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A Comparative Study of N-(O-Nitrophenyl) Maleimide Polymer and N-(M-Nitro Phenyl) Maleimide and Effect of Electron Withdrawing Group on Thermal Stability



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ABSTRACT

This article investigated a comparison study of N-(O-Nitrophenyl) maleimide polymer and N-(M-Nitro phenyl) maleimide polymers. Monomer were prepared by O-Nitro aniline and M-Nitro aniline with methyl methacrylate. synthesis homo and copolymers were characterized by FT-IR and ¹H-NMR. reaction was kept and trial for different time hours and obtained result is find out. AIBN and BPO used as a free radical initiator. THF and DMF were used as a solvent. Number average and weight average molecular weight was determined by the gel permission chromatography. Intrinsic viscosity was determined by the Hubelhod viscometer and Thermal stability was determined by the TGA Techniques and initial temperature and final temperature is recorded. Polymerization reaction is determined by the PDI index, relation in between molecular weight and intrinsic viscosity is also calculated and our main focused that what effect will come when electron group present on benzene ring and studied polyelectrolyte effect in solvent. In addition, some physical constants of polymers such as density, solubility parameter, and viscosity were determined.



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INTRODUCTION

There is a major current research interest to synthesis of new maleimides polymer. Polymaleimides represent a class of rigid polymers having excellent thermal stability, high mechanical and electrical properties beside good chemical resistance [1-3]. In spite of all these properties, poor solubility and process ability limit the applications of polyimides [4-6]. Although all the difficulties overcome by the new methods. Many efforts have been made to solve these problems since developing these properties can be an important approach to their use in many new fields [7-13]. At Present time overcome to this difficulties. We will make new homopolymer and copolymer. Thus in the present work researcher has tried to improve polymaleimides properties by two ways the first one involved introducing of bulk Schiff base moieties as pendant groups in polymeric chains of polymaleimides, while the second way involved introducing of maleimides substituted with Schiff bases into copolymerization with acrylonitrile since copolymerization is the most efficient method for modifying polymer properties [14-17]. The search for new catalysts or initiators, however, has continued due to the industry and commercial significance of the problems that previous studies on the solution polymerization of N-PMI had to deal with, such as yield losses, low molecular weights, long response times, lack of solvents, catalyst removal from resultant polymers, and extreme conditions (in the dark, under nitrogen atmosphere, or at -78 °C) (Okamoto, 1991). The present work showing that what effect will come on the thermal stability when electron group was present on the ring. Although polymer having vast applications. Our aim that comparison study of ONPMI and HONPMI in different manners like as solubility, viscosity, molecular weight. TGA.

MATERIALS

Maleicanhydride were recrystallized from acetone. Methylmethacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl₂ for 6 hours and distilled [18]. The head and tail fractions were discarded. AIBN (2,2_-azobis-isobutironitrile (spectrochem.)) was recrystallized twice from methanol prior to use. BPO (benzoyl peroxide CDH) was used as received. THF was purified by distillation after being refluxed for 2 h in the presence of sodium. Dioxane and DMSO were used after distillation. DMF and methanol used in the present work were of analytical grade and were used as received.

Measurements

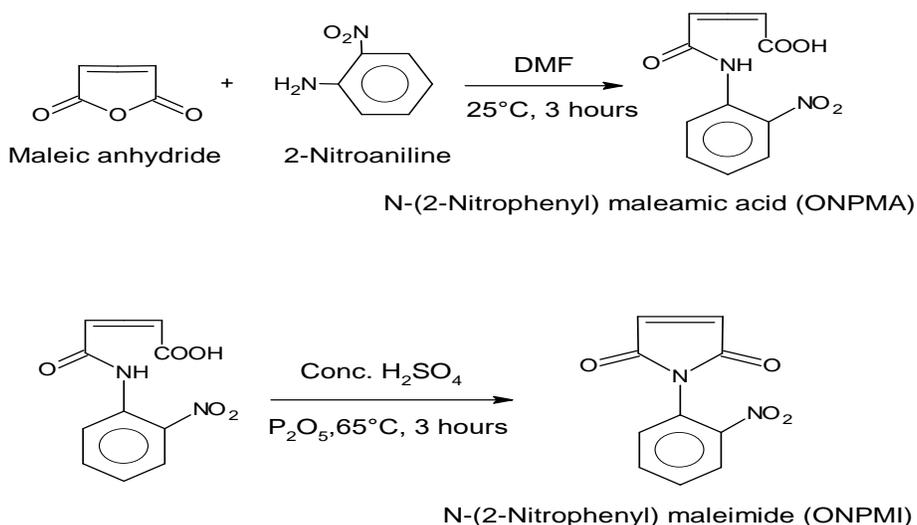
$^1\text{H-NMR}$ spectra of monomer and polymer samples were taken in DMSO- d_6 on a Bruker DPX-200/DPX-300 spectrometer at 200/300 MHz. The internal reference used was TMS. FT-IR spectra of the monomer and polymer sample were recorded on a Shimadzu 8201 PC (4000-400 cm^{-1}) FT-IR spectrometer, using KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.2 °C, using an Ubbelohde suspended level viscometer. Elemental analysis was made on Carlo Erba Model NA 500 series analyzer. The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 °C/min.

Methods

Preparation of N-(2-Nitrophenyl) maleamic acid: Nitroaniline (13.8 gm for 0.1mol) and 9.8 gm maleic anhydride were taken in 30ml DMF. The solutions kept stirring for three hours at 25°C. The reaction mixture was poured in crushed ice. Yellow solid precipitate was obtained, then filtered and dried under vacuum. It was recrystallized from methanol to obtain pure N-(2-Nitrophenyl) maleamic acid. Yield was 70%, m.p. 145°C.

N-(2-Nitrophenyl) Maleimide: Cyclodehydration of the 2-Nitromaleamic acid, an intermediate to maleimide was carried out by treating former with conc. H_2SO_4 and P_2O_5 . The solution stirring for three hours at 65°C. Then the solution poured in crushed ice or cooled water, obtained to yellow solid precipitate filtered and washed with water and dried. N-(2-Nitrophenyl) maleimide was recrystallized from ethyl alcohol solvent. The yield was 65%, m.p. 120°C. Synthesis monomer characterized by FT-IR spectra. The major characteristic FT-IR spectra with characteristic absorption frequencies 3105 (aromatic and alkene C-H stretch), 1716, 1790, (symmetric and asymmetric stretch of C=O in a five-member imide ring 1528, 1354 (symmetric and asymmetric stretch of NO_2 group), 1606(C=C, alkene) 1586, 1491, 1454 (C=C, aromatic), 1150 (C-N stretch), 957(CH=CH), 834 (1,2 disubstituted of benzene), as shown in these are consider with the structure of ONPMI [19]. $^1\text{H-NMR}$, 400 MHz, ref. TMS, solvent DMSO- d_6 , δ , ppm (a) two methine (CH=CH) protons at δ 6.93 (s) ppm and (b) one phenyl protons at δ 7.29-8.20(m). synthesis ONPMI shown in scheme-1.

