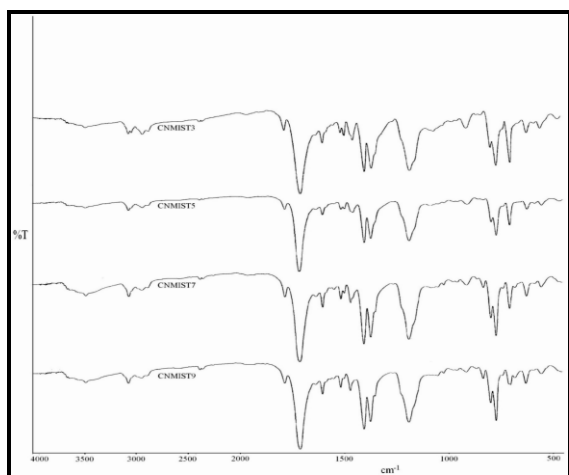
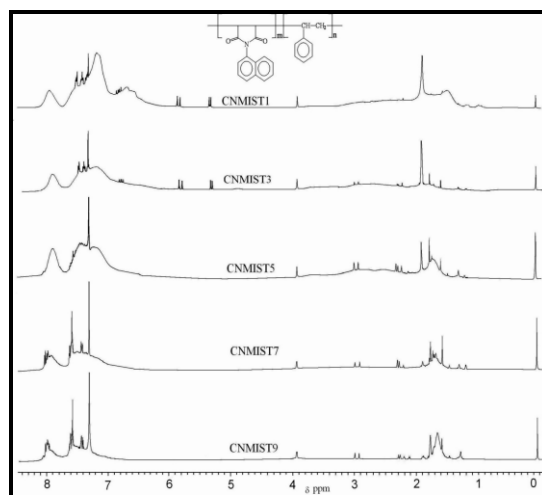**Figure 7 (b): FT-IR spectrum of CNMIST3, CNMIST5, CNMIST7 and CNMIST9**

CNMIMA1 to CNMIMA9, while for the CNMISTs the peak intensities remain almost similar, which indicates that the CNMIMAs are random one while CNMISTs alternate one.

The thermograms (TGs) were obtained by heating the polymer and copolymers samples in N$_2$ at 10°C/min. The temperatures for initial decomposition T$_i$, final decomposition T$_f$, maximum rate of weight loss T$_{max}$, fifty percent decomposition T$_{50}$, and residue at 500°C determined from TGA for few selected polymer samples are summarized in Table 6.

Figure 8 (a): ^{1}H-NMR spectrum of CNMIMA1, CNMIMA3, CNMIMA5, CNMIMA7 and CNMIMA9 at 400 MHzin CDCl$_3$

The values of integral procedural decomposition temperatures (IPDT), an index of thermal stability as proposed by Doyle [32], were determined from a mass loss curve and are included in Table 6. The maleimide polymer PNMI is a potential heat-resistant material and has a significantly higher thermal stability than PMMA. One-step degradation at temperature of over 320°C was observed for PNMI. The T$_f$ was about 480°C. The copolymersamples CNMIMA1, CNMIMA3, CNMIMA5 and CNMIMA7 also decomposed in a one-step procedure. As the content of NMI in the feed has increased, the copolymers began to decompose at higher T$_i$ and the weight loss for the degradation-step became smaller. An increase in residual char yield (%) at 500°C was also observed by increasing the NMI content in the copolymer samples. Similarly, the thermal stability of copolymers of NMI with styrene also enhanced as the NMI content increase in copolymers.

