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A Comparative Thermal stability Study of N-(4-Nitropheny) Maleimide and N-(2, 4-di-nitrophenyl) maleimide with Methylacrylate

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Abstract: In this article two type of monomers were synthesize, having different position on benzene ring one present on 4th position and second present on 2,4 position. Monomers were prepared by Maleic anhydride reaction with 2,4 dinitro aniline and 4 nitro aniline and obtained 4-Nitropheny Maleimide and 2,4-Didinitrophenylmaleimide copolymerized with Methylacrylate. Investigated a comparative study in between and what effect will come with thermal stability of the synthesis polymers. Free radical initiator AIBN and BPO were used of the polymerization and percentage yield calculated in THF and DMF solvent system under the identical conditions.

Polymerization reaction proceed at different time (12, 24, 36) hours. Prepared homopolymer and copolymer were characterized by FTIR and ^{1}H-NMR. The thermal stability and percentage degradation of the polymer were recorded by TGA Techniques. Percentage yield were obtained with given time hours and using free radical initiator and solvent systems. Synthesis polymers and their PDI values obtained range 1.5 to 10(Mw/Mn), it indicate that polymerization proceed via radical polymerization. Shape of the polymer in given solution were determined by Kuhan Mark Equations. Homopolymer shows unperturbed condition and copolymer present in rigid rods. Reduced viscosity and Intrinsic viscosity determined by the using Ubbelhod viscometer. Number average and weight average molecular weight were determined by the Gel permeation chromatography. Different feed mole ratios and percent yield were reported.

Keywords: Polymerization. Intrinsic Viscosity, TGA, DMF

I. INTRODUCTION

At present time polymer have vast demand in daily life and polymers which are having N-Phenylmaleimide in their backbones more useful and most important useful of polymer in medical sciences ,aerospace. mechanical properties, dielectric properties, thermal stability and outstanding bonding ability, epoxy resin has been widely applied as coating, insulation materials, etc, in the electronic, electrical, mechanical manufacturing, aerospace and other fields, especially polymers used in circuit board (PCB), the demand on the thermal resistance of insulation material becomes severe [1,2]. In recent study observed Styrene and maleic anhydride copolymer give excellent thermal resistance property [3,4] . It is known that N-phenyl maleimide (N-PMI) has high thermal resistance [5]. recently developed one-pot post-polymerization modification reactions using p-maleimidophenyl isocyanate (PMPI) as a modification reagent to introduce maleimide moieties into polymers with hydroxy groups and studied the polymerization reactions between the introduced N-aryl MA groups and thiol groups[6] N-Substituted Phenyl maleimide are interesting monomers for making transparent thermally stable polymeric materials [7-13]. Recently we are published 4-Nitro Phenylmaleimide copolymerized with Acrylonitrile and Ethyl acrylate . In this continuations we are interesting about the 4-Nitrophenyl maleimide and 2,4 Dinitrophenyl maleimide copolymerized with Methylacrylte (MA). Investigated comparative thermal stability, determined by the TGA Techniques and characterized by FTIR and ^{1}HNMR.

II. EXPERIMENTAL

A. Materials

Methylacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl2 for 6 hours and distilled [14]. The head and tail fractions were discarded. AIBN (2,2_-azobis–isobutironitrile (spectorchem.)) 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.

