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Research Article

RADICAL COPOLYMERIZATION AND DETERMINATION OF THERMAL STABILITY OF SOME NEW SUBSTITUTED PHENYL MALEIMIDE POLYMERS

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ABSTRACT

This article investigated a study and application of Kuhan-mark Howink Sakwada equation on some maleimides polymer and find out a relation in between intrinsic viscosity and molecular weight. Proposed work taken some maleimide substituted compounds and their study. In the research we selected some new maleimides monomer like as N-(O-Nitrophenyl) maleimide, N-(M-Nitro phenyl) maleimide and N-(P-Nitro phenyl) maleimide. Monomers were copolymerized with methyl methacrylate. Synthesized homo and copolymers were characterized by FT-IR and ^{1}H-NMR spectroscopy. Prepared monomers were polymerized at 12, 36, 48 and 72 hours on magnetic stirrer and AIBN and BPO used as a free radical initiator. THF and DMF were used as a solvent. Percentage yield were determined with time variations. 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 starting degradation temperature and final degradation temperature was recorded. Polymerization reaction proceed via free radical is determined by the PDI index. Percentage composition of N and C is calculated in monomer and polymer. This article focused that what actual shape of the homopolymer and copolymer showing in solvent and determined by Kuhan-mark Howink Sakwada equation.

Keywords: FT-IR, ^{1}H-NM R, TGA, MMA, GPC, Polymerization.

1. INTRODUCTION

For the past many years, the use of polymers has been increasing in history and today the use of polymers is increasing day by day, today we see that polymers are being produced and used in many fields. Polymer replaced the Iron which is very important in special cases like in sewerage pipe lines and many light and aeronautical parts. Polymers are useful in military and civil defense. Bullet proof jacket is well known use of maleimide polymer. In addition to that the process ability of maleimide polymer can also be enhanced by the incorporation of more flexible units within the polymer backbone [1]. Rigid imide ring hinder chair rotation, resulting in greater structural stiffness and higher thermal stability [2]. Flexibility was introduced in polymer chain by its copolymerization with vinyl monomer; copolymerization can improve the physical, mechanical and chemical properties of polymaleimides applications in different fields [3]. Maleimide and it's derivatives are a kind of very useful monomers. Their prepared homopolymer or copolymers are vastly used as coatings, adhesives, laminations and fibers because of their high heat-resistivity [4]. Polymaleimide (PMAI) can be defined as a type of high reactivity polymer often used as the polymer-based backbone of several functional materials with outstanding thermal stability. N-Phenylmaleimide (N-PMI) radical and anionic polymerization reactions have been observed [5]. N-Substituted maleimide copolymers with MMA, acrylates, butylacrylate showed excellent thermal properties accompanied by characteristic polymerization behavior and it has been approved by experimentally. But excess of N-substituted maleimide moiety, increases chain-rigidity, causes the drop of mechanical properties such as tensile strength and impact strength and achieved with enhancement of Tg-value [6-14]. Here we are focused to synthesis of some newly of N- Phenyl maleimide substituted polymer and determination of polymer shape in the solution by using of Kuhan-mark Howink Sakwada equation.

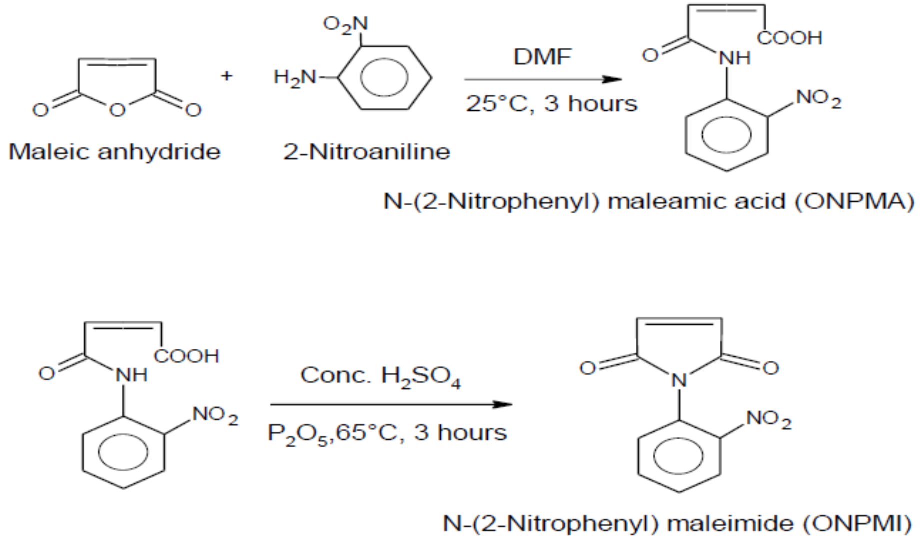
2. MATERIAL AND METHODS

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. Maleicanhydride were recrystallized from acetone. Methylmethacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous $CaCl_2$ for 6 hours and distilled [15]. The head and tail fractions were discarded. AIBN (2,2_-azobis-isobutironitrile (spector-chem)) was recrystallized twice from methanol prior to use. BPO (benzoyl peroxide CDH) was used as received ^{1}H-NMR spectra of monomer and polymer samples were taken in DMSO-d6 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.

2.1. Preparation of N-(2-Nitorphenyl) 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 was stirred for three hours at 65°C. Then the solution poured in crushed ice or cooled water, obtained a yellow solid precipitate which was 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.



Scheme-1

2.2. Synthesis of 3-Nitro phenyl maleimide

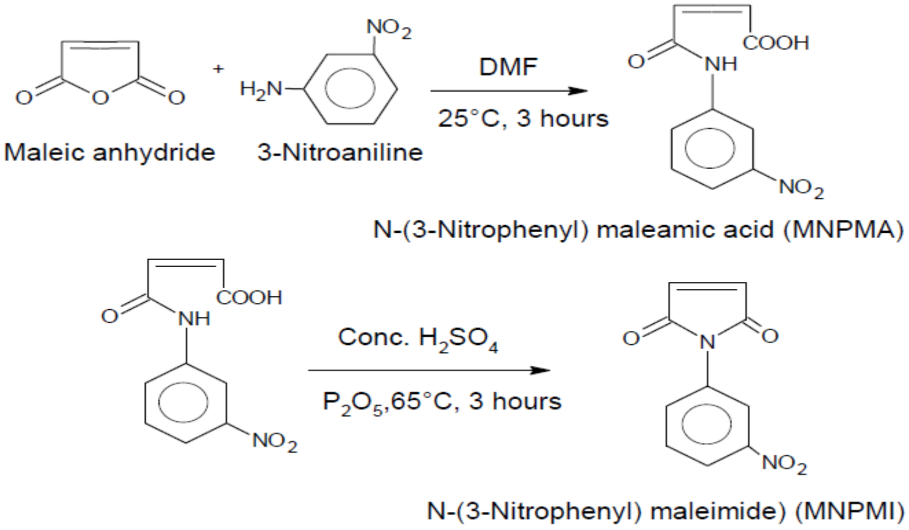
3-Nitroaniline 13.8 gm for 0.1 mol and 9.8 gm (0.1mol) maleic anhydride were taken in 30 ml DMF. The reaction mixture kept stirred for three hours at 25°C. The reaction mixture was poured in crushed ice or cooled water, yellow coloured precipitate was obtained which was filtered and dried under vacuum.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

Cyclization of N-(3-Nitrophenyl) maleamic acid : A 2.36 gm of 3-Nitrophenylmaleamic acid was taken in 30 ml DMF, in flat round bottom flask. The reaction mixture was treated with conc. H_2SO_4 and P_2O_5. The reaction mixture was stirred for three hours at 65°C, then cooled and poured into 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.

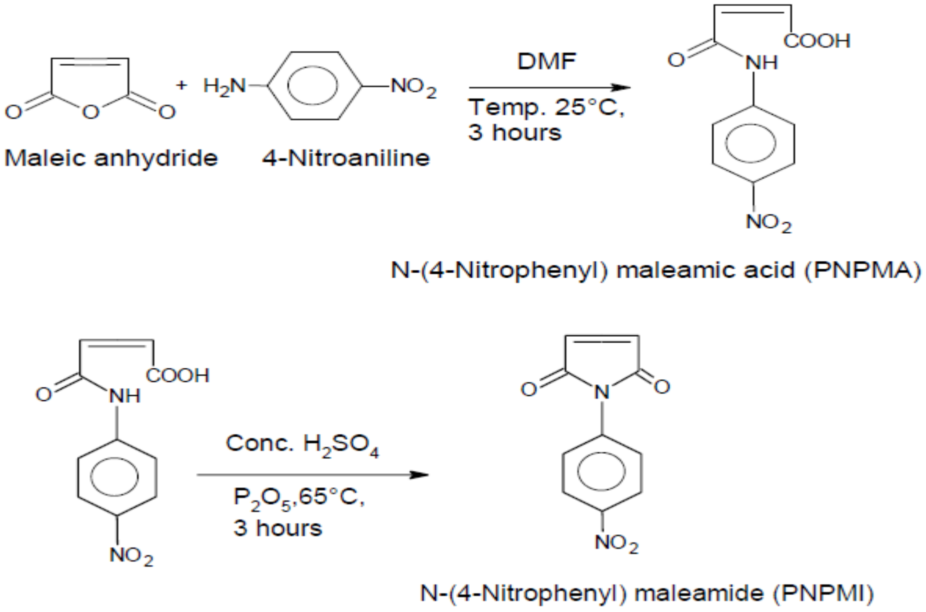
2.3. Preparation of N-(4-Nitrophenyl) maleamic acid

4-Nitroaniline 13.8 gm for 0.1mol in 30ml DMF and 9.8gm (0.1mol) maleic anhydride were taken in flat round bottom flask. The reaction mixture was stirred for three hours at 25°C. The solution was poured in cooled water. The yellow solid 4-Nitrophenylmaleamic acid was obtained. The product was filtered and dried. It was recrystallized from ethanol to obtain pure maleamic acid. Yield was 90%, m.p. 145°C.