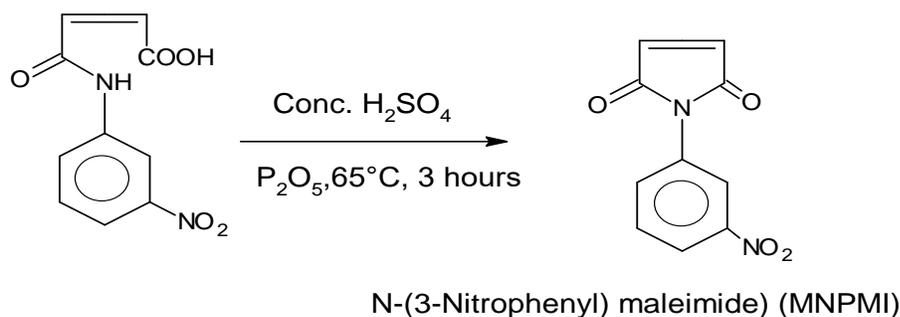
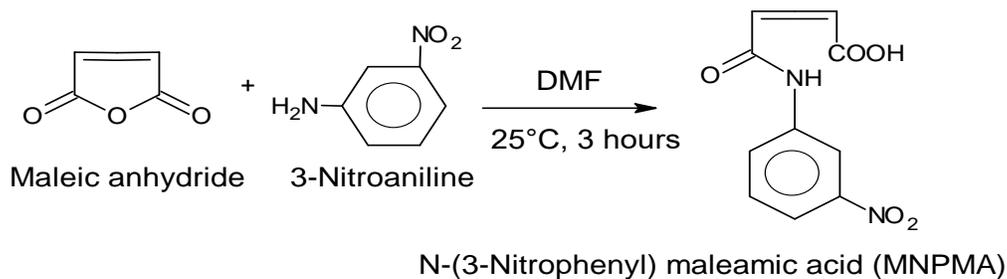
Scheme-1



Synthesis of 3-Nitro phenyl maleimide: 3-Nitroaniline 13.8 gm for 0.1 mol and 9.8 gm (0.1mol) maleic anhydride were taken in 30 ml DMF. The reaction mixture kept stirring for three hours at 25°C. The reaction mixture was poured in crushed ice or cooled water, yellow colour precipitate was obtained, then precipitate filtered and dried under vacuum. It was recrystallized from ethanol to obtained pure 3-Nitrophenylmaleamic acid. The yield was 80%, m.p. 165°C.

Cyclization of N-(3-Nitrophenyl) maleamic acid : 2.36 gm of 3-Nitrophenylmaleamic acid were taken in 30 ml DMF, in flat round bottom flask . The reaction mixture treating former with conc. H₂SO₄ and P₂O₅. The reaction mixture was stirred for three hours at 65°C, the reaction mixture was cooled and poured in to ice water. The yellow precipitate was obtained, precipitate was filtered and washed several times with water and dried. The product was recrystallized from ethanol. The yield was 70%, m.p. 192°C. Reaction of preparation are given in scheme-2.

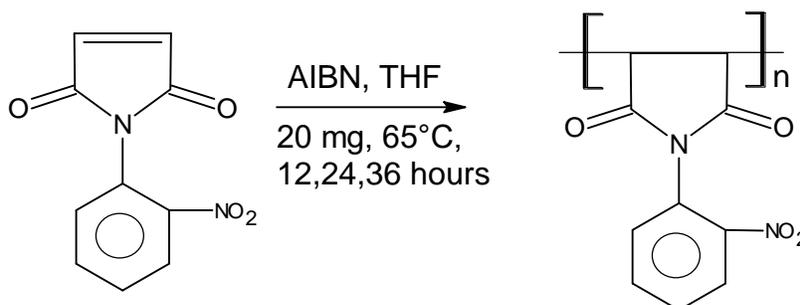
Scheme-2



Homopolymerization of N-(2-Nitrophenyl) maleimide (HONPMI)

Polymerization of N-(2-Nitrophenyl) maleimide was carried out in THF solvent. Using radical initiator AIBN 65°C. 2-Nitrophenylmaleimide (2.18 gm), 0.01 mol and THF in 30ml were placed in round bottom flask with reflux condenser. To this solution 20mg AIBN was added and the reaction mixture was refluxed on heating mantle at 65°C. For 12, 24, 36 and 48 hours. Very less polymer was formed if the reaction was carried out up to 12 hours. Yield was obtained 26.45% for 24 hours. The synthesized polymer was isolated in excess quantity of methanol water mixture. It was dried under vacuum at 60°C.

Scheme - 03



Homopolymerization of N-(3-Nitrophenyl) maleimide (HMNPMI)

Homopolymerization of N-(3-Nitrophenyl) maleimide (2.18 gm, 0.01 mol) was carried out in THF solvent using free radical initiator AIBN at 65°C. The polymerization reaction mixture was placed in round bottom flask, with reflux condenser for 24 hours. Very less polymer was formed. The reaction mixture was isolated in excess quantity of methanol water mixture it was dried under vacuum at 60°C. The yield was obtained 29.45%.

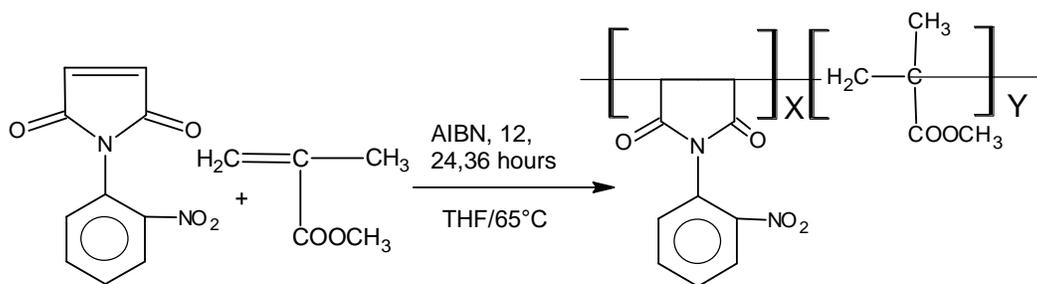
Scheme - 04



Copolymerization of N-(2-Nitrophenyl) maleimide with MMA (CONPMI)

2-Nitrophenylmaleimide (2.18 gm, 0.01 mol) and MMA (1.06 ml, 0.01 mol) in 30 ml THF solvent was taken in a round bottom flask. The copolymerization reaction was carried out at 65°C for 24 hours. Copolymer samples were isolated in water containing 20% methanol. The copolymer were purified by first dissolving in THF and then, reprecipitating in excess quantity of methanol water mixture. The precipitated copolymers were washed with methanol several times and dried at 60°C under vacuum. Yield was obtained 42.90%.

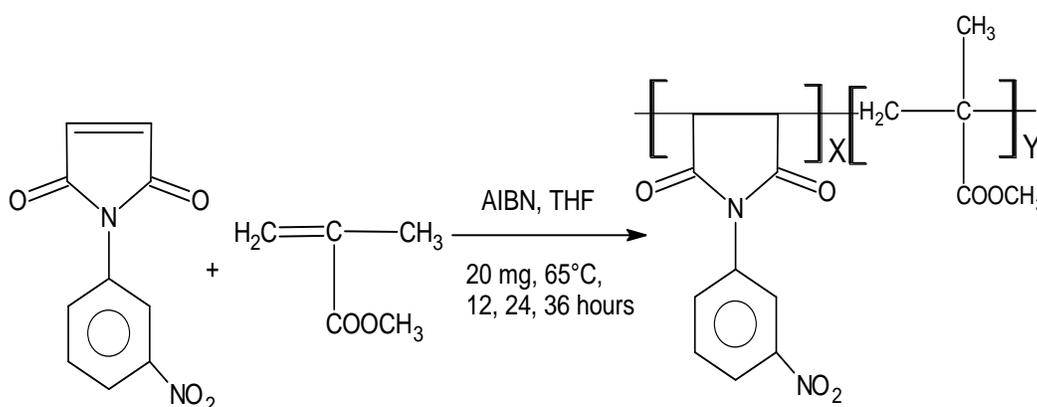
Scheme -05



Copolymerization of N-(3-Nitrophenyl) maleimide with MMA (CMNPMI)

3-Nitrophenylmaleimide (2.18 gm, 0.01 mol) and MMA (1.06 ml, 0.01 mol) in 60 ml THF solvent were taken in round bottom flask. The copolymerization reaction was carried out at 65°C for 24 hours. Copolymer samples were isolated in water containing 20% methanol. The copolymer purified by first dissolving in THF and then reprecipitating in excess quantity of methanol water mixture. The precipitated copolymers were washed with methanol several times and dried at 60°C under vacuum. The yield was obtained 39.75%.

