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Recent Study of N – (4-Methoxyphenyl) Maleimide Monomer and Copolymerized with Methylacrylate



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ABSTRACT

The 4-Methoxyphenyl maleimide monomers were prepared by Maleic anhydride reaction with 4-Methoxyaniline and obtained 4-Methoxyphenylmaleimide. Copolymerized with Methylacrylate. In order to study of thermal stability effect with Methoxy group. Free radical initiator AIBN and BPO were used duration of the reactions. THF and DMF solvent used under the appropriate atmosphere. Reaction carried out at different time hours. The chemical structures of polymers were identified by Fourier Transform Infrared Reflection (FT-IR) spectroscopy. Gel permeation chromatography equipment given the knowledge about the molecular weight. The thermal stability and degradation of the copolymer were recorded by TGA Techniques. Analysis of the TGA results revealed that the weight loss rate was starting at 220°C. The homopolymer and copolymer exhibited a significant weight loss in the range of 220–550°C. The compound weight lost at 34.80% around the 300°C.



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INTRODUCTION

Thermal stable and heat resistant polymers have wide range of multi applications. Because without polymer we can't easily feel although we know that polymer application is very harmful but we know that N-Phenylmaleimide polymers are have very important role in our daily life and well-defined polymer microstructures promise new material properties, the control of the macromolecular architecture has become an important topic of contemporary polymer science. Recently, significant progress has been made in the field of living free-radical polymerization such as nitroxide-mediated stable free radical polymerization [1–4] atom transfer radical polymerization [5–12]. Maleimide is easily prepared by reaction of Maleic anhydride with a primary amine ,after dehydration of the resulting compound to produce maleimide ring [13-17]. Additionally, the vinylene group of maleimides can be polymerized under radical conditions. Poly maleimide and its derivatives are important polymers [18]. Recently number of many articles of Substituted Phenylmaleimide and copolymerization related paper has been published [19-25]. Recently in our laboratories we are synthesis of substituted N-Phenylmaleimides. In this current series our published paper N-Substituted Phenylmaleimide polymers [26-28]. Present article our major interested to synthesized novel polymer of 4-Methoxyphenylmaleimide and copolymerized with Methylacrylate and evaluated their thermal stability, solubility and characterized by FTIR and ¹H-NMR.

EXPERIMENTAL

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. 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 [28].

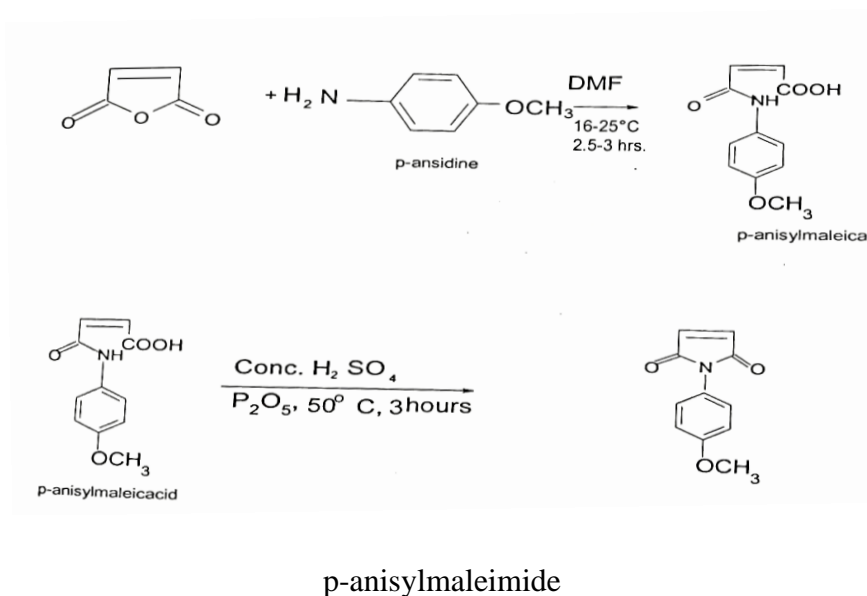
Measurements

$^1\text{H-NMR}$ 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 N-(4-Methoxyphenyl) maleimide (PAMI) : p-anisidine and maleic anhydride were taken in 30 ml DMF. The reaction mixture was stirred for three hours at 25°C. The reaction solution was insert in crushed ice. Yellow solid precipitate was obtained, then filtered and dried under vacuum. It was recrystallized from methanol to obtained pure p-anisylmaleic acid after Cyclodehydration of the p-anisylmaleic acid, the solution treated with conc. H_2SO_4 and P_2O_5 and stirred for three hours at 50°C. Then the solution poured in crushed ice or cooled water, obtained to green solid precipitate filtered and washed with water and dried. The yield was 70%, m.p. 129°C.