Cyclodehydration of the 4-Nitrophenylmaleamic acid: Obtained acid was treated with conc. H_2SO_4 and P_2O_5 followed by stirring for three hours at 65°C. Then the solution was poured in crushed ice and yellow colour precipitate obtained which was filtered and washed with water and dried. N-(4-Nitrophenyl) maleimide was recrystallized from ethyl alcohol solvent. Yield was 80%, m.p. 205°C.



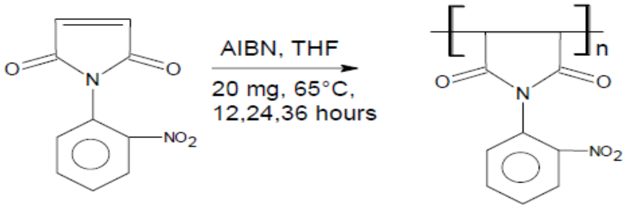
Scheme-2



Scheme-3

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

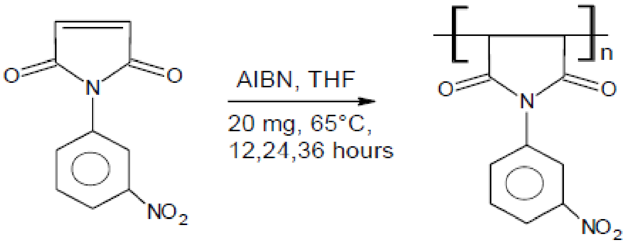
Polymerization of N-(2-Nitrophenyl) maleimide was carried out in THF solvent using radical initiator AIBN at 65°C. 2-Nitrophenylmaleimide (2.18 gm), 0.01 mol and THF in 30ml were placed in round bottom flask with reflux condenser. To this solution, 20mg AIBN was added and the reaction mixture was refluxed on heating mental 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 as 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- 04

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

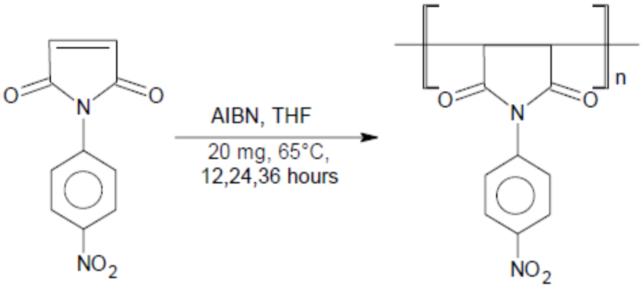
Homopolymerization of N-(3-Nitrophenyl) maleimide (2.18 gm, 0.01mol) was carried out in THF solvent using free radical initiator AIBN at 65°C. The polymerization reaction mixture was placed in round bottom flask, with reflux condenser for 24 hours. Very less polymer was formed. The reaction mixture was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



Scheme - 05

2.6. Homopolymerization of N-(4-Nitrophenyl) maleimide (HPNPMI)

Polymerization of 4-Nitrophenylmaleimide was carried out in THF solvent using radicals initiator AIBN at 65°C. 4-Nitrophenylmaleimide (2.18 gm, 0.01mol) and THF in 30 ml were placed in round bottom flask with reflux condenser. To this solution, 20 mg AIBN was added and the reaction mixture was refluxed on heating mental at 65°C for 12, 24, 36 and 48 hours. No polymer or very less polymer was formed if the reaction was carried out up to 12 hours. Yield was obtained as 32.33% for 24 hours. The synthesized polymer was isolated in excess quantity of methanol water mixture. It was dried under vacuum at 55°C.



Scheme - 06

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

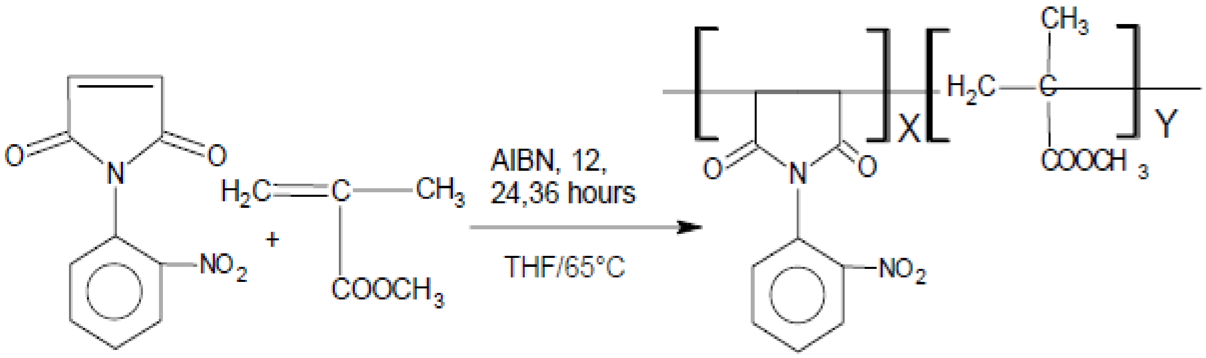
2-Nitrophenylmaleimide (2.18 gm, 0.01 mol) and MMA (1.06 ml, 0.01 mol) in 30 ml THF solvent was taken in a round bottom flask. The copolymerization reaction was carried out at 65°C for 24 hours. Copolymer samples were isolated in water containing 20% methanol. The copolymer were purified by first dissolving 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 as 42.90%.

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

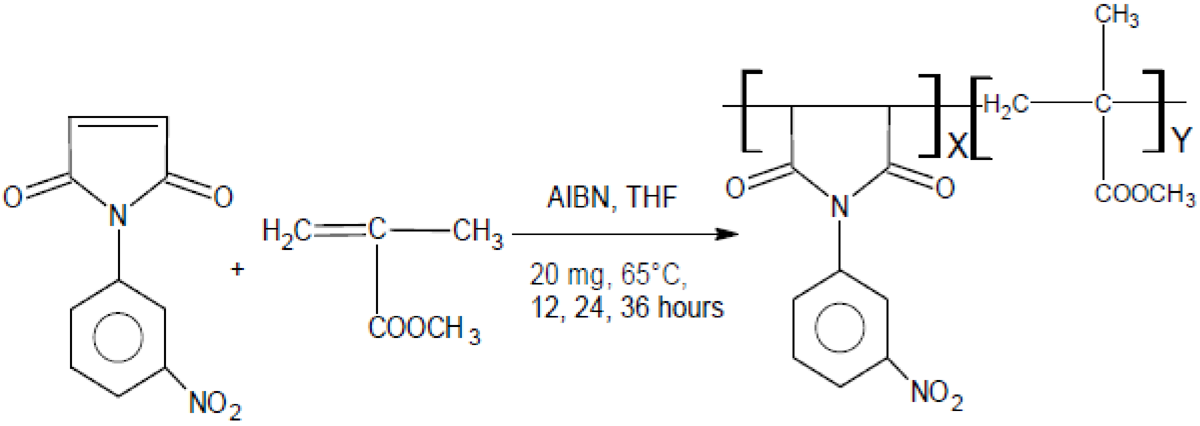
3-Nitrophenylmaleimide (2.18 gm, 0.01 mol) and MMA (1.06 ml, 0.01 mol) in 60 ml THF solvent were taken in round bottom flask. The copolymerization reaction was carried out at 65°C for 24 hours. Copolymer samples were isolated in water containing 20% methanol. The copolymer was purified by first dissolving 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 as 39.75%.

2.9. Copolymerization of N-(4-Nitrophenyl) maleimide with MMA (CPNPMI)

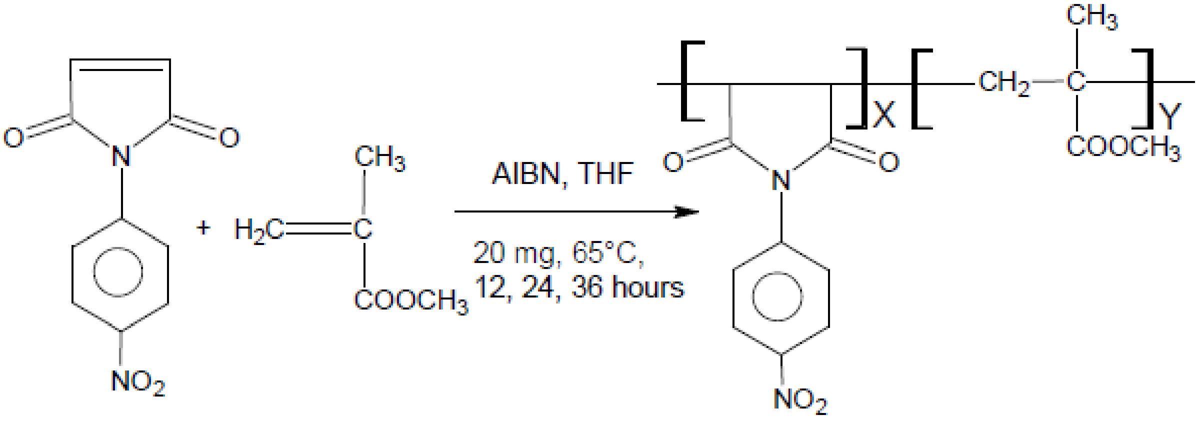
Calculated amount of 4-Nitrphenylmaleimide (2.18 gm, 0.01 mol) and (1.06 ml, 0.01 mol) MMA in 30 ml THF solvent were taken in a round bottom flask. The copolymerization reaction was carried out at 65°C for 24 hours. Copolymer samples were isolated in water containing 20 % methanol. The copolymer were purified by first dissolving in THF and then reprecipitated 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 48.81%.