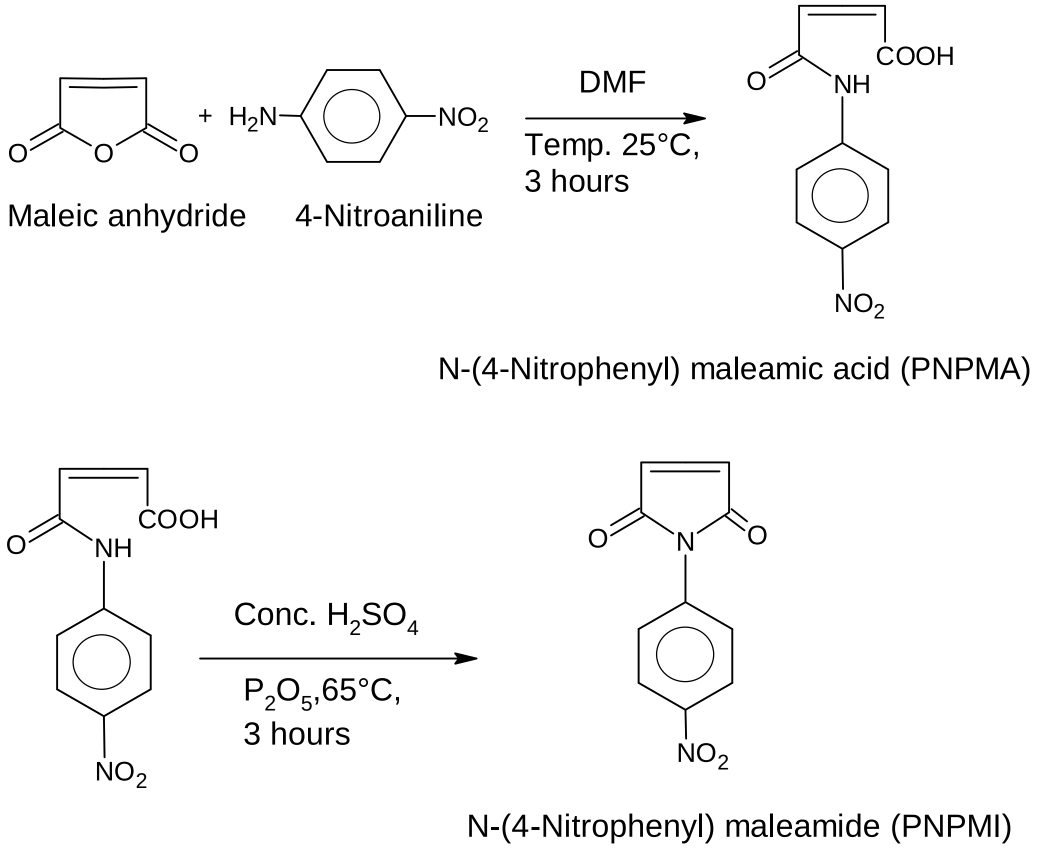
B. *Measurements*

^{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

C. *Methods*

Preparation N-(4-Nitrophenyl) maleimide (MNPMI**) :** 4-Nitro aniline (13.8 gm for 0.1mol) and 9.8 gm maleic anhydride were taken in 30 ml DMF. The reaction mixture was stirred 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 obtained pure N-(4-Nitrophenyl) maleamic acid. Cyclodehydration of the 4-Nitromaleamic acid, this solution treated with conc. H_2SO_4 and P_2O_5 and stirred 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-(4-Nitrophenyl) maleimide was recrystallized from ethyl alcohol solvent. The yield was 65%, m.p. 120°C.

SCHEME-I



Maleic anhydride

4-Nitroaniline

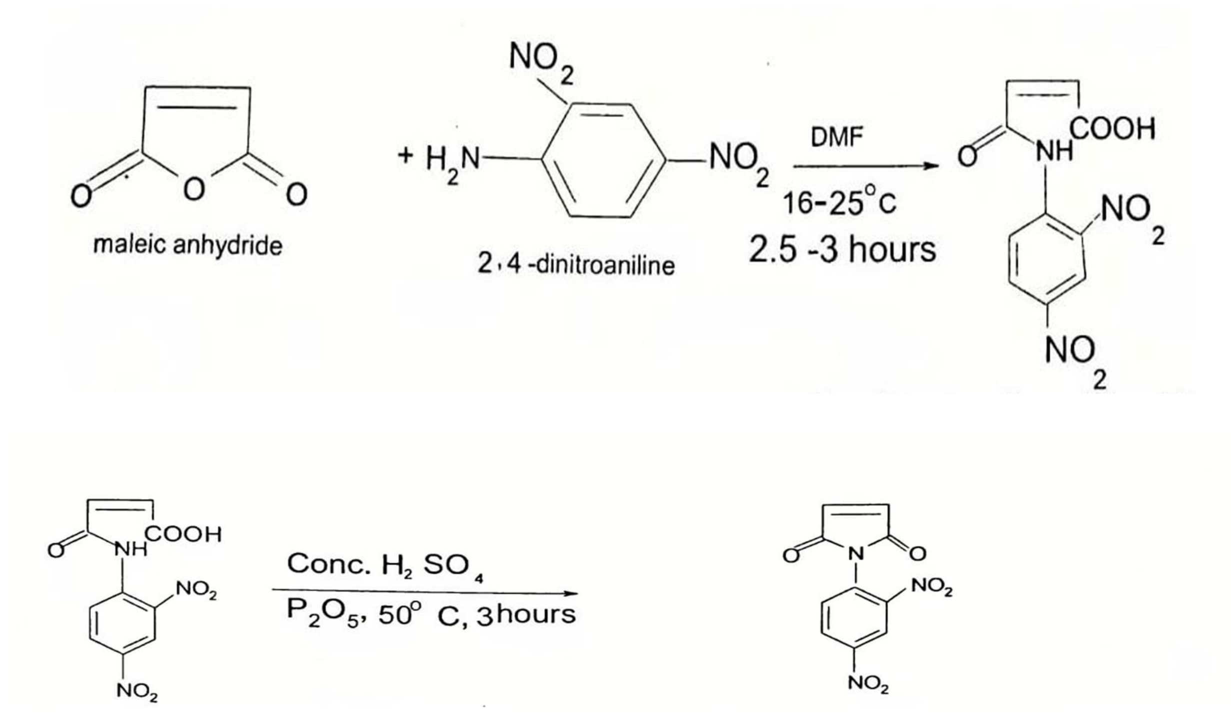
N-(4-Nitrophenyl) maleamic acid (PNPMA)

N-(4-Nitrophenyl) maleamide (PNPMI)

D. *Preparation N-(2,4-Dinitrophenyl) maleimide (OPNPMI)*

Equal amount of 2,4 Dinitrophenyl maleimide and equal amount maleic anhydride were taken in 30 ml DMF. The reaction mixture was stirred 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. Cyclodehydration of the 2,4-diNitrophenylmaleamic acid, treated with conc. H_2SO_4 and P_2O_5 and stirred for three hours at 65°C. Then the solution poured in crushed ice or cooled water, obtained to yellow solid product.

SCHEME-II

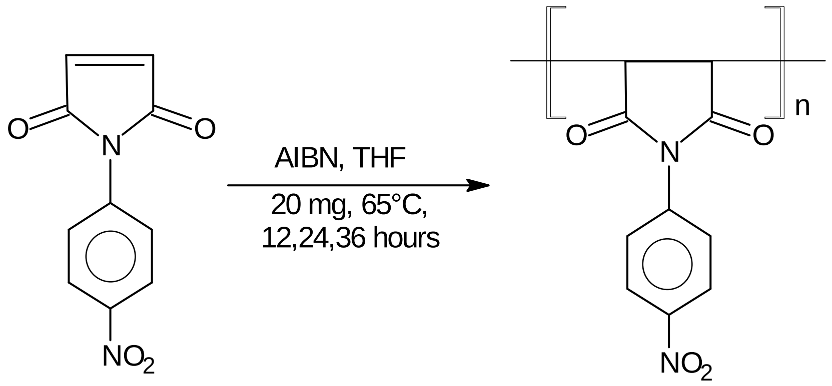


2,4 Dinitrophenyl maleimide

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

4-Nitrophenylmaleimide (2.18 gm, 0.01 mol) were taken in 30 ml THF solvent in round bottom flask with fitted reflux condenser. Free radical 20 mg AIBN was added and the reaction mixture was refluxed on heating mental at 65°C for 12, 24, 36 and 48 hours. Product was occurred 32.33% for 24 hours. Prepared polymer was separated in excess amount of methanol water mixture. It was dried under vacuum at 55°C then kept under dedicator free from moisture.