Scheme – 06



ONPMI

FT-IR spectra with characteristic absorption frequencies 3105 (aromatic and alkene C–H stretch), 1716, 1790, (symmetric and asymmetric stretch of C=O in a five-member imide ring [19,20,21]. 1528, 1354 (symmetric and asymmetric stretch of NO₂ group), 1606(C=C, alkene)

1586,1491,1454 (C=C, aromatic) [22,23]. 1150 (C–N stretch) [23]. 957(CH=CH), 834 (1,2 disubstituted of benzene), as shown in (Fig. 1 in cm^{-1}) these are considered with the structure of ONPMI.

ONPMI

$^1\text{H-NMR}$,400 MHz , ref. TMS, solvent DMSO- d_6 , δ ,ppm) (a) two methine (CH=CH) protons at δ 6.93 (s) ppm and (b) one phenyl protons at δ 7.29-8.20(m). showing in Fig.2.

MNPMI

FT-IR spectra with characteristic absorption frequencies 3134 (aromatic and alkene C–H stretch), 1785, 1716 (symmetric and asymmetric stretch of C=O in five-member imide ring [19,20,21]. 1528, 1351 (symmetric and asymmetric stretch of $-\text{NO}_2$ group), 1623 (C=C, alkene), 1590,1437 (C=C, aromatic), 1150 (C-N-C stretch) [22,23]. 972(CH=CH),855(1,3disubstituted of benzene) as shown in (Fig.3 in cm^{-1}) these are consistent with the structure of MNPMI.

$^1\text{H-NMR}$ of MNPMI is observed : (a) two methine (CH=CH) protons at δ 7.23 ppm (s). and (b) one phenyl protons at δ 7.29-8.58 ppm (m). showing in Fig. 4.