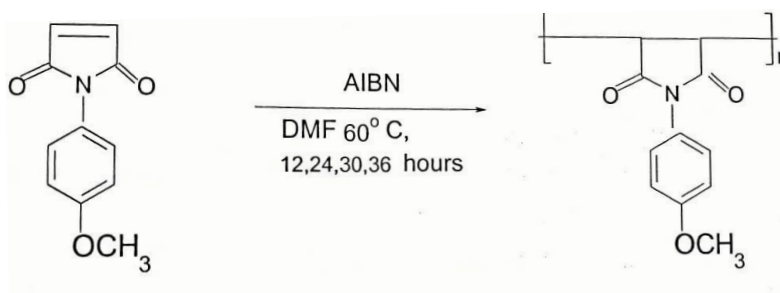
SCHEME-I



Homopolymerization of N-(4-Methoxyphenyl) maleimide (PPAMI)

N-(4-Methoxyphenyl) maleimide (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 solution was refluxed on heating mantle at 60°C for 12, 24, 30 and 36 hours. Product was obtained 52.43% 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 desiccator free from moisture.

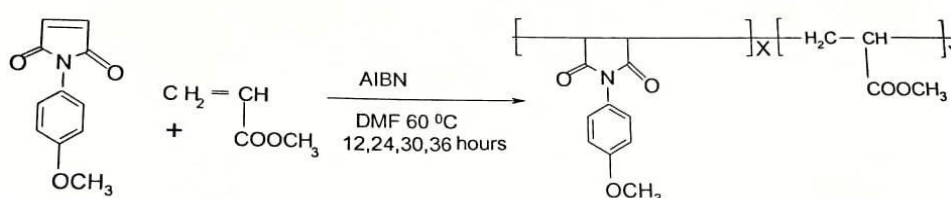
SCHEME - 02



Copolymerization of N-(4-Methoxyphenyl) maleimide with Methylacrylate

Equal amount of N-(4-Methoxyphenyl) maleimide and Methylacrylate in 30 ml THF solvent were taken in a round bottom flask. The reaction was carried out at 60°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-3



RESULTS AND DISCUSSION

PPAMI

Fig.1 Shows, 3074 cm^{-1} (aromatic C-H stretching) , $1778,1714$ (C=O group), $1621, 1588, 1439\text{ cm}^{-1}$ represent (C=C) ring stretching. $1549, 1353$ (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). The multiple in the range at δ 7.23–7.35 ppm corresponds to the four aromatic protons. Two protons in –CH–CH– group have appeared at δ 4.02–3.05 ppm. $^1\text{H-NMR}$ of PPAMI monomer shows chemical shift δ at 7.15 (s) ppm characteristic of –CH=CH– group [26-28].

PAMCMA

The purity and structure of PAMCMA was ascertained by IR and $^1\text{H-NMR}$ spectra $2032,2932$ (CH=CH), $1780, 1715$ (C=O), 1513 (-CH-Stretching of imide) 1461.9 (C-H band, –CH₂), 1389 (C-N, Stretching of maleimide), 1160 (C-O-C), 1512 -CH-stretching, 832 (1,2-disubstituted benzene) and 662 cm^{-1} (out of plane C-H band of benzene ring), and 650 (aromatic ring C=C band). $^1\text{H-NMR}$ of PAMCMA In Fig.2, δ values from 6.9 to 8.0 due to present of phenyl ring protons and a signal of showing δ at 4.1 present of MA, δ values obtained in 3.2 to 3.7 ppm, polymerization precede via single bond [28-29].