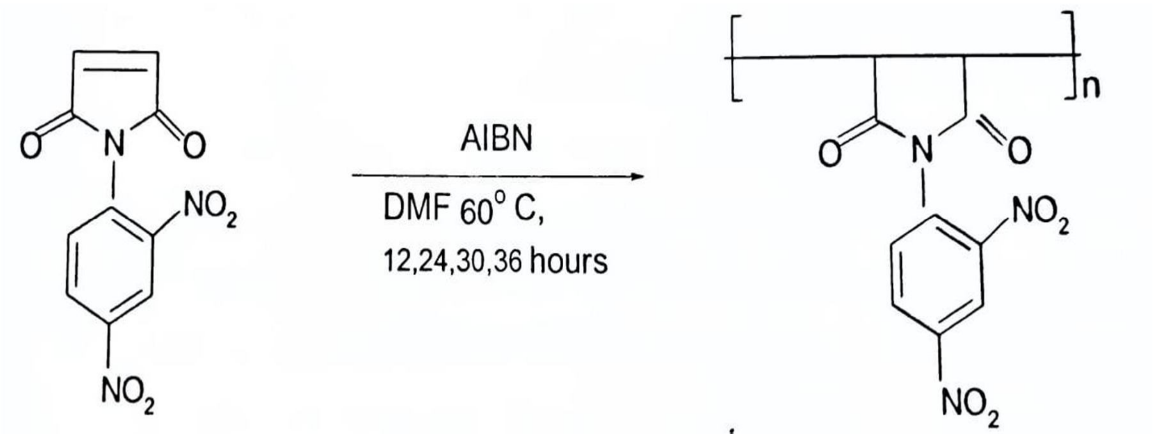
SCHEME - 03



F. Homopolymerization of N-(2,4 Dinitrophenyl) Maleimide (HOPNPMI)

2, 4-Dinitrophenylmaleimide (0.01 mol) were taken in 30 ml THF solvent in round bottom flask with fitted reflux condenser. Free radical 20 mg AIBN was added and the reaction mixture was refluxed on heating mental at 65°C for 12, 24, 36 and 48 hours. Product was obtained. Prepared polymer was separated in excess amount of methanol water mixture. It was dried under vacuum at 55°C then kept under dedicator free from moisture.

SCHEME - 04

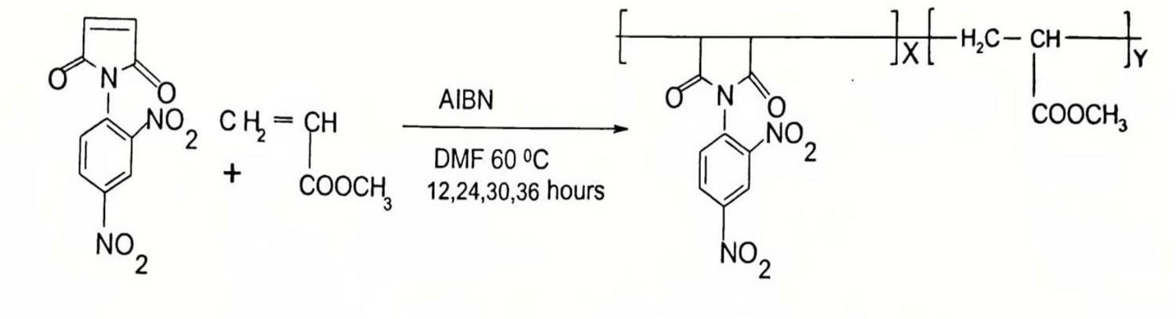


2, 4 Di -(Nitrophenyl) maleimide

G. Copolymerization of N-(2,4-Dinitrophenyl) Maleimide with Methylacrylate(OPNPMCMA)

Equal amount of 2,4-Nitrophenylmaleimide and Methylacrylate in 30 ml THF solvent were taken in a round bottom flask. The reaction was carried out at 65°C for 12, 24 ,36 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.

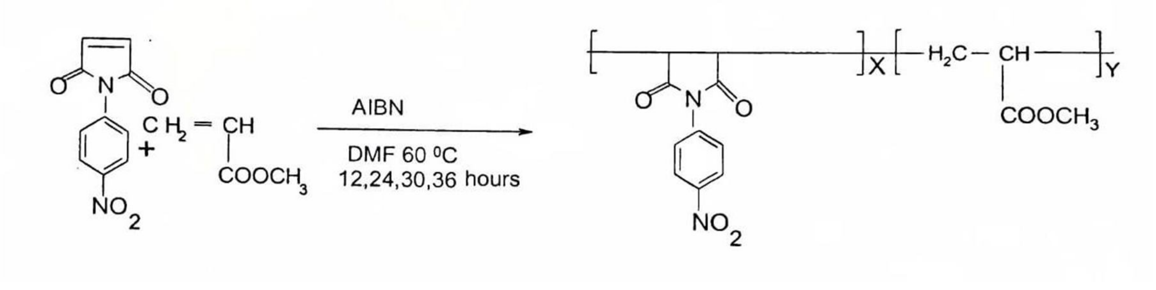
Scheme-5



H. Copolymerization of N-(4-Nitrophenyl) maleimide with Methylacrylate (PNPMCMA)

Equal amount of 4-Nitrophenylmaleimide and Methylacrylate in 30 ml THF solvent were taken in a round bottom flask. The reaction was carried out at 65°C for 12, 24 ,36 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.