Figure 8 (b): ^{1}H-NMR spectrum of CNMIST1, CNMIST3, CNMIST5, CNMIST7 and CNMIST9 at 400 MHzin CDCl$_3$

Table 6: Thermal Behavior of Homo and Copolymer Samples in N_2 Atmosphere

Polymer code	degrad. Step	T_i ^0C	T_{max} ^0C	T_f ^0C	T_{50} ^0C	IPDT at 500^0C	Residue At 500^0C %	E_a kcal/mol	n
PNMI	I	320.0	400.0	480.0	397.0	377.0	20.0	41.5	1.0
PMMA	I	236.0	282.0	318.0	337.0	323.0	1.1	27.5	1.0
	II	318.0	401.0	439.0	---	---	---	35.5	1.0
CNMIMA1	I	270.0	370.0	430.0	349.0	330.0	5.1	29.2	1.0
CNMIMA3	I	300.0	370.0	430.0	355.0	340.0	9.7	31.2	1.0
CNMIMA5	I	300.0	370.0	460.0	367.0	349.0	17.3	33.3	1.5
CNMIMA7	I	310.0	380.0	460.0	374.0	358.0	18.1	34.7	1.0
CNMIST1	I	300.0	370.0	430.0	349.0	340.0	10.9	34.9	1.0
CNMIST3	I	310.0	370.0	430.0	363.0	351.0	11.7	37.1	1.0
CNMIST5	I	310.0	380.0	450.0	379.0	359.0	14.8	37.7	1.0
CNMIST7	I	320.0	390.0	480.0	386.0	368.0	18.2	38.7	1.0
CNMIST9	I	330.0	400.0	480.0	398.0	373.0	18.6	39.7	1.0

T_i= initial decomposition,T_{max} = maximum rate of weight loss,T_f= final decomposition, T_{50} = fifty percent decomposition T_{50}, IPDT = value of integral procedural decomposition temperatures (IPDT),and $E_a$and n stands for energy of activation and order of thermal degradation.

The results in Table 6 clearly indicate that the thermal stability of vinyl polymers is greatly enhanced by copolymerizing them with NMI and it tends to increaseas the NMI content is increased in the copolymers. This is because of the incorporation of five member planner cyclic structure in the chain of copolymer enhances the thermal stability of copolymer [11]. The activation energy Ea of thermal degradation, also given in Table6, was estimated by employing the Broido method[33]. The value of Ea, 41.50 kcal mol^{-1}, for the first step degradation of PNMI is higher than 27.5 and 35.50 kcal mol^{-1} for PMMA. The values of Ea for the first step degradation for CNMIMA1-CNMIMA9 varied from 29.16 to 34.68 kcal mol^{-1}. In case of CNMIST the values of Ea for the first step degradation vary from 34.91 to 39.68 kcal mol^{-1}. The order of degradation reaction for PNMI, CNMIMAs and CNMISTs determined by Horowitz-Matzger method[34]isone, except the first and second step of CNMIMA5. For latter step it is one and half.

Gel Permeation Chromatography

$\overline{M}_n$, $\overline{M}_w$, $\overline{M}_v$ and polydispersity index (PD) from the GPC are determined for few selected polymer samples of CNMIMA andCNMIST. Table 7 shows that the values of $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_v$ for copolymer CNMIST are in the range from 33125 to 9856, 38376 to 11290 and 37520 to 11079 g/mol, respectively, and $\overline{M}_n$ and $\overline{M}_w$ are in the range from 4793 to 1591 and 5960 to 1660g/mol, respectively, for CNMIMA. Thus, the average molecular weights decrease with the increase in the content of maleimide in copolymers. It is due to increase in steric

hindrance, the degree of polymerization decreases. The average molecular weight of series CNMIST is higher compared to CNMIMA may be as a result different duration of polymerization. In former case it was 14 hrs while in later case it was only 9 h. The polydispersity index is in the range 1.04 to 1.28, quite close to unity.

Table 7: GPC Data for Copolymaleimides

Polymer code	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}v$	PD*
CNMIMA1	4793	5960	----	1.24
CNMIMA9	1591	1660	----	1.04
CNMIST1	33125	38376	37520	1.16
CNMIST3	25699	30741	29934	1.19
CNMIST5	17324	20798	20234	1.2
CNMIST7	10992	14102	13617	1.28
CNMIST9	9856	11290	11079	1.15

* PD represents polydispersity index $\overline{M}_w$ / $\overline{M}_n$.