Scheme - 07



Scheme - 08



Scheme - 09

2.10. Characterization of Monomer

2.10.1. ONPMI

3105 (aromatic and alkene C-H stretch), 1716, 1790, (C=O) [16-18]. 1528, 1354 (-NO_2 group), 1606(C=C, alkene) 1586, 1491, 1454 (C=C, aromatic) [19, 20], 1150 (C-N stretch) [21]. 957(CH=CH), 834 (1,2 disubstituted of benzene), these are considered with the structure of ONPMI. ^{1}H-NMR, 400 MH_z, 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 δ7.29-8.20(m).

2.10.2. MNPMI

3134 (aromatic and alkene C-H stretch), 1785, 171 (C=O)[16-18], 1528, 1351 (-NO_2 group), 1623 (C=C, alkene), 1590, 1437 (C=C, aromatic), 1150 (C-N-C stretch) [21], 972(CH=CH), 855 (1,3-disubstituted of benzene). ^{1}H-NMR of MNPMI is observed: (a) two methine (CH=CH) protons at δ7.23 ppm (s) and (b) one phenyl protons at δ7.29-8.58 ppm (m).

2.10.3. PNPMI

3091.3, 2980.8 (aromatic and alkene C-H stretch), 1797 and 1708 (C=O) [22,23] 1634 (CH=CH), 1564 1456 (C=C) [23-25], 1.335, 1504 (-NO_2) [25], 967 (CH=CH) [23], 856(1,4 disubstituted benzene) these are consistent with the structure of PNPMI. ^{1}H-NMR spectra of PNPMI obtained two methine (CH=CH) protons at δ 6.82 (s) ppm; two aromatic protons (o-group in phenyl ring) at δ7.13-7.15 (d) ppm; two aromatic proton (m-group in phenyl ring) at δ7.63-7.64 (d) ppm [25, 26].

3. RESULTS AND DISCUSSION

3.1. CONPMI

In Fig.1, 3150-2951 (Aromatic, C-H stretch, CH_3, and CH_2 in MMA), 1721, 1770 (C=O), 1602, 1535 (C=C), 1487, 1444 (C-H band, -CH_2), 1352 (due to overlapping of C-N stretch and C-H band of -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 [16]. ^{1}H-NMR δ value obtained for four aromatic proton at 7.29-8.20 ppm. for 2H (-CH-CH-) and -OCH_3 signals at δ 3.60-3.79 ppm and -CH_3 signals at 0.85-1.23 ppm, 2H for (-CH_2-) observed at 1.83-2.49 ppm (Fig.2).

3.2. CMNPMI

In Fig.3, 2952-2996 (C-H stretch, CH_3, and CH_2 in MMA), 1731-1775 (C=O), 1599, 1536 (C=C), 1441, 1488 (C-H band, -CH_2), 1353 (due to over lapping of C-N stretch and C-H band of -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). Showed 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.4, showing chemical shift for CMNPMI observed at 7.24-7.79 ppm (4 Ar-H), 2H (-CH-CH-) and –OCH_3 signals at 3.54-3.75 ppm and -CH_3 protons observed at δ 0.86-1.24 ppm. Two protons for -CH_2- were observed around 1.85-1.26 ppm.

3.3. CPNPMI

Fig.5, (C=O) 1775-1731 cm^{-1}, 2998-2953 (C-H stretching) [16].1597 (C=C) 1497, 1446 (C-H band, -CH_2), 1339 (due to overlapping of C-N stretch and C-H band of -CH_3 group), 1268, 1150 (C-O-C), 852 (1,4-disubstituted benzene), 751 (out of plan), 687-606 (out of plane aromatic ring C=C band) these bands confirm that units of both the monomers PNPMI and MMA are present in the copolymer samples. In Fig. 6, the chemical shift for four aromatic protons observed δ at 7.28-8.08 ppm and 2H (-CH-CH-), -OCH_3 observed δ at 3.60-3.72 ppm and δ 0.84-1.13 observed for -CH_3 protons and 1.80-2.06 ppm for two methylene protons. These data confirm the presence of both units present in the copolymer sample.

3.4. HONPMI

Fig.7, 2935 (C-H stretch, alkane), 1785, 1721 (C=O), 1661, 1608, 1587, 1437 (C=C), 1502, 1386 (Ar-NO_2 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) [23] are consistent with the structure of HONPMI. Fig.8 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. ^{1}H-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 [24-27].

3.5. HMNPM

Fig.9, 3074 cm^{-1} (C-H stretching) [24, 25]. 1778, 1714 (C=O group), 1621, 1588, 1439 cm^{-1} represent C=C ring stretching, 1549, 1353 (Ar-NO_2 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. The chemical shift δ for HMNPMI is observed at 7.23-7.35 (m) and 4.02-3.05 (d). The multiple are 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. ^{1}H-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 [26-28] (Fig.10).

3.6. HPNPMI

In Fig.11, 3088 (C-H aromatic), 2981 (C-H stretch alkene), 1778, 1715 (C=O group) 1614, 1651, 1563, 1444, 1596 (C=C stretch aromatic), 1504, 1331 (Ar-NO_2 group), 1255 (C-O-C), 1110, 1168 (symmetric C-O-C stretch), 856 (1,4 disubstituted benzene) and 690, 605 (out of plane aromatic ring C=C bend) are consistent with the structure of HPNPMI. In Fig. 12, the ^{1}H-NMR spectrum of HPNPMI is observed at δ 7.50-8.08 (d). 2H in -CH-CH- group have appeared at 3.5-4.0 ppm. ^{1}H-NMR of HPNPMI monomer shows chemical shift δ at 6.82 (s) ppm characteristic of CH=CH group. The disappearance of this in polymer HPNPMI shows that the radical polymerization proceed through the double bond [27-29].