Scheme-6



III. RESULTS AND DISCUSSION

A. PNPMI

FTIR spectra observed at 3091.3,2980.8 (aromatic and alkene C-H stretch), 1797 and 1708 (C=O), 1634(CH=CH, alkene), 1564 1456 (C=C, aromatic) , 1335,1504 ($-NO_2$), 967 (CH=CH), 856(1,4 disubstituted benzene) these are consistent with the structure of PNPMI. ^{1}H-NMR: (CH=CH) protons at δ 6.82 (s) ppm, Aromatic protons at δ7.13-7.15 (d) ppm; two aromatic proton (m-group in phenyl ring) at δ7.63-7.64 (d) ppm [15-20] .

B. HPNPMI

3088 (C-H aromatic), 2981 (C-H stretch alkene), 1778, 1715(C=O) 1614, 1651, 1563, 1444, 1596 (C=C stretch aromatic), 1504, 1331 (Ar-NO_2), 1255 (asymmetric C-O-C stretch), 1110, 1168 (symmetric C-O-C stretch), 856 (1,4 disubstituted benzene) and 690, 605 (out of plane aromatic ring C=C bend). the ^{1}H–NMR δ 7.50–8.08 (d). 2H,at 3.5–4.0 ppm [21-23].

C. PNPMCMA

In fig.1, 3050,3190 (Aromatic,C-H), (CH=CH), 1750, 1790 (C=O), 1548 (-NO_2 group) 1461.9 (C-H band, $-CH_2$), 1380 (C-N, Stretching of maleimide),1189 (C-O-C), 1540,1548 (-NO_2), 832 (1,2-disubstituted benzene) and 780.3,850 cm^{-1} (out of plane C-H band of benzene ring), and 630 (aromatic ring C=C band). ^{1}H-NMR of PNPMCMA, In Fig.2, δ values from 7.5 to 8.1 due to present of phenyl ring protons and a signal of showing δ at 4.0 present of MA, δ values obtained in 3.3 to 3.5 ppm, polymerization precede via single bond.

D. OPNPMCMA

3070,3200 (Aromatic,C-H) 1740, 1800 (C=O), 1570 (-NO_2 group) 1484 (C-H band, $-CH_2$), 1320,1380 (C-N, Stretching of maleimide), 1100 (C-O-C), 1531 (-NO_2), 890 (1,2-disubstituted benzene) and 700,750 cm^{-1} (out of plane C-H band of benzene ring), and 670 (aromatic ring C=C band). ^{1}H-NMR of PNPMCAA, In Fig.3, δ values from 7.5 to 8.1 due to present of phenyl ring and a signal of showing δ at 4.0 present of MA, δ values obtained in 3.3 to 3.5ppm.