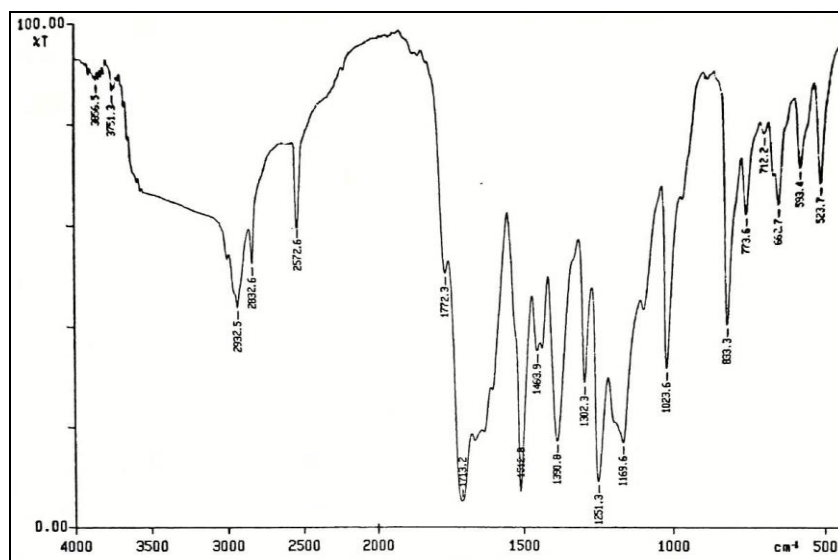


Fig. 1 FTIR Spectra of PPAMI

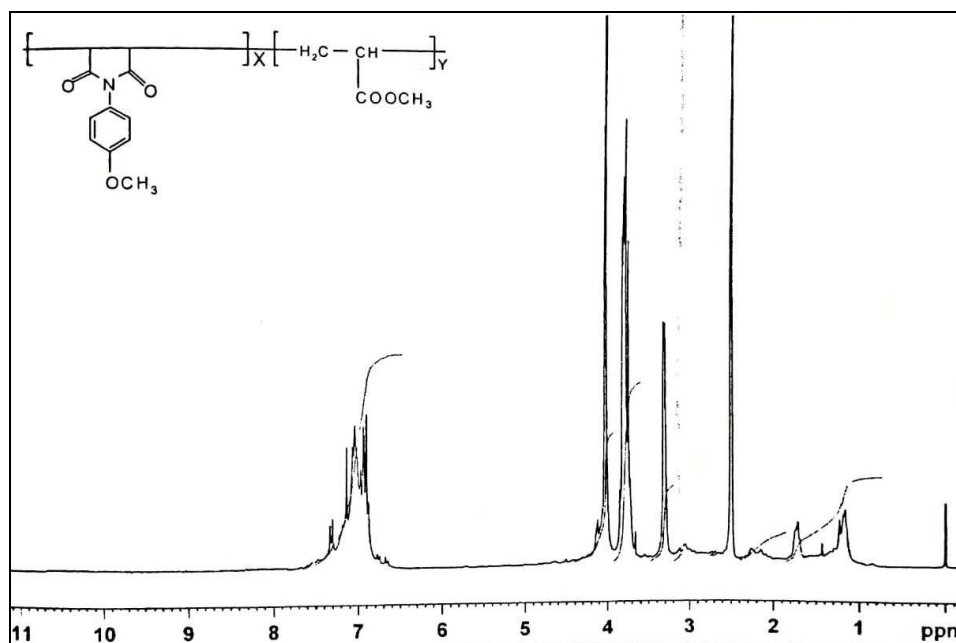


Fig. 2 ¹H NMR Spectra of PAMCMA

Effect of Feed ratio of monomer

The nine copolymer samples were synthesized by using different feed ratios. Synthesis monomers copolymerized with Methylacrylate and percentage yield summarized in table. 1.

Table. 1 shows copolymer of PAM with Methylacrylate using free radical AIBN

Polymer code	PAMI	MA	Polymer Time	Yield	Appearance
PAMCMA1	0.1	0.9	24	63.8	Cream
PAMCMA2	0.2	0.2	24	63.1	Cream
PAMCMA3	0.3	0.3	24	62.4	Cream
PAMCMA4	0.4	0.4	24	61.7	Cream
PAMCMA5	0.5	0.5	24	61.1	Cream
PAMCMA6	0.6	0.6	24	60.4	Cream
PAMCMA7	07	0.7	24	59.7	Cream
PAMCMA8	0.8	0.8	24	59.0	Cream
PAMCMA9	0.9	0.9	24	58.4	Cream

Effect of time on Yield and solvent initiator systems

Prepared monomers were copolymerized with different time hours and percent yield were observed.

Table. 2 Percentage Yield of Homopolymer of PPAMI given in table with respect to time Hours.