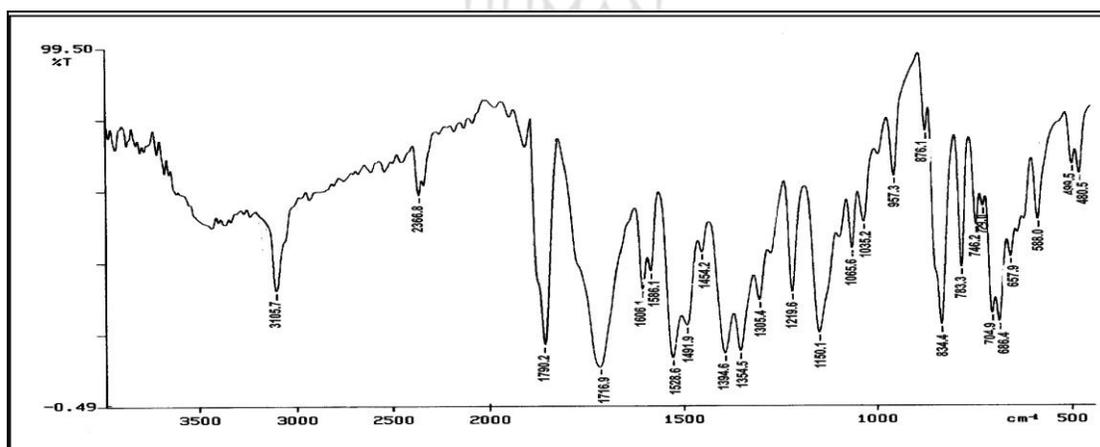


Fig.1 FTIR spectra of ONPMI

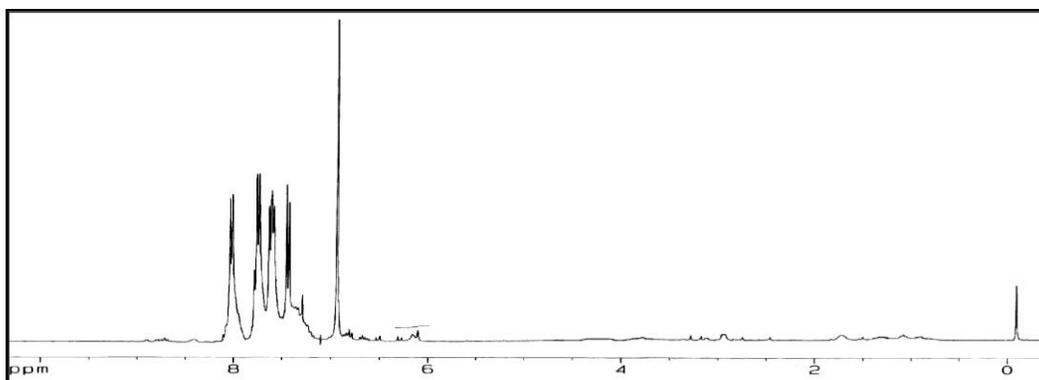


Fig.2 ¹H NMR of ONPMI

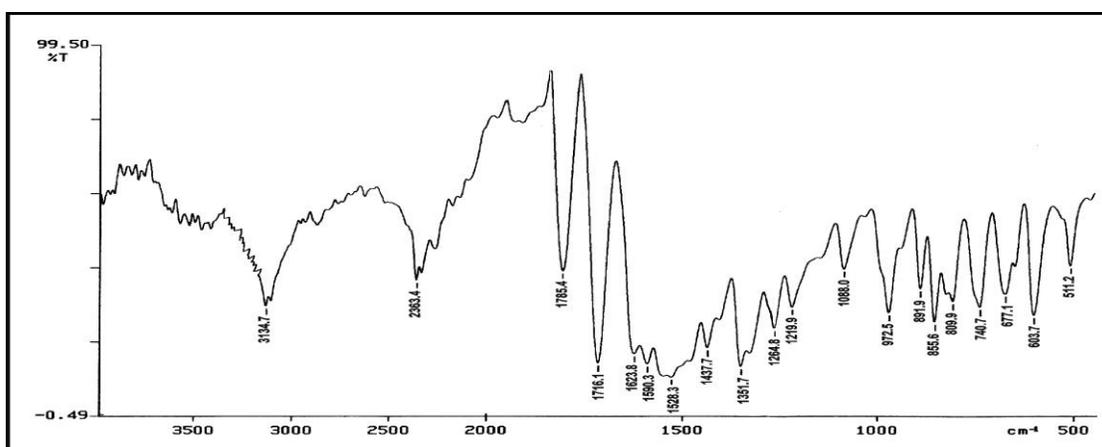


Fig.3 FTIR spectra of MNPMI

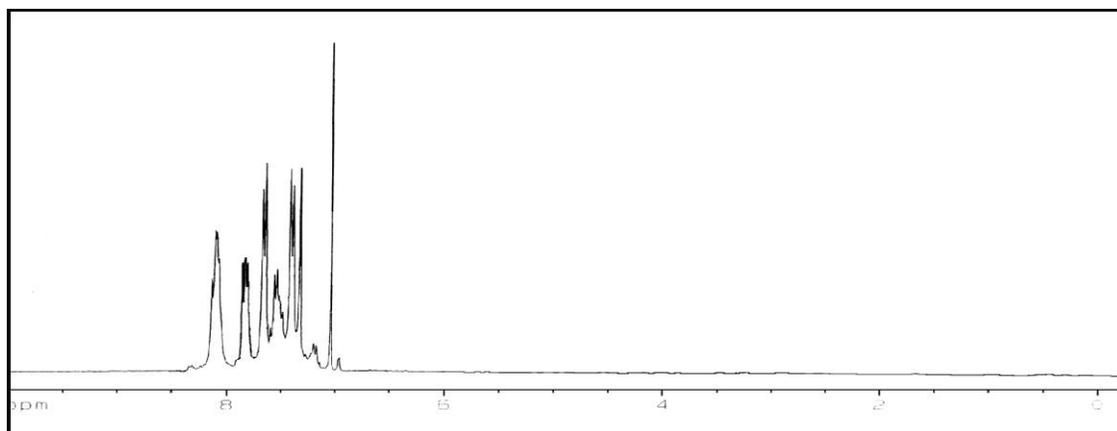


Fig. 4 ¹H NMR of MNPMI

RESULT AND DISCUSSION

CONPMI

In Fig. 5, showing absorption bands (in cm^{-1}) are calculated at 3150–2951 (Aromatic, C-H stretch, CH_3 , and CH_2 in MMA), 1721, 1770 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1602, 1535 (C=C stretch, aromatic), 1487, 1444 (C-H band, $-\text{CH}_2$), 1352 (due to overlapping of C-N stretch and C-H band of $-\text{CH}_3$ group), 1299, 1190, 1150 (asymmetric and symmetric C-O-C stretch, 831 (1,2-disubstituted benzene) and 781, 741 cm^{-1} (out of plane C-H band of benzene ring, and 699 (out of plane (aromatic ring C=C band). These values summarized of monomers of ONPMI and MMA are present in the copolymer. The absence of band of vinyl group at 957 cm^{-1} indicates the polymer formation via vinyl group. $^1\text{H-NMR}$ δ value in fig.6, obtained for four aromatic proton at 7.29–8.20 ppm. for 2H ($-\text{CH}-\text{CH}-$) and $-\text{OCH}_3$ signals at δ 3.60–3.79 ppm and $-\text{CH}_3$ signals at 0.85–1.23 ppm, 2H for ($-\text{CH}_2-$) observed at 1.83–2.49 ppm.

CMNPMI

In Fig.7, showing bands (in cm^{-1}) are at 2952–2996 (C-H stretch, CH_3 , and CH_2 in MMA), 1731–1775 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1599, 1536 (C=C stretch, aromatic), 1441, 1488 (C-H band, $-\text{CH}_2$), 1353 (due to overlapping of C-N stretch and C-H band of $-\text{CH}_3$ group), 1245, 1195 1148 (asymmetric and symmetric C-O-C stretch), 898 (1,3 disubstituted benzene), 799, 742 cm^{-1} (out of plane C-H band of benzene ring), 673, 602 (out of plane aromatic ring C=C band). Showing data indicated that both are unit and the absence of characteristic band of vinyl group at 972 cm^{-1} indicates the polymer formation via vinyl group. Fig.8 showing Chemical shift for CMNPMI is observed at 7.24–7.79 ppm (4 Ar-H), 2H ($-\text{CH}-\text{CH}-$) and $-\text{OCH}_3$ signals at 3.54–3.75 ppm and $-\text{CH}_3$ protons observed at δ 0.86–1.24 ppm. Two protons for $-\text{CH}_2-$ observed around 1.85–1.26 ppm.

HONPMI

The FT-IR spectrum of HONPMI is shown in Fig. 9, The major characteristic absorption IR frequencies (in cm^{-1}) 2935 (C-H stretch, alkane), 1785, 1721 (symmetric and asymmetric stretching of C=O in a five member imide ring, 1661, 1608, 1587, 1437 (C=C stretch, aromatic),

1502, 1386 (symmetric and asymmetric, Ar-NO₂ group), 1257 (asymmetric C-O-C stretch), 1189, 1102 (symmetric C-O-C stretch), 851 (1, 2 disubstituted benzene) 620 (out of plane aromatic ring C=C bend)[24] are consistent with the structure of HONPMI.

HONPMI

Fig.10 shows the chemical shift δ for HONPMI at 7.50–7.90 ppm 4H (m). 2H in –CH–CH– at 3.50–3.90 ppm. ¹H–NMR of HONPMI monomer chemical shift δ at 6.93 (s) ppm of –CH=CH– group. The disappearance of this peak in HONPMI shows that the radical polymerizations proceed through the double bond [26,27,28].

HMNPMI

The FT-IR spectrum of HMNPMI is shown in Fig.11, The major absorption bands observed at 3074 cm⁻¹ that correspond to aromatic C-H stretching[25,26]. 1778,1714 (asymmetric and symmetric C=O group), The bands appeared at 1621, 1588, 1439 cm⁻¹ represent C=C ring stretching. 1549, 1353 are shows the Ar-NO₂ group (asymmetric and symmetric group). 1265, 1221 (asymmetric C-O-C stretch), 1091 symmetric C-O-C stretch), 856 (1,3 disubstituted benzene) and 683 (out of plane aromatic ring C=C bend) are consistent with the structure of HMNPMI.

HMNPMI

The chemical shift δ for HMNPMI is shows in fig.12, observed at 7.23–7.35 (m) and 4.02–3.05 (d). The multiple in the range at δ 7.23–7.35 ppm. Two protons in –CH–CH– group have appeared at δ 4.02–3.05 ppm. ¹H–NMR of HMNPMI monomer shows chemical shift δ at 7.15 (s) ppm characteristic of –CH=CH– group. The disappearance of this in polymer HMNPMI shows that the radical polymerizations proceed via an opening of the double bond [26,27,28].