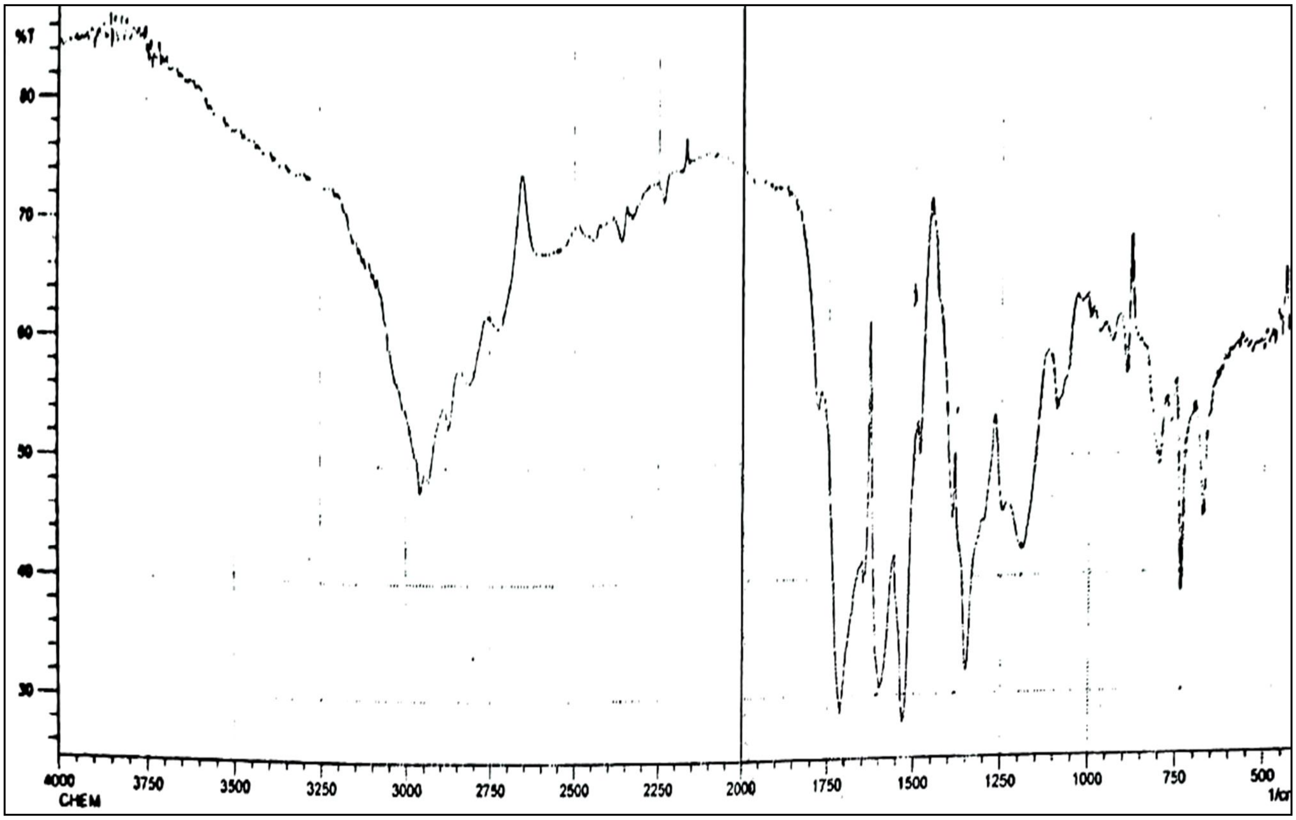


Fig. 1 FTIR spectra of PNPMCAM

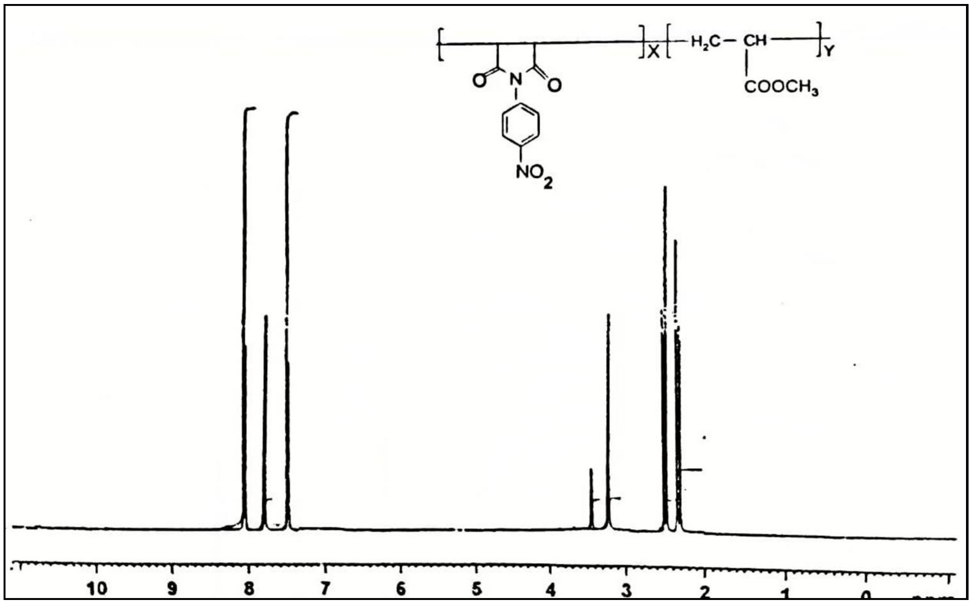


Fig. 2 ^{1}H-NMR of PNPMCAM

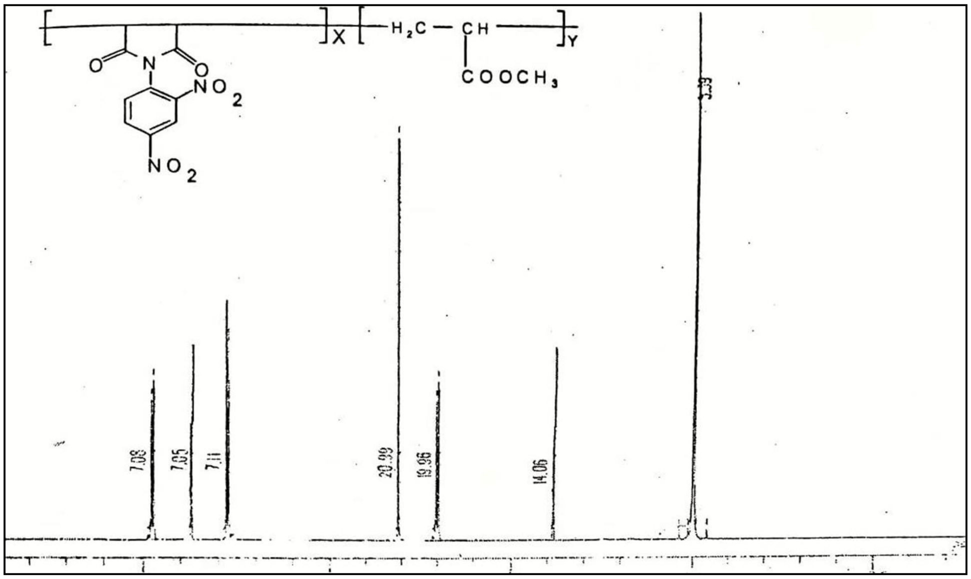


Fig. 3 ^{1}H-NMR of OPNPMCM

E. Effect of time on yield

Percentage yield were obtained at different time hours and any polymeric material very useful for industries purpose and percentage yield was given in table. 1 and from the table we are observed that percentage yield was increases with time hours.

Table 1. Percentage Yield of Homopolymer and copolymers given in table with respect to time Hours.

Polymer Code	12Hrs.	24Hr.	30Hrs.	36Hrs.	Colour
HPNPMI	18.78	33.23	38.12	40.78	Yellow
PNPMCMA	42.7	43.8	44.9	45.2	Yellow
OPNPMCMA	27.6	28.20	29.0	30.20	Yellow

F. Effect of solvent and Initiator on percentage yield

Percentage yield of synthesis polymer are calculated with respect using Free radical AIBN and BPO and results are summarized in table 2. Indicate that the percent yield in the AIBN-DMF system is more suitable as the comparable BPO-DMF solvent system. AIBN-DMF system gives higher yield.