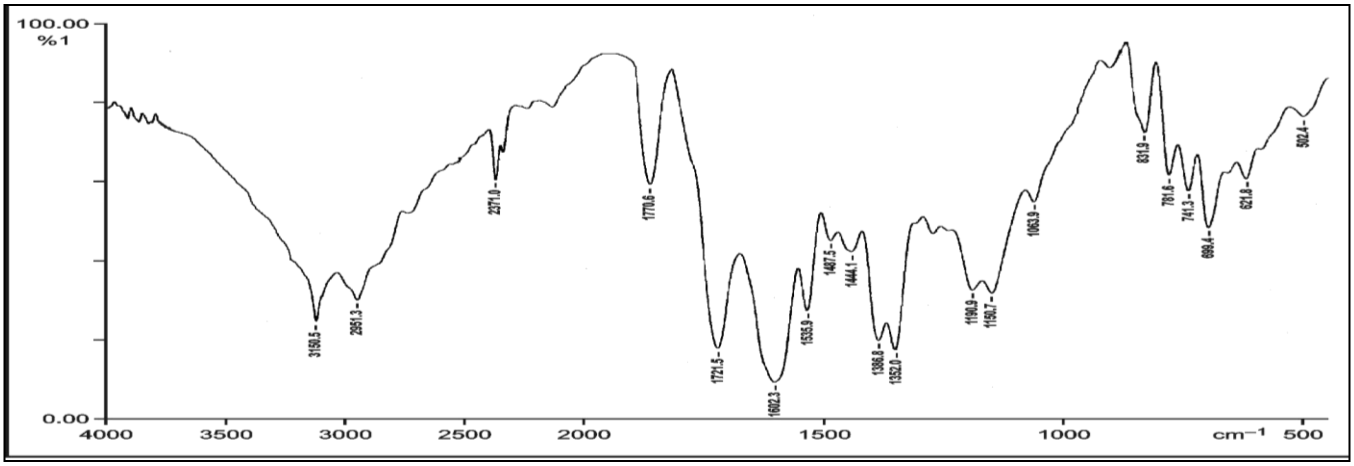


Fig. 1: IR spectra of CONPMI

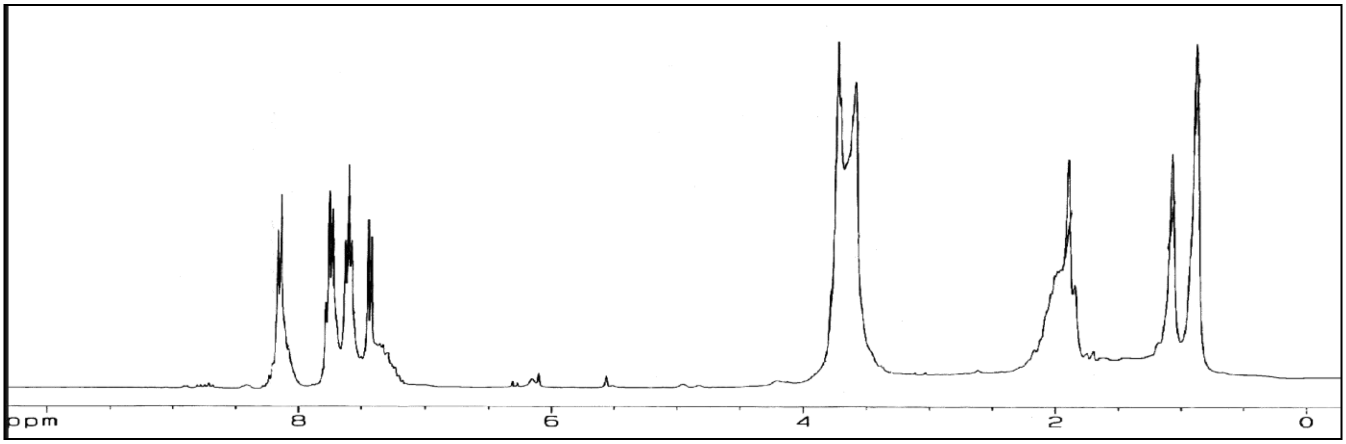


Fig. 2: ^{1}HNMR of CONPMI

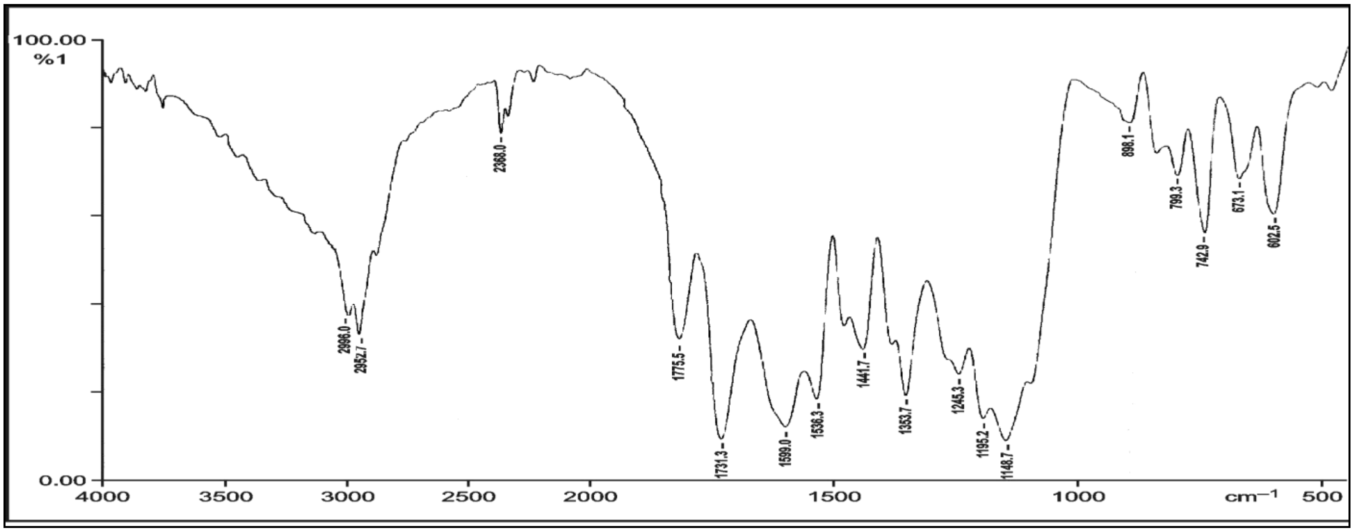


Fig. 3: FTIR spectra of CMNPMI

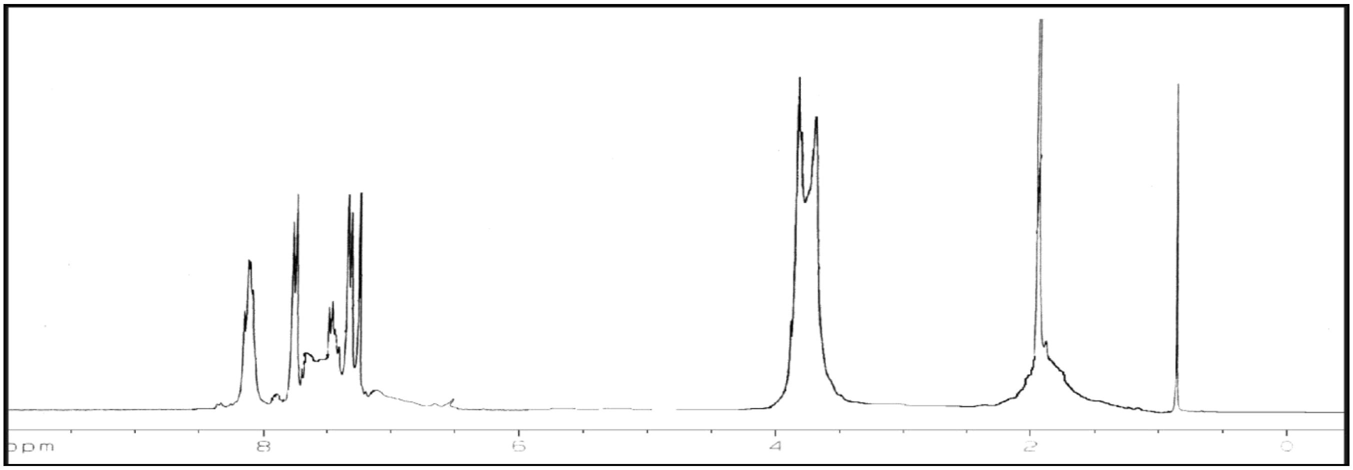


Fig. 4: ^{1}HNMR of CMNPMI

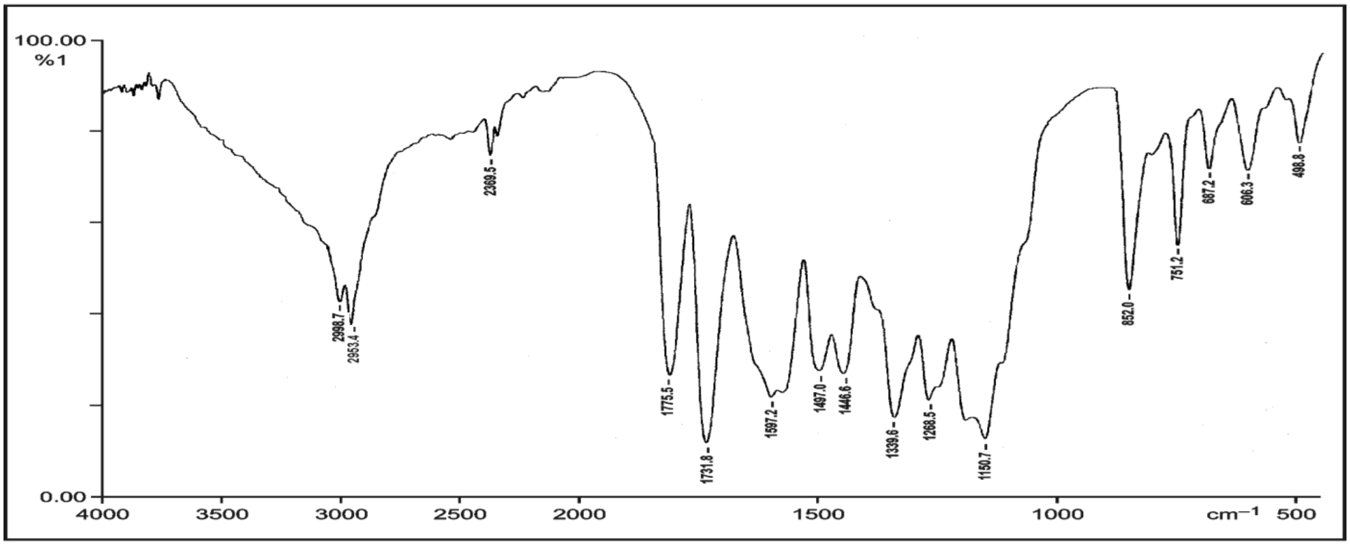


Fig. 5: FTIR spectra of CPNPMI

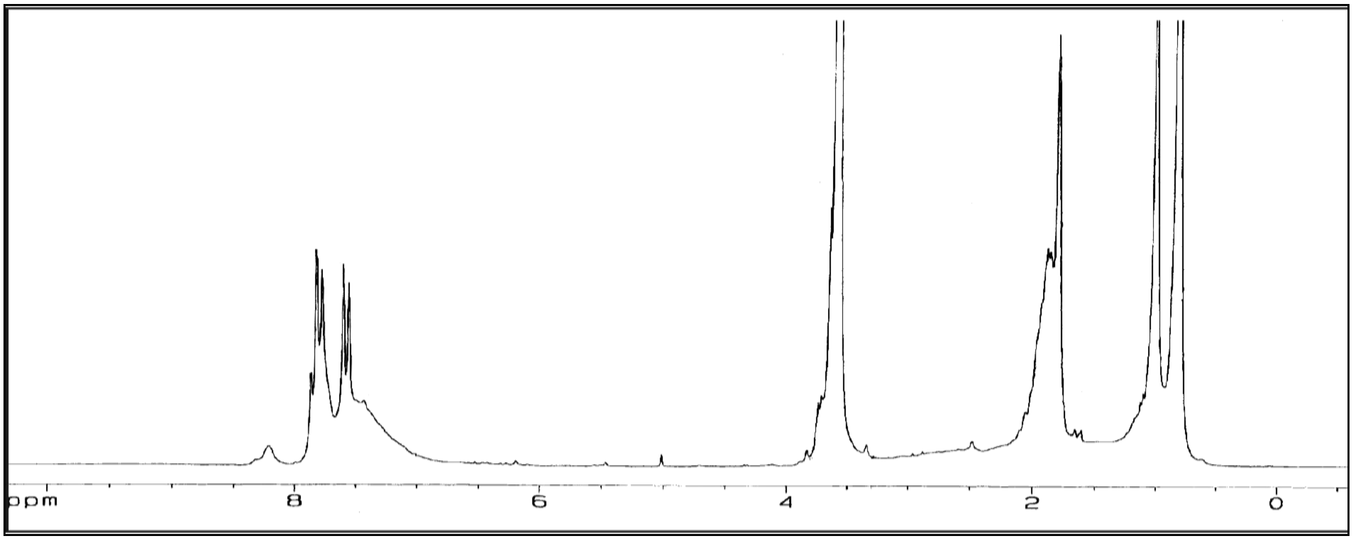


Fig. 6: ^{1}HNMR of CPNPMI

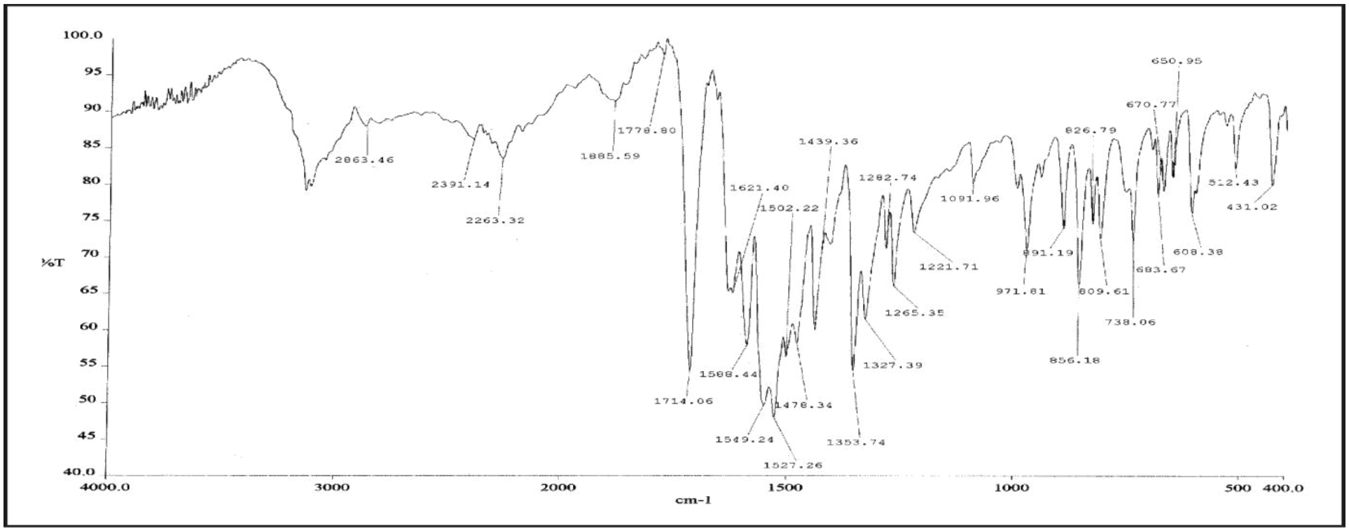


Fig. 7: FTIR spectra of HONPMI

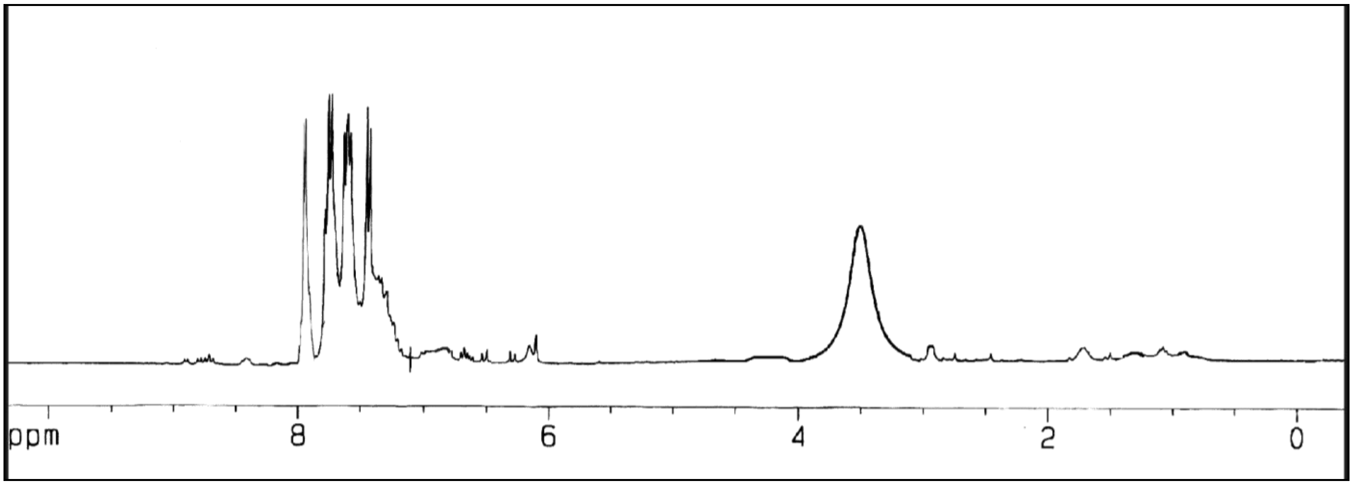


Fig. 8: ^{1}HNMR of HONPMI

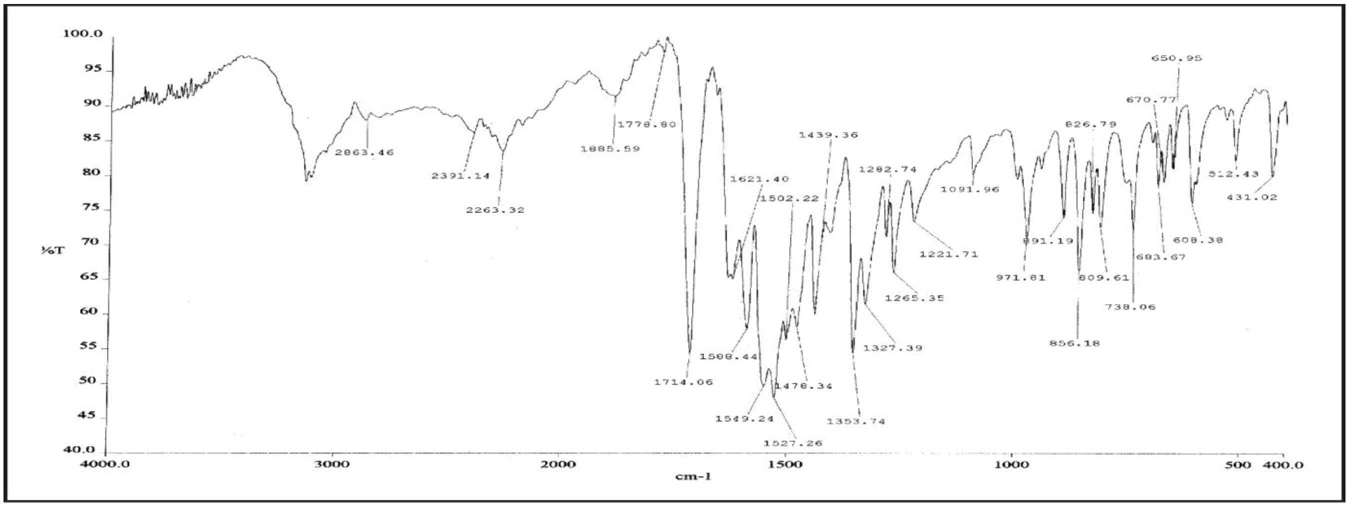


Fig. 9: FTIR spectra of HMNPMI

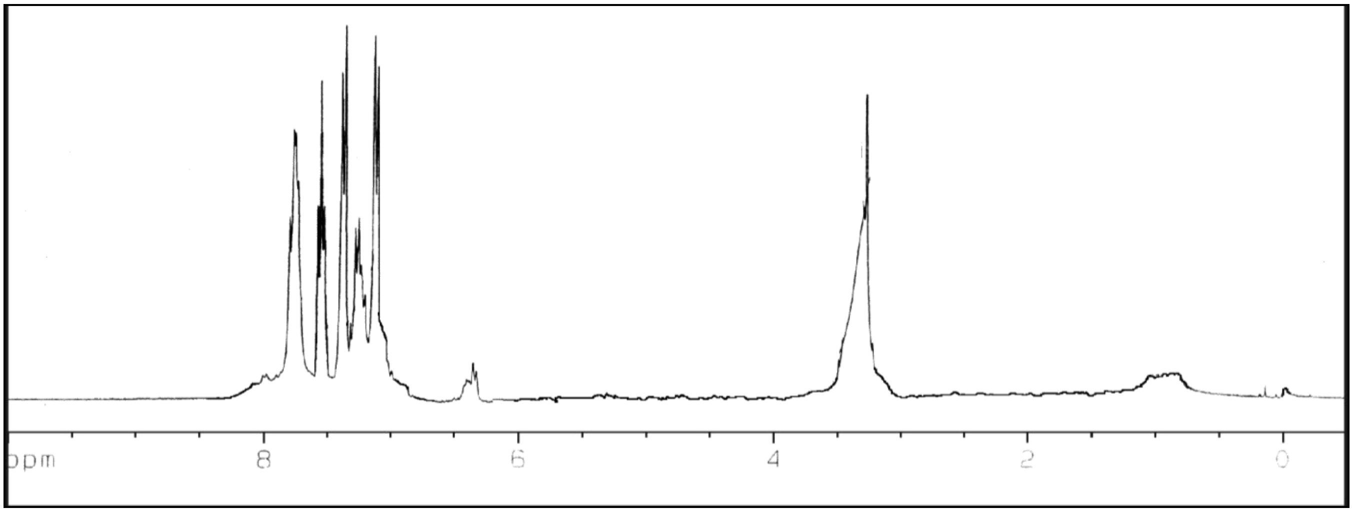


Fig. 10: ^{1}HNMR of HMNPMI

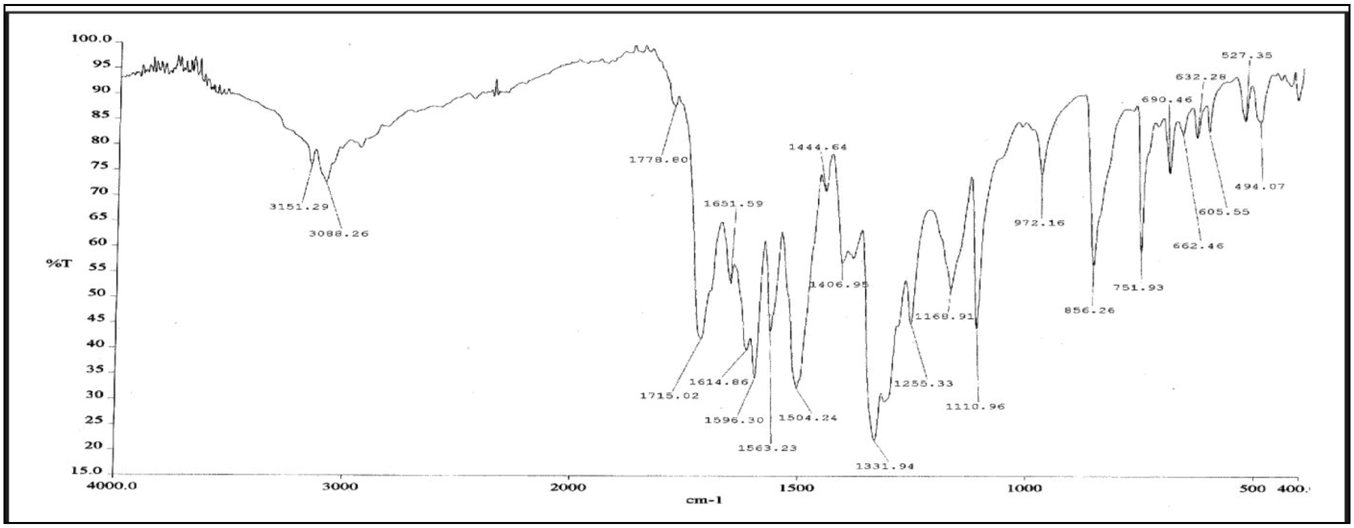


Fig. 11: FTIR spectra of HPNPMI

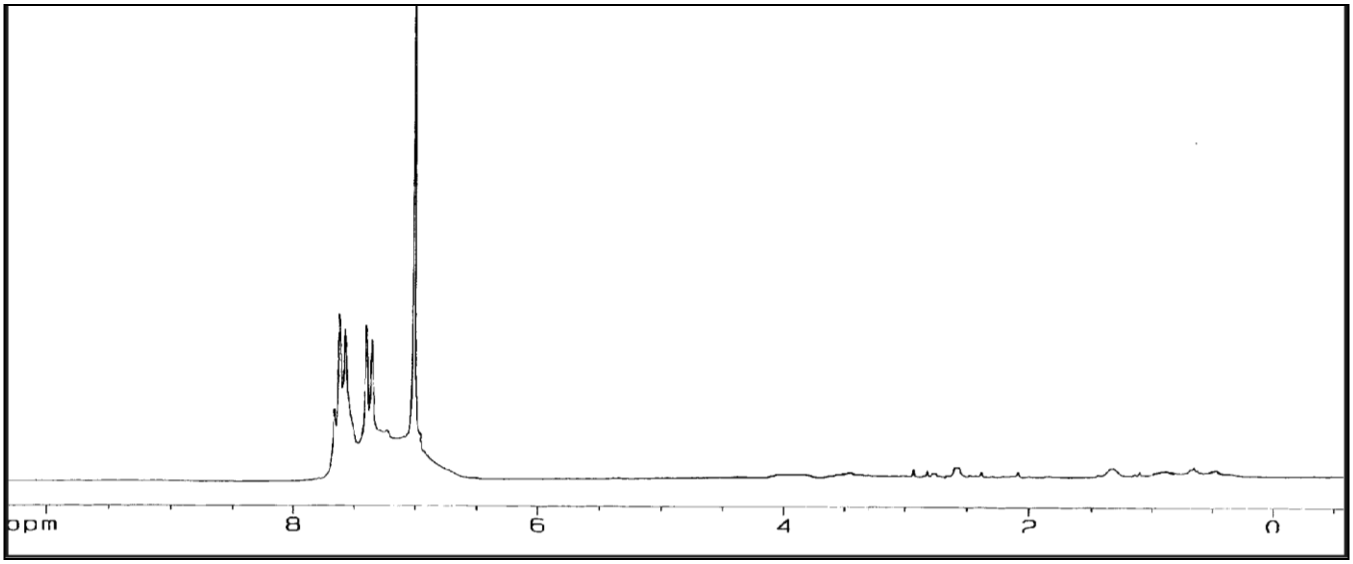


Fig. 12:^{1}**H-NMR of HPNPMI**

3.7. Copolymer Composition

The properties of copolymer largely depend upon their composition, therefore, determination of copolymer composition is very important and necessary. Here copolymer composition was determined by the elemental analysis. The weight percentage of monomers and their copolymers was calculated [30, 31].