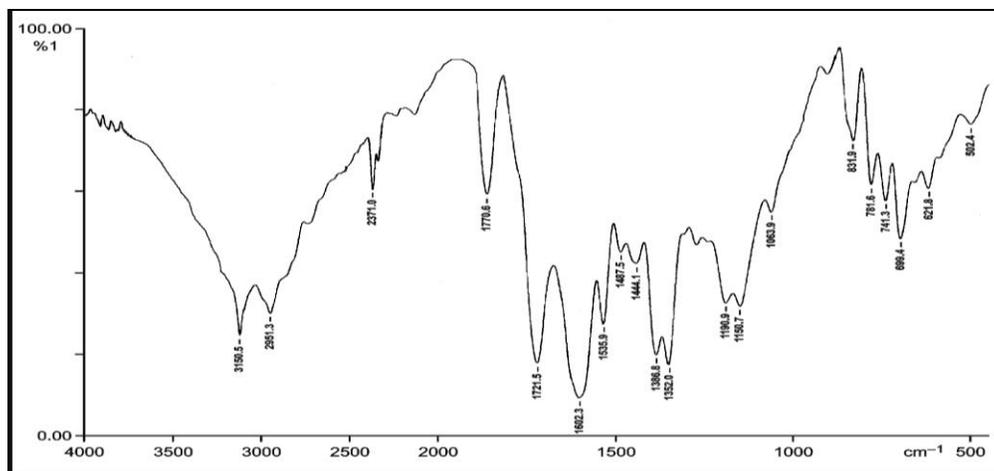


Fig.5 CONPMI

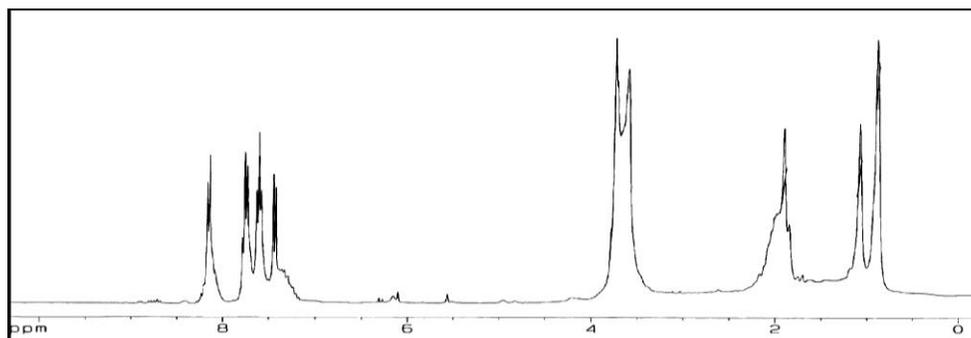


Fig.6 ¹H NMR of CONPMI

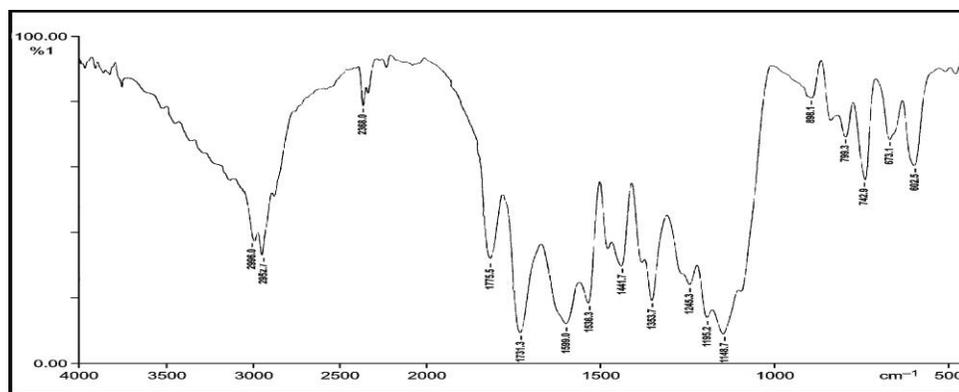


Fig.7 CMNPMI

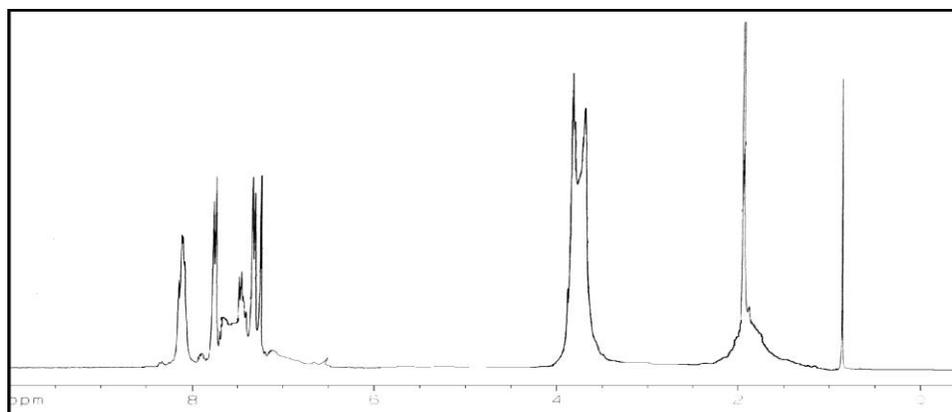


Fig.8 ¹H NMR of CMNPMI

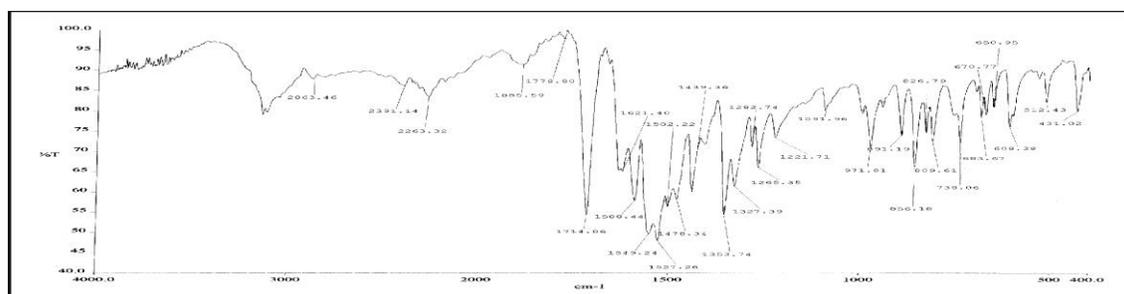


Fig.9 IR of HONPMI

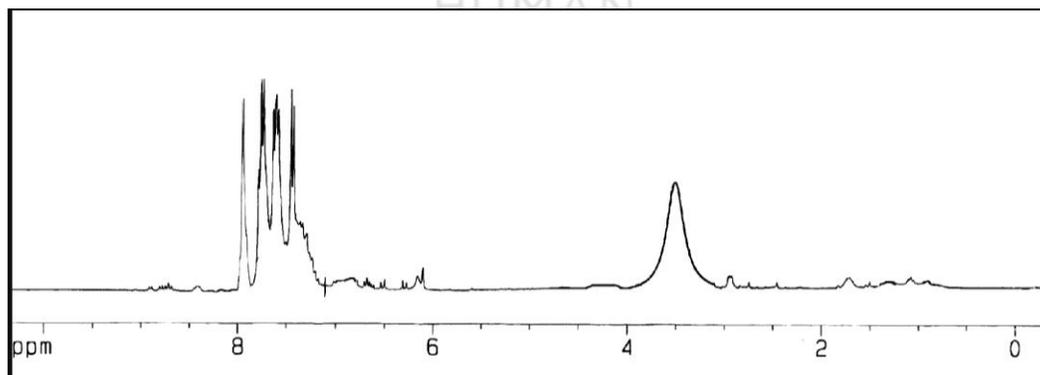


Fig.10 ¹H NMR of HONPMI

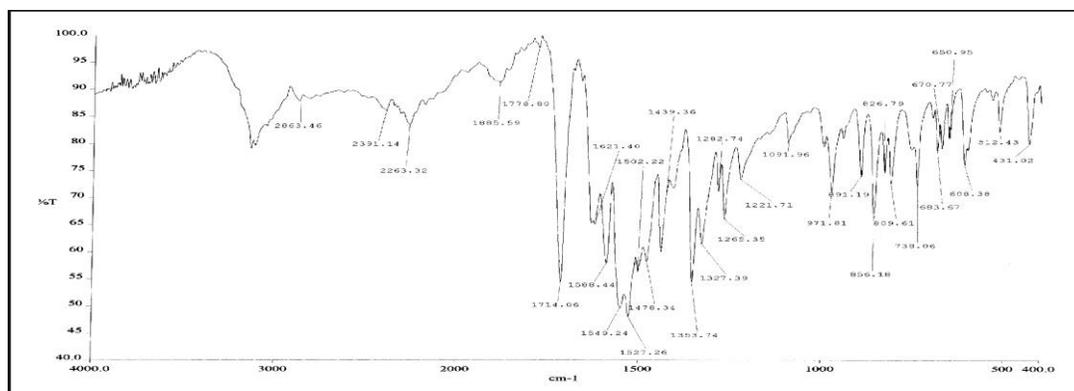


Fig.11 FT-IR of HMNPMI

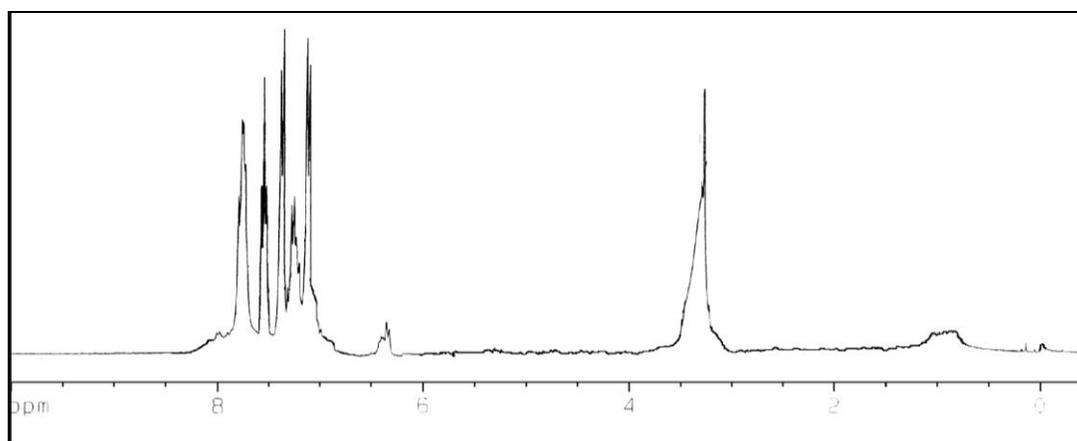


Fig.12 HMNPMI

Viscosity behavior and electrolyte behavior

Intrinsic viscosity $[\eta]$ 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. Effect of concentration is effected the viscosity. Graph plotted in between (η) reduced viscosity and concentration with a positive slope. The results of the viscosity measurement show linear relationship in all cases This clearly indicate non-electrolyte behavior of all the polymers solution under study. This could be understood from the fact that the Benzene and NO_2 groups have a very low dissociation constant and such groups in non-aqueous media may not dissociate appreciably to show any polyelectrolyte behavior. As size of monomer increases intrinsic viscosity increases. Intrinsic viscosity evaluation by following relations. Flow time of the concentration was measured by the Ubbelohde viscometer, where flow time of solution (t) and solvent t_0 ,