Table 2. Shows the result of percentage yield in DMF-AIBN and DMF-BPO Solvent system

Polymer Code	Solvent	AIBN	BPO	Colour
PNPMCMA	DMF	47.0	46.0	Yellow
	THF	44.0	44.4	Yellow
OPNPMCMA	DMF	30.2	29.8	brown
	THF	29.2	29.4	Yellow

G. Intrinsic viscosity

Intrinsic viscosity determined by Ubbelohde suspended viscometer. Intrinsic viscosity depends on molecular weight as well as on the size of the polymer coil in a given solution. it is a measure of hydrodynamic volume. Molecular weight of synthesis compounds determined by the Gel Permeation Chromatography and relation find out in between molar mass and intrinsic viscosity. The relation between the molecular weight and intrinsic viscosity of polyvinyl alcohol observed [21] . The viscosity measurements were carried out with an Ubbelohde suspended level type viscometer[22].From the flow time of solution (t) and solvent t_0, the specific viscosity (ηsp) was evaluated by the following relationship.

$$\eta_{sp} = \frac{t - t_0}{t_0}$$

This was used to find reduced viscosity, η reduced.

$$\eta_{reduced} = \frac{\eta_{speific}}{C}$$

The intrinsic viscosity [η] was obtained from the plots of reduced viscosity versus concentration by extrapolating the curve at c → 0. Intrinsic viscosity (η) of homopolymers and copolymers are summarized in table. 3 and 4

Table 3. Typical data of Viscosity measurements of HPNPMI summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	*Intrinsic viscosity*
HPNPMI	0.1	1.0055	.0055	0.055	0.0423
	0.2	1.0138	.0138	0.069	
	0.3	1.0255	.0255	0.085	
	0.4	1.0380	.0380	0.095	
	0.5	1.0560	.0560	0.112	
	0.6	1.0732	.0732	0.122	

Table 4 . Typical data of Viscosity measurements of PNPMCAN summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	*Intrinsic viscosity*
PNPMCMA	0.1	1.0291	0.0291	0.291	0.284
	0.2	1.0590	0.0590	0.295	
	0.3	1.0915	0.0915	0.305	
	0.4	1.1252	0.1252	0.313	
	0.5	1.1560	0.1560	0.317	
	0.6	1.1938	0.1938	0.323	

Table 3 and 4 are shows that intrinsic viscosity of Copolymer is more than of Homopolyer. it is due to present of both are unit in the structure of copolymer.

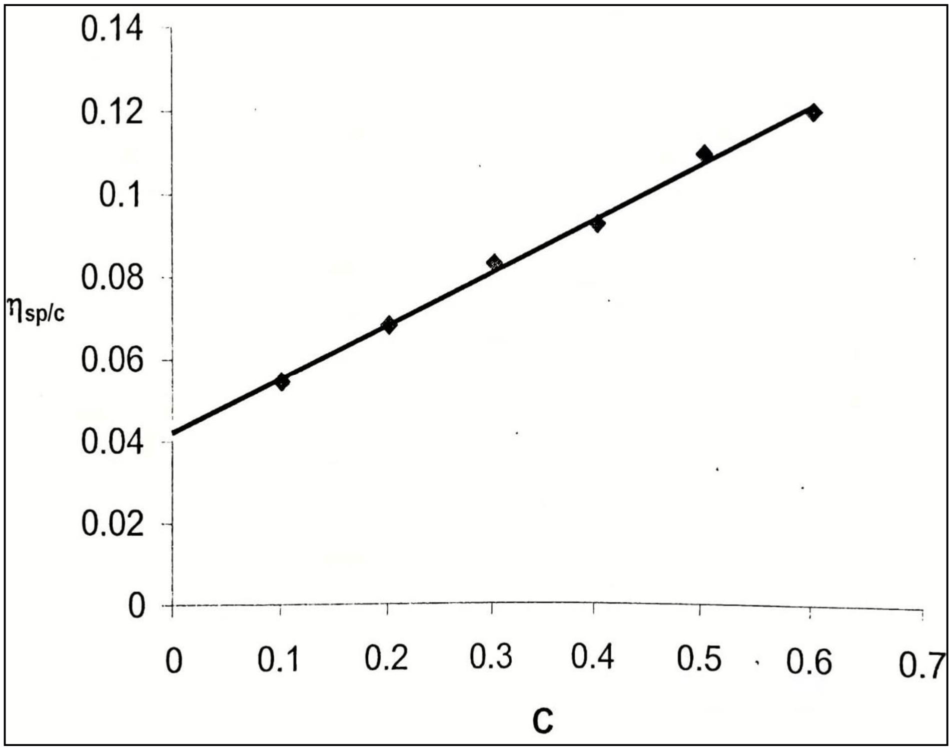


Fig. 4 for HPNPMI

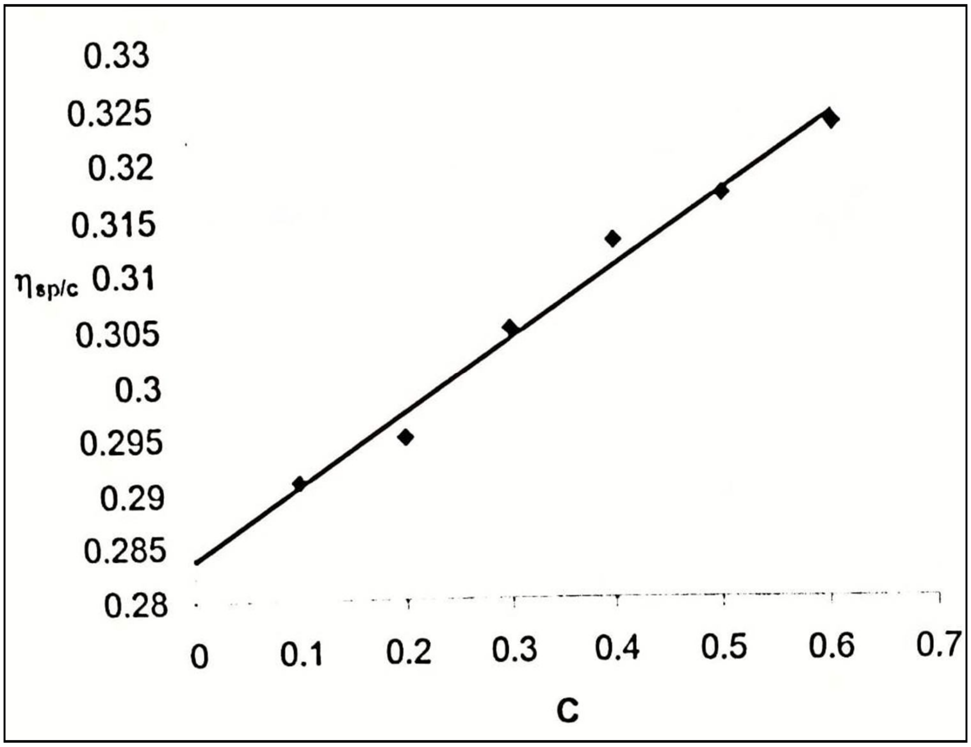


Fig. 5 for PNPCMA

I. Effect of Feed Ratio of Monomers

Synthesized monomers and substituted vinyl monomers were copolymerize taking initial different mole ratios. Results are summarized in table 5 and 6.