3.8. Relation in between intrinsic viscosity and molar mass

The measurement of the viscosity of polymer solutions in organic solvents gives us a value that is directly related to the molecular mass of the polymer. In other words, the higher the viscosity, the higher the molecular weight, although the correlation is not direct. The molecular weight is an essential characteristic that determines some mechanical and thermal behaviors of polymers. As the size of monomer increases, intrinsic viscosity increases. Relation in between intrinsic viscosity and molar mass describe by Kuhan -mark Howink Sakwada equation. The exponent α=0 it knowledge to us spheres,$\alpha = 0.5$ the polymer would in unperturbed dimensions $\alpha = 0.764$ polymer in coils and $\alpha = 2$ for rigid rods. Synthesis of homopolymer study are gave $\alpha \approx 0.48741$. It shows homopolymer is in unperturbed dimensions. In case of copolymers, α value ≈ 1.4921which shows polymers are in shape of rigid rods.

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

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

Table 1: Copolymer composition of CONPMI

Polymer code	Feed mol ratio	Feed composition	N%	Mole fraction of ONPMI in copolymer	Wt % of ONPMI
CONPMI	0.1 : 0.0	0.0	12.84	0.0	100.00
CONPMIMMA1	0.1 : 0.9	0.1	2.10	0.087	16.35
CONPMIMMA2	0.2 : 0.8	0.2	3.10	0.134	24.14
CONPMIMMA3	0.3 : 0.7	0.3	4.30	0.197	33.48
CONPMIMMA4	0.4 : 0.6	0.4	5.71	0.281	44.47
CONPMIMMA5	0.5 : 0.5	0.5	5.91	0.294	46.02
CONPMIMMA6	0.6 : 0.4	0.6	6.31	0.321	49.14
CONPMIMMA7	0.7 : 0.3	0.7	7.51	0.408	58.41
CONPMIMMA8	0.8 : 0.2	0.8	8.72	0.509	67.91
CONPMIMMA9	0.9 : 0.1	0.9	9.35	0.567	72.81

Table 2: Copolymer composition of CMNPMI

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: 06	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

Table 3: Copolymer composition of CPNPMI

Polymer code	Feed mole ratio	Feed composition	N%	Mole fraction of PNPMI in copolymer	Wt % of PNPMI
CPNPMI	1.0: 0.0	0.0	12.84	0.0	100.00
CPNPMIMMA1	0.1: 0.9	0.1	2.30	0.0966	17.91
CPNPMIMMA2	0.2: 0.8	0.2	3.15	0.137	24.53
CPNPMIMMA3	0.3: 0.7	0.3	4.40	0.203	34.26
CPNPMIMMA4	0.4 : 0.6	0.4	5.85	0.290	45.56
CPNPMIMMA5	0.5 : 0.5	0.5	6.90	0.362	53.73
CPNPMIMMA6	0.6 : 0.4	0.6	7.20	0.384	56.07
CPNPMIMMA7	0.7 : 0.3	0.7	8.90	0.525	69.31
CPNPMIMMA8	0.8 : 0.2	0.8	9.60	0.592	74.76
CPNPMIMMA9	0.9 : 01	0.9	11.20	0.769	87.22