Conclusion

The investigated copoly(vinyl-co-maleimide)s show excellent solubility in acetone, dioxane, THF, DMF, DMSO, benzene, nitrobenzene, chloroform, 2-butanone, chlorobenzene and ethyl acetate. They are partially soluble in aniline and carbontetrachloride. The average value of reactivity ratios r_1 and r_2 are 0.85 and 1.06 in NMI/MMA system, 0.80 and 0.15 in NMI/ST system. Alfrey-Price Q-e values for NMI were calculated as Q = 0.84 and e = 0.72 in NMI/MMA system, Q = 0.79 and e = 1.85 in NMI/ST

system. The thermal stability of vinyl polymers is greatly enhanced by polymerizing them with NMI and it tends to increase as the NMI content is increased in copolymer samples. The intrinsic viscosity of copolymer solutions decreases as we increase the maleimide content in the the copolymer sample. Molecular weights of CNMISTs are higher than the CNMIMAs. Incorporated five member planner cyclic structure in the chain of copolymer enhances the thermal stability of copolymer. Thus, the copolymers of N-1-naphthylmaleimide with MMA/ST of desired properties can be obtained by suitable choice of feed ratio.

References
1.Critchley J., Knight G., and Wright W., Heat Resistant Polymers, Plenum press, New York. **(1983)**

2.Mittal K., Polyimides in Synthesis, Characterization and Applications Ed(s), Plenum Press, New York, Vols. **1&2, (1984)**

3.Feger C., Khojasteh M., McGrath J., Ed(s). Polyimides: Materials, Chemistry and Characterization, Elsevier Science Publishers B. V., Amsterdam, **(1989)**

4.Lupinski J., Moore R., Ed(s). Polymeric Materials for Electronics Packaging and Interconnection. in ACS Symposium Series 407, American Chemical Society, Washington, DC **(1989)**

5.Patel C.B., Malek N.I., Oswal S.L., Synthesis and radical polymerization of N-[4-N'-(Phenylamino-carbonyl) phenyl]maleimide and its copolymerization with methyl methacrylate, *J. Macromol. Sci., Part A, Pure & Appl. Chem.,* **43(2)**, 289-303 **(2006)**

6.Oswal S.L., Patel C.B., Malek N.I., Synthesis and radical coplymerization of ethyl acrylate and butyl acrylate with N-[4-N(phenylamino-carbonyl) phenyl] maleimide, *Int. J. Polym. Mater.,***56(1)**, 27-41 **(2007)**

7.Riddick J., Bunger W., Sakano T., Organic Solvents Physical Properties and Methods of Purification. Wiley Interscience, New York **(1986)**

8.Searle N., U. S. Patent 2, 444, 536, United State of America (E. I. Dupont de Nemours and Co.) **(1948)**

9.Hoyt A., Benicewicz B.,Rigid rod molecules as liquid crystal thermosets. I. Rigid rod amides, *J. Polym. Sci., Part A, Polym. Chem.,* **28(12)**, 3403-3415 **(1990)**

10.Barrales-Rienda J., Gonzalez de la, Campa J., Gonzalez Ramos J, Free radical copolymerization of N-phenyl maleimide, *J. Macromol. Sci. Chem.,* **A11(2)**, 267-286 **(1977)**

11.Oswal S.L., Bhandari V.K., Bhamore P., Malek N.I., free radical copolymerization of methyl methacrylate and styrene with N-(4-carboxyphenyl) maleimide, *Int. J. Polym. Mater.,* **56(4)**, 412-435 **(2007)**

12.Fineman M., Ross S., Linear method for determining monomer reactivity ratios in copolymerization, *J. Polym. Sci.,* **5(2)**, 259-262 **(1950)**