Table. 5 Feed mole ratio for copolymer of PNPMI with Methylacrylate in DMF solvent

Polymer code	PNPMI	MA	Time in hrs.	Yield	Appearance
PNPMCMA1	0.1	0.9	24	45.5	Brown
PNPMCMA2	0.2	0.8	24	45.1	Brown
PNPMCMA3	0.3	0.7	24	44.7	Brown
PNPMCMA4	0.4	0.6	24	44.2	Brown
PNPMCMA5	0.5	0.5	24	43.8	Brown
PNPMCMA6	0.6	0.4	24	43.4	Brown
PNPMCMA7	0.7	0.3	24	43.0	Brown
PNPMCMA8	0.8	0.2	24	42.5	Brown
PNPMCMA9	0.9	0.1	24	42.0	Brown

Table. 6 Feed mole ratio for copolymer of OPNPMI with Methylacrylate in DMF solvent

Polymer code	OPNPMI	MA	Time in hrs.	Yield	Appearance
PNPMCMA1	0.1	0.9	24	29.8	Light Brown
OPNPMCMA2	0.2	0.8	24	29.1	Light Brown
OPNPMCMA3	0.3	0.7	24	28.8	Light Brown
OPNPMCMA4	0.4	0.6	24	28.5	Light Brown
OPNPMCMA5	0.5	0.5	24	28.2	Light Brown
OPNPMCMA6	0.6	0.4	24	27.9	Light Brown
OPNPMCMA7	0.7	0.3	24	27.6	Light Brown
OPNPMCMA8	0.8	0.2	24	27.3	Light Brown
OPNPMCMA9	0.9	0.1	24	27.0	Light Brown

J. Solubility Behavior of Homopolymer and copolymer

Synthesis homopolymer and Copolymers were finely grounded and polymer powder insert and placed into test tube and two to three ml solvent was added and stirred at 30C. same procedure repeat again and again for each sample. Solvents were taken as follows THF,DMF,DMSO,Benzene.Methylacetate,,1,4Dioxane,Xylene,dichloromethane,2Butanol,cyclohexanon,water,methanol and carbon tetrachloride. Knowing about information very important for any industrial purpose because today's times a lot of paints made by the plastic coated materials. Solubility of any polymeric materials depends upon the composition of polymer structure. Solubility of homopolymer is less than copolymer while always is not same . Result of Solubility is summarized in table. 7

Table . 7 Relative solubility of homopolymer and copolymer are summarized

Solvents	HPNPMI	PNPMCMA	OPNPMCMA	Colour
Chloroform	Soluble	Soluble	Soluble	Yellow
THF	Soluble	Soluble	Soluble	Yellow
DMF	Soluble	Soluble	Soluble	Yellow
DMSO	Soluble	Soluble	Soluble	Yellow
Dioxane	Soluble	Soluble	Soluble	Yellow
Acetone	Soluble	Soluble	Soluble	Yellow
Ethyl acetae	Soluble	Soluble	Soluble	Yellow
Xylene	In Soluble	Insoluble	PartialSoluble	Yellow
Toluene	Soluble	PartialSoluble	PartialSoluble	Yellow
Carbon tetrachloride	Soluble	PartialSoluble	PartialSoluble	Yellow
Cyclohexanone	Partial Soluble	Partial Soluble	Insoluble	Yellow
Dichloromethane	Soluble	Soluble	Soluble	Yellow
n-Hexane	Partial Soluble	Partial Soluble	In Soluble	Yellow
Ethanol	Soluble	Soluble	Soluble	Yellow
Methanol	Soluble	Soluble	Soluble	Yellow
Benzene	Soluble	Partial Soluble	Soluble	Yellow

K. Thermal behavior of Homo and Copolymer

Synthesis homopolymer and copolymer and their thermal stability were determined by the Thermogravemetric analysis. Thermograms of synthesis HPNPMI ,PNPMCMA and OPNPMCMA are shown in Fig.6,7 and 8. Thermal stability were determined by Perkin Elmer USA Pyris TGA-A Techniques. Initial temperature Ti and Final temperature Tf. Degradation of the polymer range shown in Table .8 and 9. The results of percentage weight loss suffered from 100 °C to 550 °C .

Table . 8 Thermal degradation of Homopolymer and copolymer samples

Polymer Code	Degradation step	Ti °C	Tmax °C	Tf °C	Residue at 500 °C
PPNPMI	I	240	340	370	20.88
	II	370	410	550	
OPNPMCMA	I	210	395	442	15.01
	II	442	480	560	
PNPMCMA	I	217	292	345	21.33
	II	345	398	550	

Table. 9 Percentage weight loss of Homopolymer and copolymer at various temperature.