The specific viscosity was determined by following relations this was used to find reduced

$$\eta_{\text{reduced}} = \frac{\eta_{\text{specific}}}{C}, \quad \eta_{\text{sp}} = \frac{t-t_0}{t_0}$$

The intrinsic viscosity $[\eta]$ was obtained from the plots of reduced viscosity versus concentration by extrapolating the curve at $c \rightarrow 0$. Intrinsic viscosity (η)

The prepared different concentration solution of homopolymer and copolymers are summarized in Table.1.

Table.1 Typical data of viscosity measurements for Homopolymer and copolymers in DMF at 30°C

Homopolymer Code	Conc.(c) (g/dl)	Flow time sec.	η_{sp}	η_{sp}/c (dl/g)
HONPMI	0.1	286	0.0035	0.0350
	0.2	288	0.0105	0.0526
	0.3	291	0.0210	0.0701
	0.4	294	0.0315	0.0789
	0.5	297	0.0421	0.0842
	0.6	300	0.0526	0.0877
HMNPMI	0.1	287	0.0070	0.0701
	0.2	290	0.0175	0.0877
	0.3	293	0.0280	0.0930
	0.4	296	0.0385	0.0960
	0.5	300	0.0528	0.1050
	0.6	304	0.0666	0.1110
CONPMI	0.1	288	0.0105	0.1052
	0.2	292	0.0245	0.1228
	0.3	296	0.0385	0.1286
	0.4	300	0.0526	0.1315
	0.5	306	0.0736	0.1473
	0.6	312	0.0947	0.1578
CMNPMI	0.1	288	0.0152	0.1052
	0.2	293	0.0280	0.1403
	0.3	298	0.0456	0.1520
	0.4	304	0.0666	0.1666
	0.5	309	0.0842	0.1684
	0.6	317	0.1122	0.1871