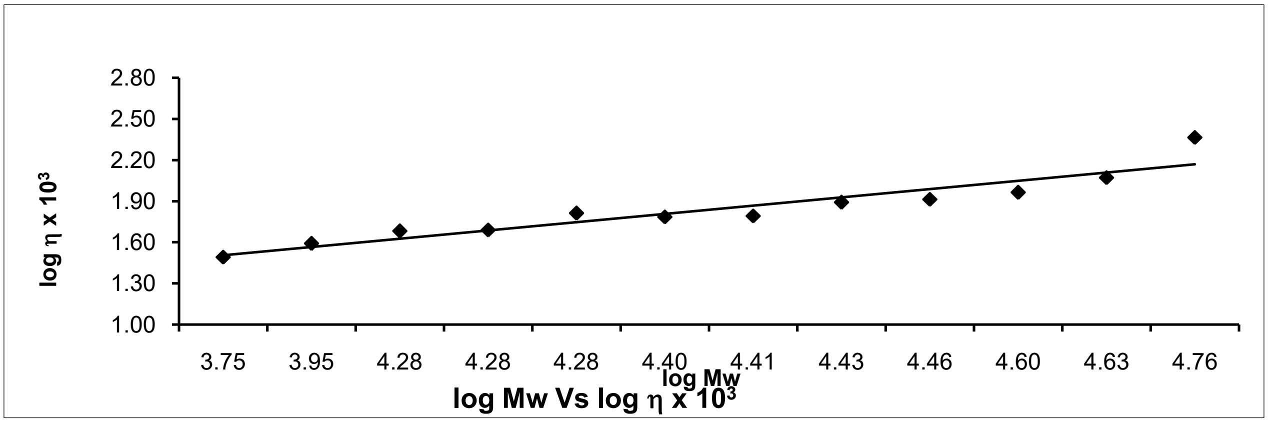


Fig. 13: Relation Log η x 10^3 and η x 10^3 dl/gm

3.9. 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 Fig. 13 to 18. The percentage weight loss of Homopolymer and Copolymer are summarized in table 5 and 6.

On comparing both the tables *i.e.* 5 and 6, it appears that the percentage degradation is very low in homopolymer units while the percentage degradation is very high in copolymer units. This is because, only one unit is present in Homopolymer whereas two units are present in co-polymer, so the percentage degradation in co-polymer is more than that of homopolymer. 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 groups present at Ortho position which make highly favorable for satiric hindrance therefore HONPMI and CONPMI thermal stability is less stable than having meta position.

Table 4: Typical data of number average and weight average and log values of Homopolymer and copolymer are given

Polymer	Mw	Log Mw	η x 10^3 dl/gm	Log η x 10^3
HPMI	5675	3.754	31	1.4914
HNMI	8946	3.9516	39	1.5911
HONPMI	18984	4.2784	48	1.6812
CNPMI	19063	4.2802	49	1.6902
HMNPMI	19063	4.2802	65	1.8129
HBMI	25340	4.4038	61	1.7853
CPMI	25581	4.4079	62	1.7924
HPNPMI	26751	4.4273	78	1.8921
CBMI	29017	4.4627	82	1.9138
CONPMI	39908	4.6011	92	1.9638
CMNPMI	42238	4.6257	118	2.0719
CPNPMI	57391	4.7588	232	2.3655

Table 5: Percentage weight loss of homopolymer and copolymer

Polymer code	200°**C**	300°**C**	400°**C**	500°**C**	550°**C**
HONPMI	-1.48	-17.94	-86.16	-89.84	-91.17
HMNPMI	-1.54	-17.94	-87.17	-90.85	-92.17
HPNPMI	-1.48	-17.94	-89.17	-90.83	-93.18

Table 6: Percentage weight loss of homopolymer and copolymer

Polymer code	185°**C**	200°**C**	300°**C**	400°**C**	500°**C**	550°**C**
CONPMI	-1.34	-4.96	-52.36	-68.59	-72.61	-74.80
CMNPMI	-5.10	-7.21	-40.29	-50.06	-57.82	-61.10
CPNPMI	-	-4.29	-40.97	-95.89	-96.55	-97.30