Polymer Code	200 °C	300 °C	400 °C	500 °C	550 °C
PPNPMI	-0.8	-20.8	-72.8	-79.1	-79.2
OPNPMCMA	--0.72	-7.73	-50.73	-84.99	-88.67
PNPMCMA	-2.98	-52.29	-78.99	-79.67	-81.28

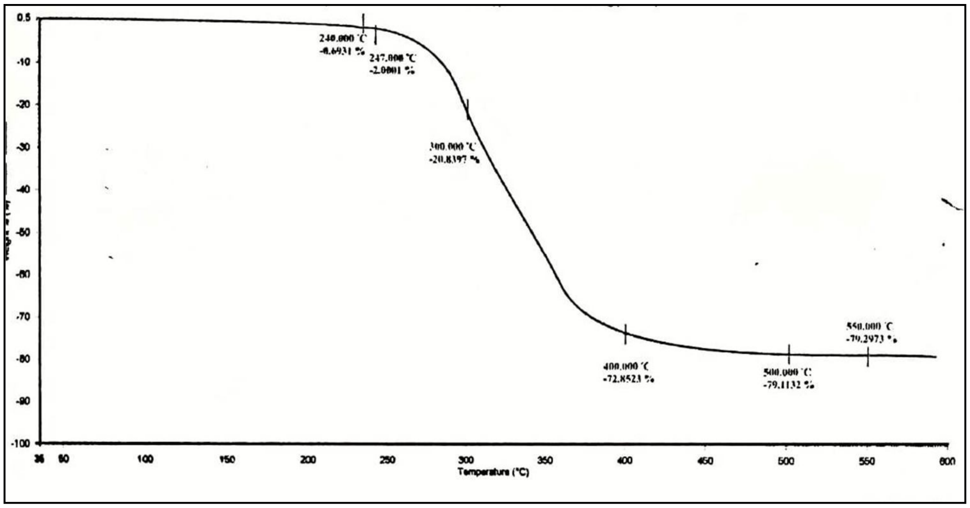


Fig. 6 TGA curve of HPNPMI

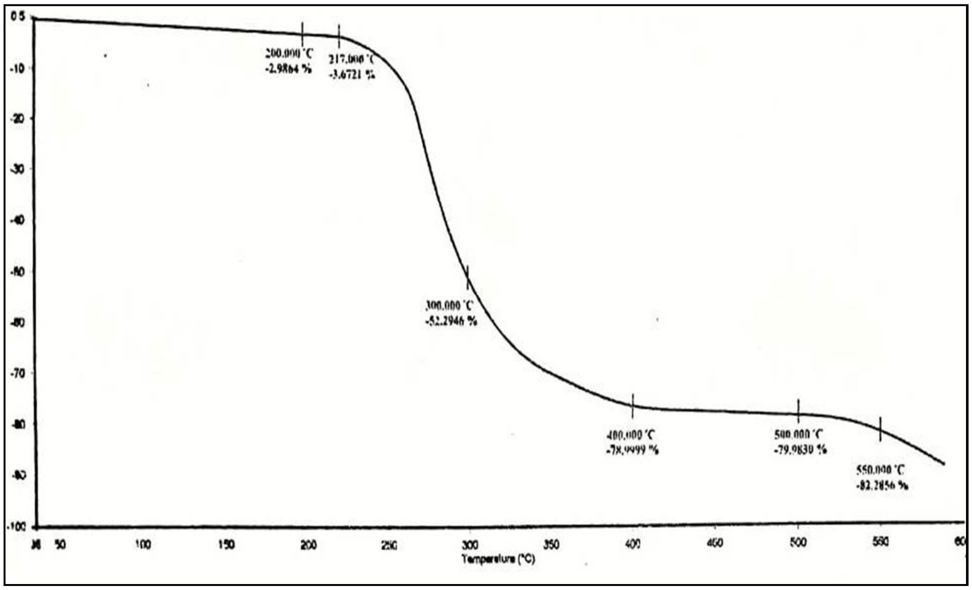


Fig. 7 TGA curve of PNPMCMA

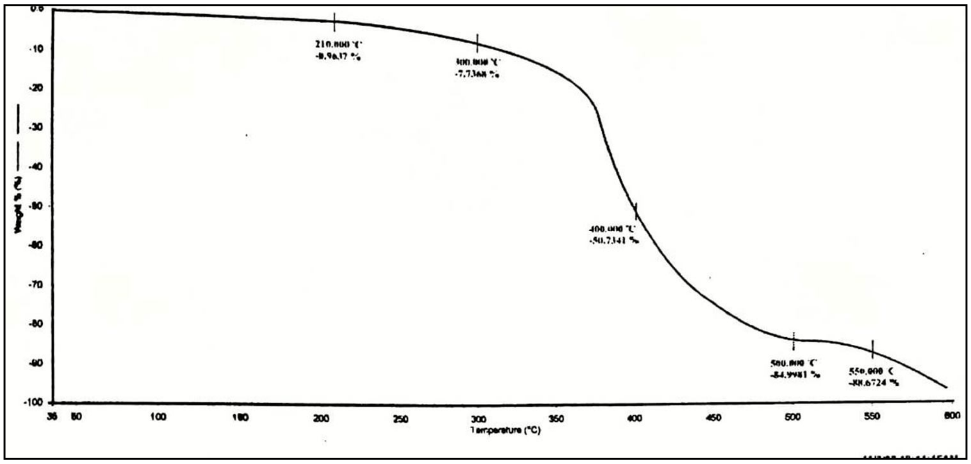


Fig. 8 TGA curve of OPNPMCMA

IV. CONCLUSION

Synthesis homopolymer and copolymer shows the excellent solubility in THF,DMF ,DMSO, Chloroform .Ethyl acetate and solubility of any polymeric materials depends on the composition like as texture and length ,molecular weight, Intrinsic viscosity. It is observed that polymerization reactions completed via radical polymerization this is approved by the Polydispersity index. Copolymer shows highly molecular weight more than of homopolymer it is due to copolymer having both are unit. Weight average and number average molecular weight determined by the Gel permeation chromatography. Polymers exhibit highly thermal stability due to present of imide ring and Homopolymer shows highly thermal stability than copolymers because homopolymer contain only single unit in their backbones.

V. ACKNOWLEDGEMENT

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