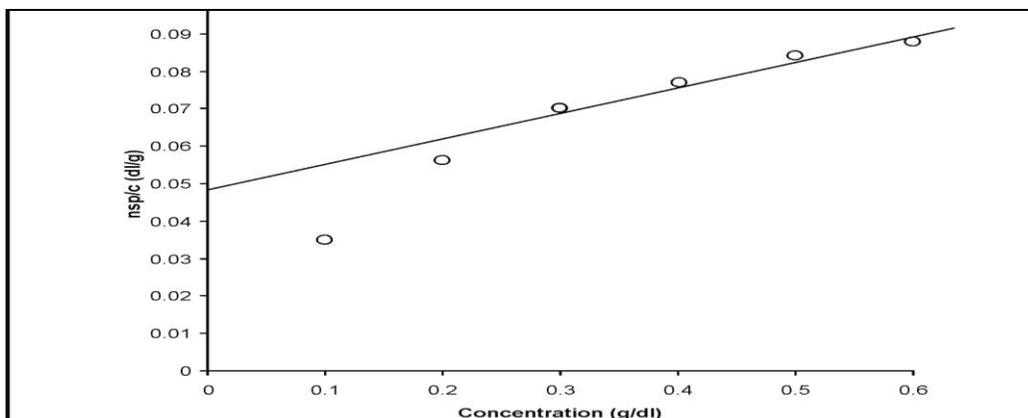


Figure. 13 Intrinsic viscosity of HONPMI

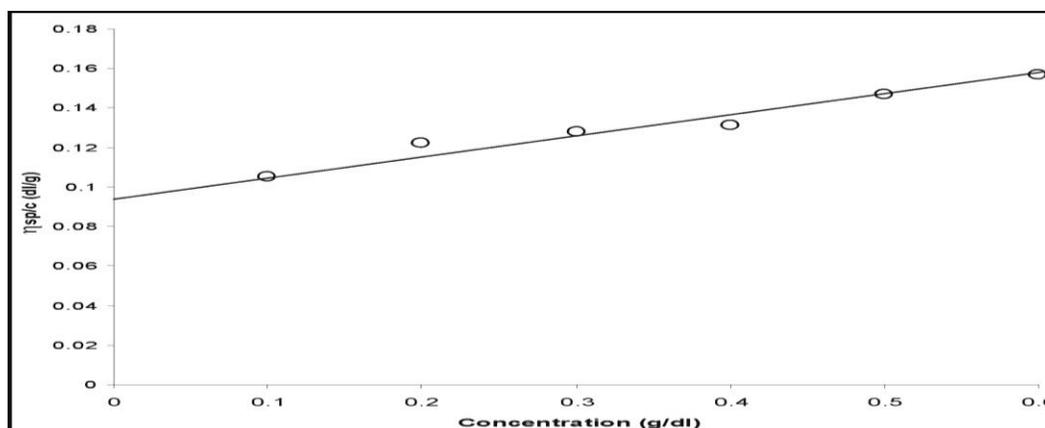


Figure.14 Intrinsic viscosity of CONPMI

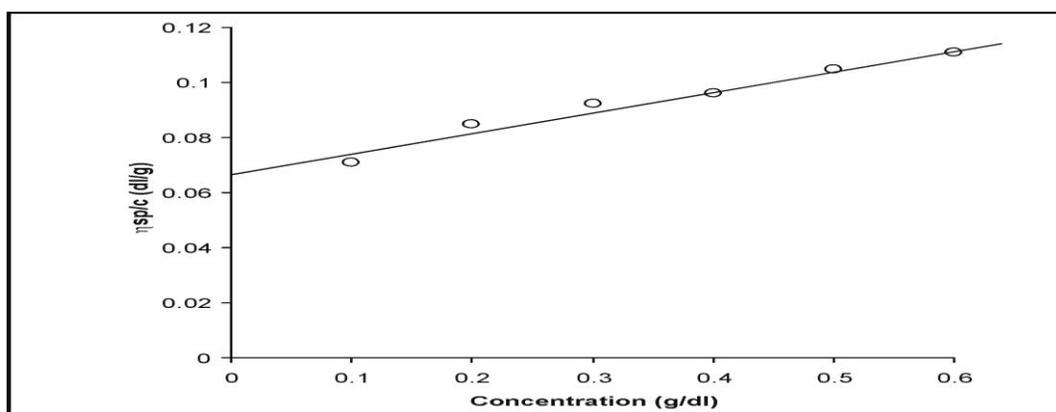


Fig. 15 Intrinsic viscosity of HMNPMI

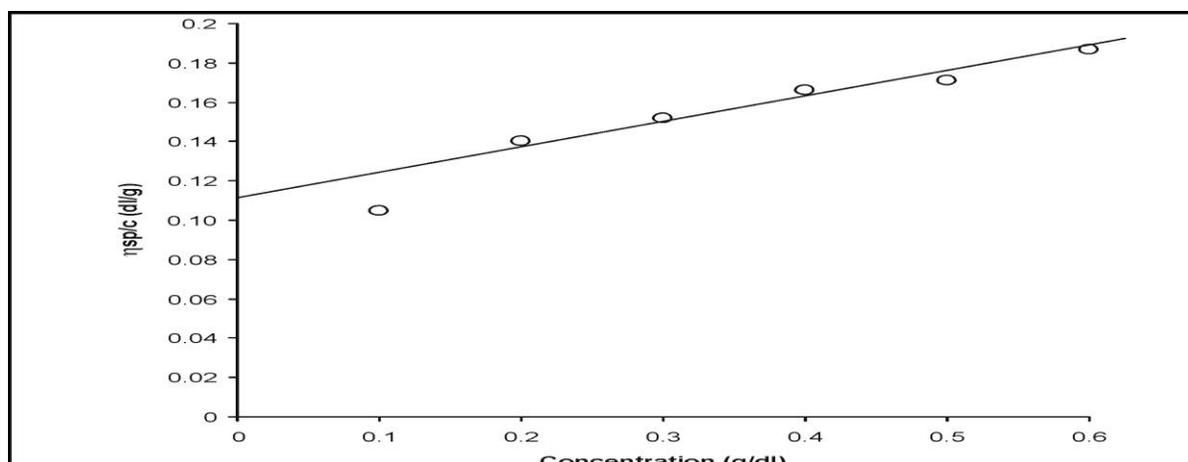


Fig. 16 Intrinsic viscosity of CMNPMI

From above fig.13,14,15 and 16 are showing that graph plotted in between reduced viscosity verses concentration, than positive slop is obtained and intrinsic viscosity of CONPMI is 0.092 and CMNPMI is 0.118 and Homopolymer of HONPMI is 0.048 ,HMNPMI is 0.065 and comparison of the intrinsic viscosity show that value of intrinsic viscosity copolymer having more than homopolymer. It is due to presence of both are unit in copolymer, while homopolymer having single repeat unit.

Viscosity-Molecular Weight Relationship

Kuwan –mark Howink Sakwada equation find out a relation in between intrinsic viscosity and molar mass. by this equation find out shape of polymers in given solution here if, The exponent α value is 0 it means polymer would be in spheres, $\alpha = 0.5$ when the polymer chain acquires unperturbed dimensions $\alpha = 0.764$ for perturbed coils and $\alpha = 2$ for rigid rods. The system in which α is close to 0.5 can be regarded to exist in θ conditions, (when the polymer coil has no interaction with the solvent molecule, it acquires unperturbed dimensions). Plot of $\log [\eta]$ versus $\log M_w$ gives straight line. In the present study when only homopolymers are taken $\alpha \approx 0.48741$. It shows homopolymer in unperturbed dimensions. In case of copolymers α value ≈ 1.4921 . Hence molecules shows are in shape of rigid rods.

$$[\eta] = K_{\eta} M^{\alpha}$$

$$\log [\eta] = \log K_{\eta} + \alpha \log M$$

log value is shown in the table.2

Table no 2: Typical data of number average and weight average and log values of Homopolymer and copolymer are given in Table .2

Polymer	Mw	Log Mw	$\eta \times 10^3$ dl/gm	Log $\eta \times 10^3$	Intrinsic viscosity
HONPMI	18984	4.2784	48	1.6812	0.048
HMNPMI	19063	4.2802	65	1.8129	0.065
CONPMI	39908	4.6011	92	1.9638	0.092
HONPMI	42238	4.6257	118	2.0719	0.118

Solubility behavior:

Solubility of synthesis homo and copolymer is very good parameter and its provided the solvent interactions with solvent. it gives more information about the solubility of polymers. Synthesis homo and copolymer showing very excellent solubility of polymer are summarized in table.3.

Table.3 Solubility of Homo and Copolymers are given in

Solvents	HONPMI	HMNPMI	CONPMI	CMNPMI
THF	Soluble	Soluble	Soluble	Soluble
DMF	Soluble	Soluble	Soluble	Soluble
DMSO	Soluble	Soluble	Soluble	Soluble
Dioxane	Soluble	Soluble	Soluble	Soluble
Acetone	Soluble	Soluble	Soluble	Soluble
Chloroform	Soluble	Soluble	Soluble	Soluble
Methyl acetate	Soluble	Soluble	Soluble	Soluble
Ethyl acetate	Soluble	Soluble	Soluble	Soluble
Benzene	Soluble	Soluble	Soluble	Soluble
Toluene	Soluble	Soluble	Soluble	Soluble
Chloroform	Soluble	Soluble	Soluble	Soluble
CCl ₄	P Soluble	In Soluble	Soluble	Soluble
CH ₂ Cl ₂	Soluble	Soluble	Soluble	Soluble

Effect of time on yield formation:

The homopolymerization and copolymerization carried out in THF Solvent at different time hours and obtained data revealed that the percentage yields are increased with time hours. Table.4, 5 are given.

Table 4: Percentage yield of HONPMI and CONPMI

Polymer code	Time hrs.	Yield %	State	Color
HONPMI	12	16.17	Solid	Yellow
	24	26.45	Solid	Yellow
	36	28.46	Solid	Yellow
	48	39.42	Solid	Yellow
CONPMI	12	17.25	Solid	Yellow
	24	42..90	Solid	Yellow
	36	52.50	Solid	Yellow
	48	54.55	Solid	Yellow

Table.5 Percentage yield of HONPMI and CONPMI

Polymer code	Time hrs.	Yield %	State	Color
HMNPMI	12	17.18	Solid	Yellow
	24	29.45	Solid	Yellow
	36	32.00	Solid	Yellow
	48	37.41	Solid	Yellow
CMNPMI	12	18.20	Solid	Yellow
	24	39.75	Solid	Yellow
	36	48.25	Solid	Yellow
	48	51.25	Solid	Yellow

Table.6 Copolymers of ONPMI with MMA (Time 12 hrs. initiator AIBN)

CONPMIMMA	Feed mol ratios ONPMI:MMA	Yield%	State	Colour
CONPMIMMA1	1:9	38.2	Viscous liquid	Light yellow
CONPMIMMA2	2:8	38.3	Viscous liquid	Light yellow
CONPMIMMA3	3:7	40.3	Viscous liquid	Light yellow
CONPMIMMA4	4:6	41.1	Solid powder	Light yellow
CONPMIMMA5	5:5	42.9	Solid powder	Light yellow
CONPMIMMA6	6:4	41.3	Solid powder	Light yellow
CONPMIMMA7	7:3	44.2	Solid powder	Light yellow
CONPMIMMA8	8:2	46.3	Solid powder	Light yellow
CONPMIMMA9	9:1	48.9	Solid powder	Light yellow

Table. 7 Copolymer composition for CMNPMI with MMA

Polymer code	Feed mole ratio	Feed composition	N%	Mole fraction of MNPMI in copolymer	Wt % of MNPMI
CMNPMI	MNPMI: MMA	X ₁	12.84	0.0: 0.0	100.00
CMNPMIMMA1	0.1: 0.9	0.1	2.20	0.092	17.13
CMNPMIMMA2	0.2: 0.8	0.2	3.12	0.135	24.29
CMNPMIMMA3	0.3: 0.7	0.3	4.35	0.200	33.87
CMNPMIMMA4	0.4: 0.6	0.4	5.82	0.288	45.32
CMNPMIMMA5	0.5 : 0.5	0.5	6.30	0.320	49.06
CMNPMIMMA6	0.6: 0.4	0.6	7.80	0.431	60.74
CMNPMIMMA7	0.7: 0.3	0.7	8.82	0.518	68.69
CMNPMIMMA8	0.8: 0.2	0.8	9.35	0.567	72.81
CMNPMIMMA9	0.9: 0.1	0.9	10.82	0.724	84.26

Thermal behavior of Homo and Copolymer:

The thermograms (TG) were obtained by heating the polymer and co-polymers samples in air at a rate of 10°C/min. typical curves of synthesis HONPMI, CONPMI, HMNPMI and CMNPMI are presented in Figs 7–10. The temperatures for initial decomposition T_i , final decomposition T_f , maximum rate of weight loss T_{max} , and decomposition rate, integral procedural decomposition temperatures and residue at 550°C determined. From TGA evaluated data are showing maximum weight loss at 400 °C minimum weight loss at 200°C.