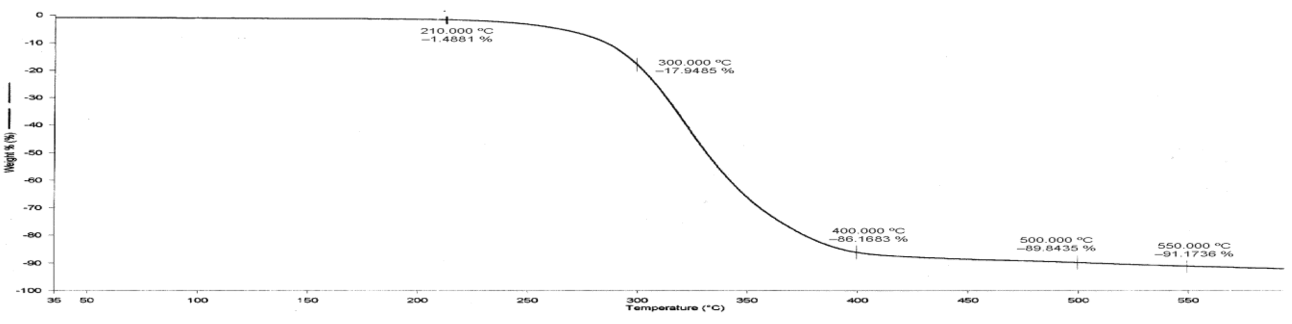


Fig. 13: Thermogram of HONPMI

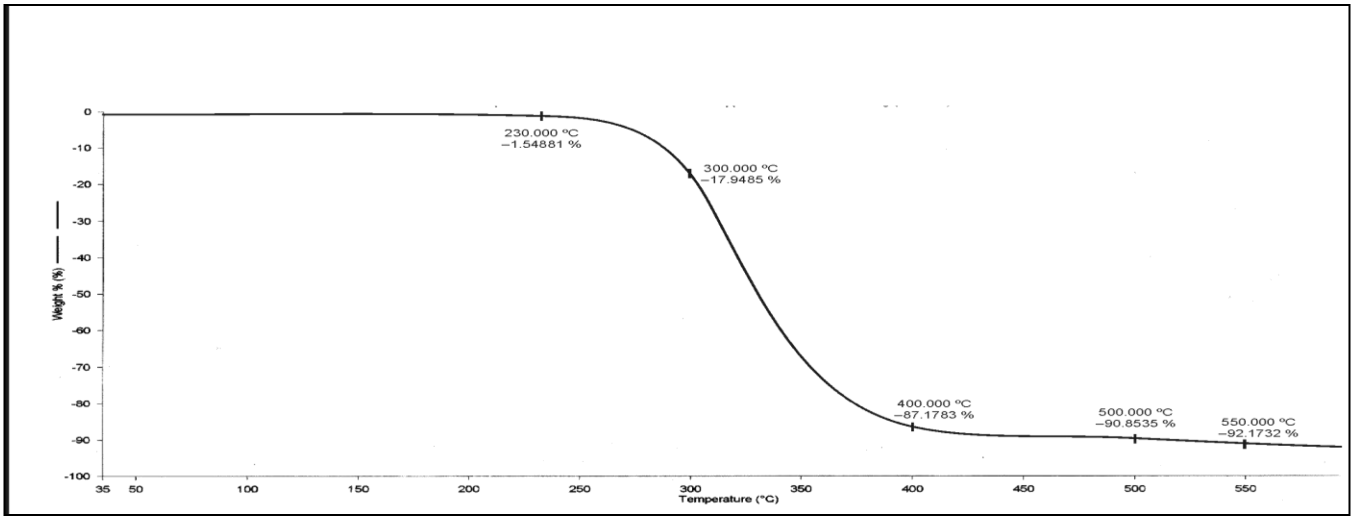


Fig. 14: Thermogram of HMNPMI

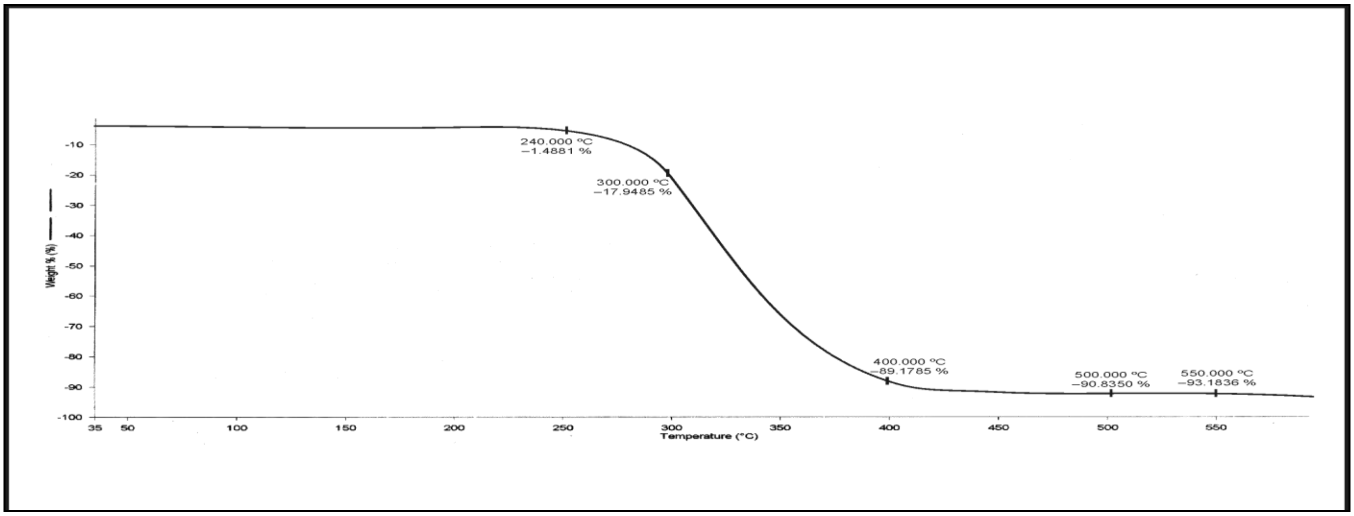


Fig. 15: Thermogram of HPNPMI

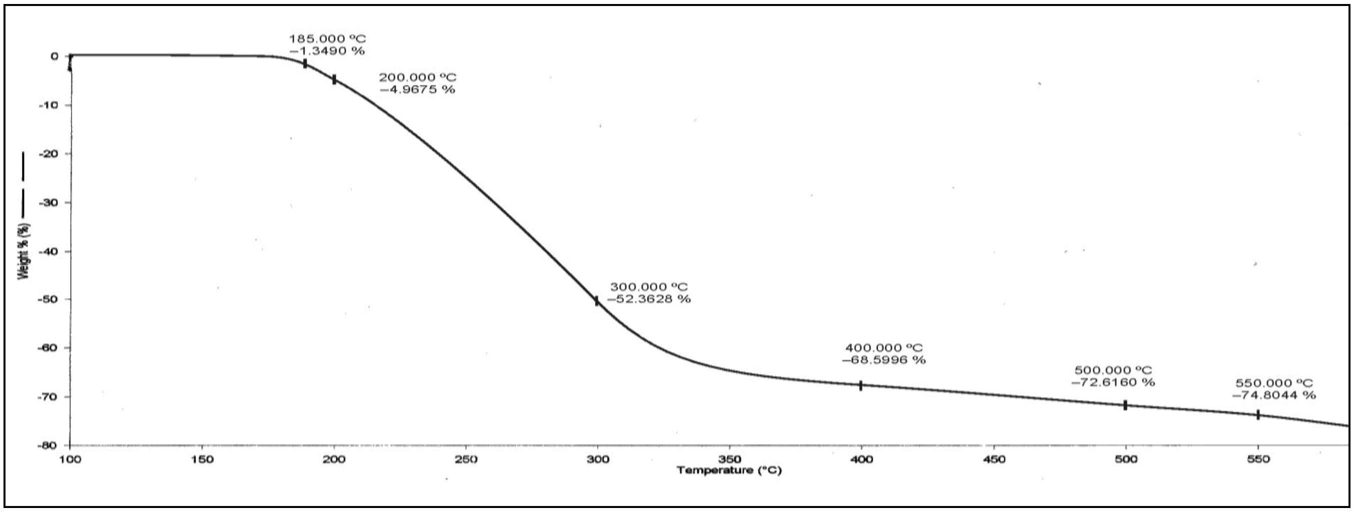


Fig. 16: Thermogram of CONPMI

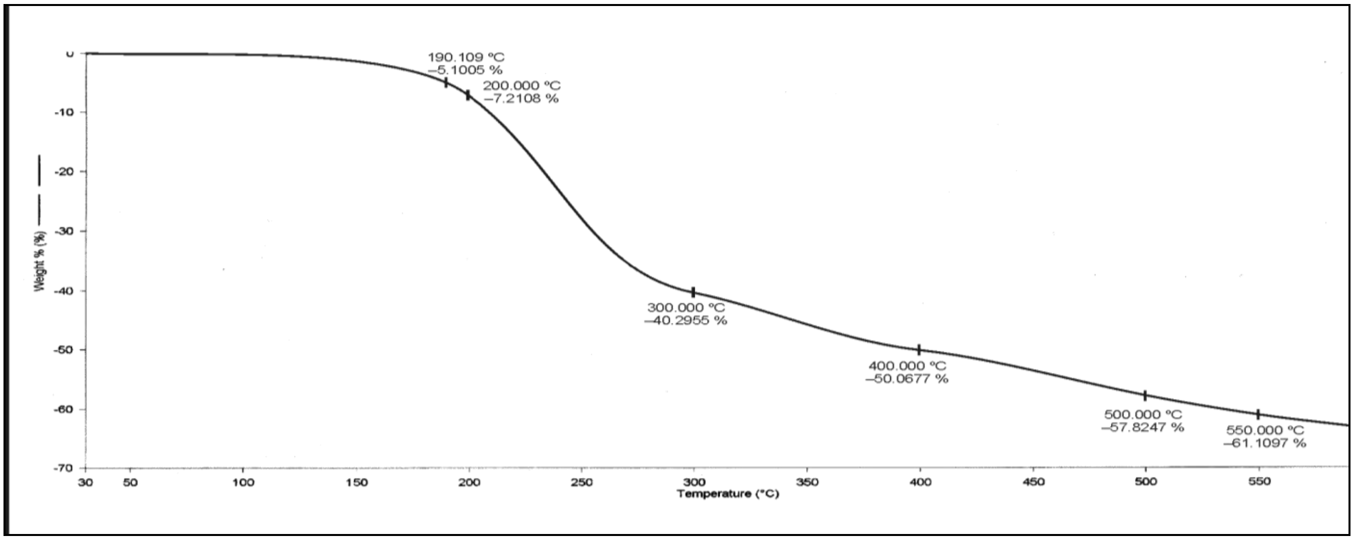


Fig. 17: Thermogram of CMNPMI

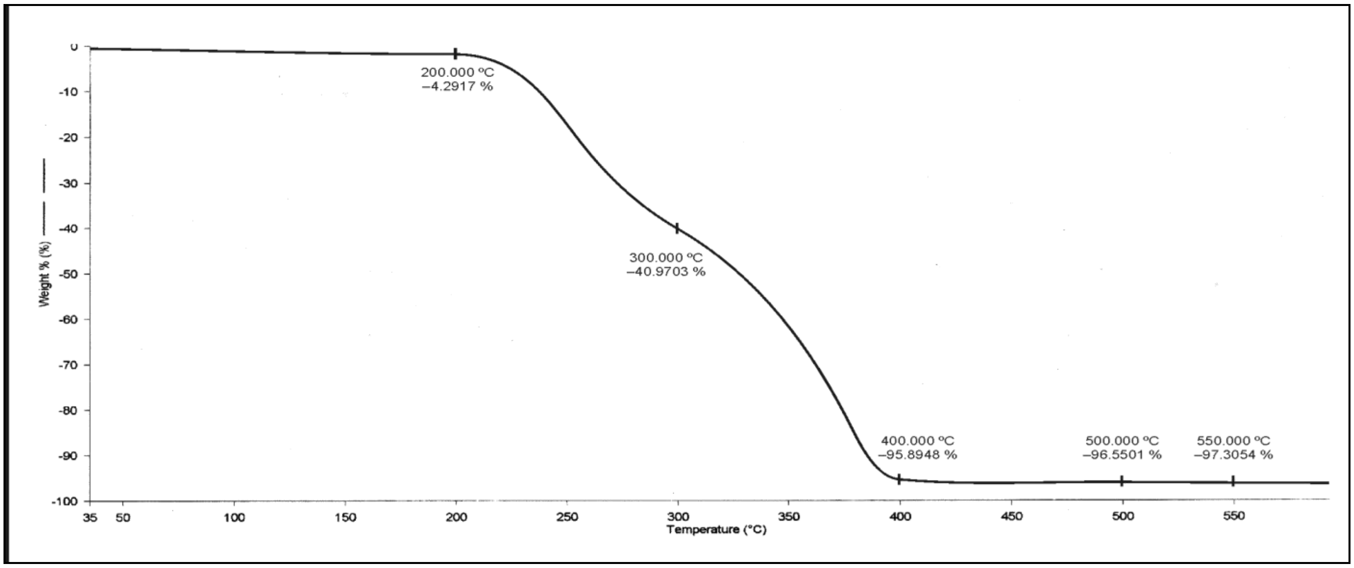


Fig. 18: Thermogram of CPNPMI

4. CONCLUSION

Synthesis of homopolymer and copolymer showing excellent thermal stability and thermal stability was determined by the TGA techniques. Shape of the homopolymer and copolymer were determined by Kuhan-mark Howink Sakwada equation and by this equation we find out that all the polymer present in rigid road shape in solvent. Homopolymerization and copolymerization reaction proceed through the free radical polymerization which is confirmed by the polydispersity index. Weight average and number average values were identified by the PDI. Molecular weight of homopolymer is less than copolymer because homopolymer contain single repeat unit,while copolymer having both are unit in their back bone. Synthesis of polymer showing excellent solubility in THF, DMF, DMSO, CH_2Cl_2, Chloroform, Acetone, Dioxane, methylacetate and Ethyl acetate.

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Conflicts of interests

The authors have no conflict of interest.

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