13.Kelen T., Tudos F., Analysis of linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method, *J. Macromol. Sci., Chem.,* **A9(1)**, 1-27 **(1975)**

14.Alfrey T., Price C., Relative reactivities in vinyl copolymerization, *J. Polym. Sci.,***2(1)**, 101-106 **(1947)**

15.Patel M.H., Oswal S.B., Synthesis and Characterization of Homo and Copolymers of N-4-Azodiphenyl maleimide with Methyl Methacrylate and Styrene, *Int. J. Polym. Mater.,* **60(8)**, 542-561 **(2011)**

16.Huggins M.L., The viscosity of dilute solutions of long-chain molecules. IV. Dependence on Concentration, *J. Amer. Chem. Soc.,* **64(11)**, 2714-2718 **(1942)**

17.Kraemer E., Molecular weights of celluloses and cellulose derivatives, *Ind. Eng. Chem.,* **30(10)**, 1200-1203 **(1938)**

18.Gowarikar V., Vishvanathan N., Sreedhar J., Polymer Science, Wiley Eastern Ltd. **(1986)**

19.Solomon O., Ciuta I., Determination de la viscosite intrinseque de polymers par une simple determination de la viscosite, *J. Appl. Polym. Sci.,* **6(24)**, 683-686 **(1962)**

20.Deb P., Chatterjee S., On polynomial expansion of log relative viscosity, *Die Makromol. Chem.,* **125(1)**, 283-285 **(1969)**

21.Rudin A., Wagner R., A new one-point intrinsic viscosity method, *J. Appl. Polym. Sci.,* **19(12)**, 3361-3367 **(1975)**

22.Ram Mohan Rao M., Yaseen M., Determination of intrinsic viscosity by single specific viscosity measurement, *J. Appl. Polym. Sci.,* **31(8)**, 2501-2508 **(1986)**

23.Khan H.U., Gupta V.K. and Bhargava G.S., Determination of intrinsic viscosity of high polymers through a single specific viscosity measurement, *Polym. Comm.,* **24(6)**, 191-192 **(1983)**

24.Raju K.V.S.N. and Yaseen M.,New equation for estimating [η] from single-viscosity measurement in dilute solution, *J. Appl. Polym. Sci.,* **45(4)**, 677-681 **(1992)**

25.Gracia D., FTIR studies of PMR-15 polyimides, *J.*

Polym. Sci. B, **25**(**11**), 2275-2282 **(1987)**

26.Park J., Jang S., Synthesis and characterization of bismaleimides from epoxy resins, *J. Polym. Sci., Part A, Polym. Chem.,* **30**(**5**), 723-729 **(1992)**

27.Oishi T., Fujimoto M.,Synthesis and polymerization of *N*-[4-*N* ⁻ - (α -methylbenzyl) aminocarbonylphenyl] maleimide, *J. Polym. Sci., Part A, Polym. Chem.,* **30**(**9**), 1821-1830 **(1992)**

28.Hocking M., Syme D., Axelson D., Miclaelian K., Water-Soluble imide-amide copolymers. II. Preparation and characterization of poly (acrylamide-co-*p*-maleimidobenzoic acid), *J. Polym. Sci., Part A, Polym.*

Chem., **28**(**11**), 2969-2982 **(1990)**

29.Silverstain R., Bassler G., Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., New York. **(1991)**

30.Oswal S.L., Patel M.H., Patel S.M., Copolymerization of methyl methacrylate, ethyl acrylate and butyl acrylate with N-2-Anisylmaleimide and characterization of the copolymers, *Int. J. Polym. Mater.,* **56**(**11**), 307-326 **(2007)**

31.Otsu T., Yasuhara T., Masumoto A, Synthesis, characterization and application of poly[substituted methylene] S., *J. Macromol. Sci. Chem.,* **A25**(**5-7**), 537-554 **(1988)**