Table 8: Thermal degradation of Homopolymer and copolymer samples

Polymer Code	% Weight loss at various temperature (°C)				
	163-240	300	400	500	550
HONPMI	1.48% at 210°C	17.94	86.16	89.84	91.17
HMNPMI	1.54% at 230°C	17.94	87.17	90.85	92.17
CONPMI	1.34% at 185°C	4.96	52.36	68.59	72.61
CMNPMI	5.10% at 190°C	7.21	40.29	50.06	57.82

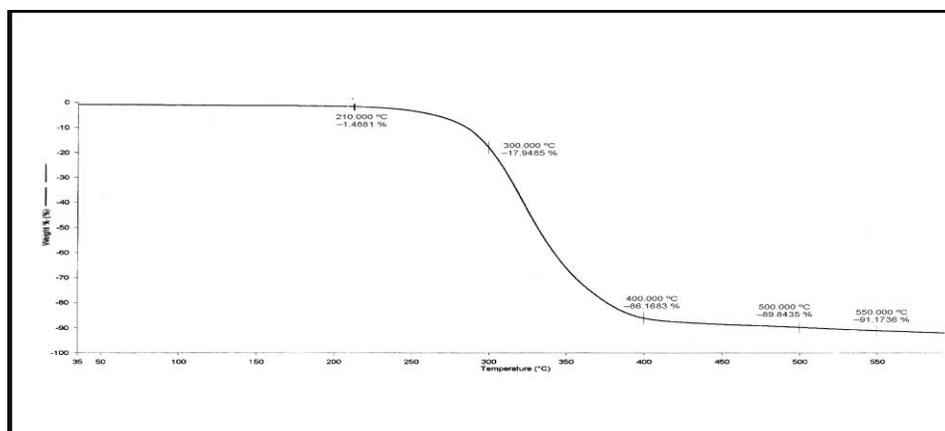


Fig.17 Thermogramh of HONPMI

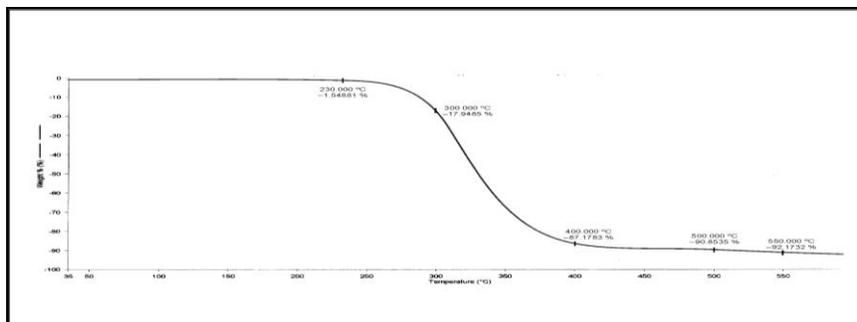


Fig.18 Thermogram of HMNPMI

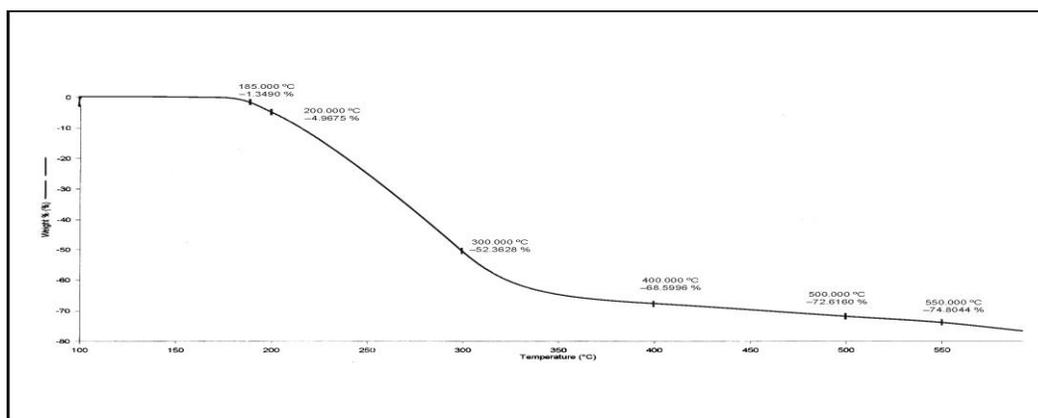


Fig.19 Thermogram of CONPMI

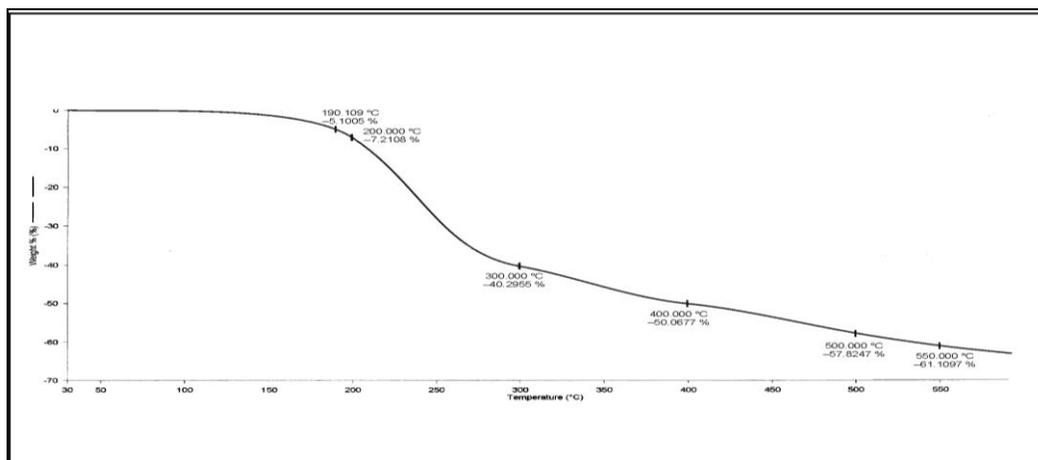


Fig.20 Thermogram of CMNPMI

CONCLUSION

Prepared homo and copolymers are showing the excellent thermal stability and thermal stability was recorded by thermogravimetric analysis. From the data table 8 are showing homopolymer is more stable than copolymer, because homopolymer having single repeat unit but in case of copolymer having both unit. From the comparison study of homo and copolymer which are affected by position of $-NO_2$ groups. In compound of CONPMI inductive effect is main major factor for stabilization, while in case of CMNPMI having $-NO_2$ groups, situated at meta position and $-NO_2$ group is meta directing, hence by resonance this compound is more stable. In case of HONPMI and CONPMI, $-NO_2$ groups present at Ortho position which make highly favorable for steric hindrance therefore HONPMI and CONPMI thermal stability is less stable than having meta position. Solubility of synthesis homo and copolymer shows excellent solubility in THF, DMF, DMSO, CCl_4 . The polymer having non electrolyte behavior in solvent it is approved by Huggins graphs.

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