Polymer Code	Feed Mole	Time in hr.	Yield	State	Colour
PPAPMI	0.01	12	48.72	Solid	Brown
		24	52.43	Solid	Brown
		30	56.23	Solid	Brown
		36	61.32	Solid	Brown

Table. 3 Percentage Yield of PAPMI in different free radical solvent system given in table

Polymer Code	Solvent	AIBN	BPO	State	Colour
		Yield Percentage			
PPAPMI	THF	58.14	56.71	Solid	Brown
	DMF	61.38	60.31	Solid	Brown
	1,4Dioxane	58.74	58.78	Solid	Brown

Table. 4 Shows the result of percentage yield in DMF-AIBN and DMF-BPO Solvent system

Polymer Code	Solvent	AIBN	BPO	Colour
PAMCMA	DMF	65.2	64.8	Brown
	THF	63.8	63.0	Light green

From comparison of the table 2 and 3 indicate that the percent yield in AIBN-DMF system is more suitable as the comparable BPO-DMF solvent system. AIBN-DMF system gives higher yield.

Intrinsic viscosity and molar mass

Prepared polymer and their molar mass analysis by Gel permeation chromatography equipment and Intrinsic viscosity determined by Ubbelohde suspended viscometer. Intrinsic viscosity depends on molar mass, as well as on the size of the polymer coil in a given solution. It is a measure of hydrodynamic volume. As well as the molecular weight increases intrinsic viscosity is also increases. The graph drawn shows a direct relationship between the concentration and viscosity.

Table 5. Typical data of Viscosity measurements of PPAPMI summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PPAMI	0.1	1.00345	0.00345	0.0354	0.028
	0.2	1.01032	0.01032	0.516	
	0.3	1.02007	0.02007	0.0669	
	0.4	1.03152	0.03152	0.0788	
	0.5	1.04200	0.04200	0.0840	
	0.6	1.05580	0.05580	0.0930	

Table 6. Typical data of Viscosity measurements of PAMCMA summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PAMCMA	0.1	1.0234	0.0234	0.234	0.230
	0.2	1.0484	0.0484	0.242	
	0.3	1.0741	0.0741	0.247	
	0.4	1.1024	0.1024	0.256	
	0.5	1.1295	0.1295	0.259	
	0.6	1.1560	0.1560	0.260	

It is observed that copolymer shows high intrinsic viscosity as compare to Homopolymer it means that both are unit present in copolymer.

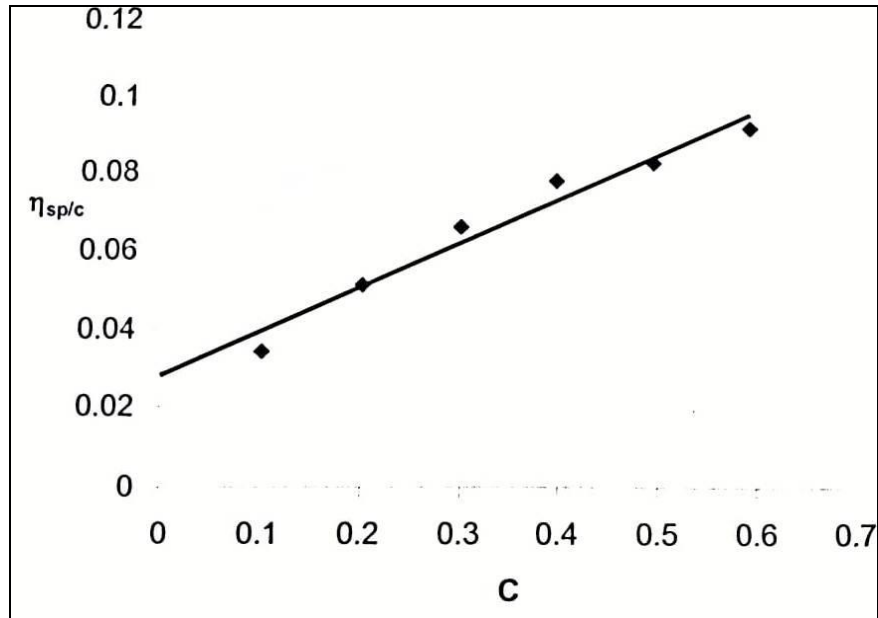


Fig. 3. for PPAMI

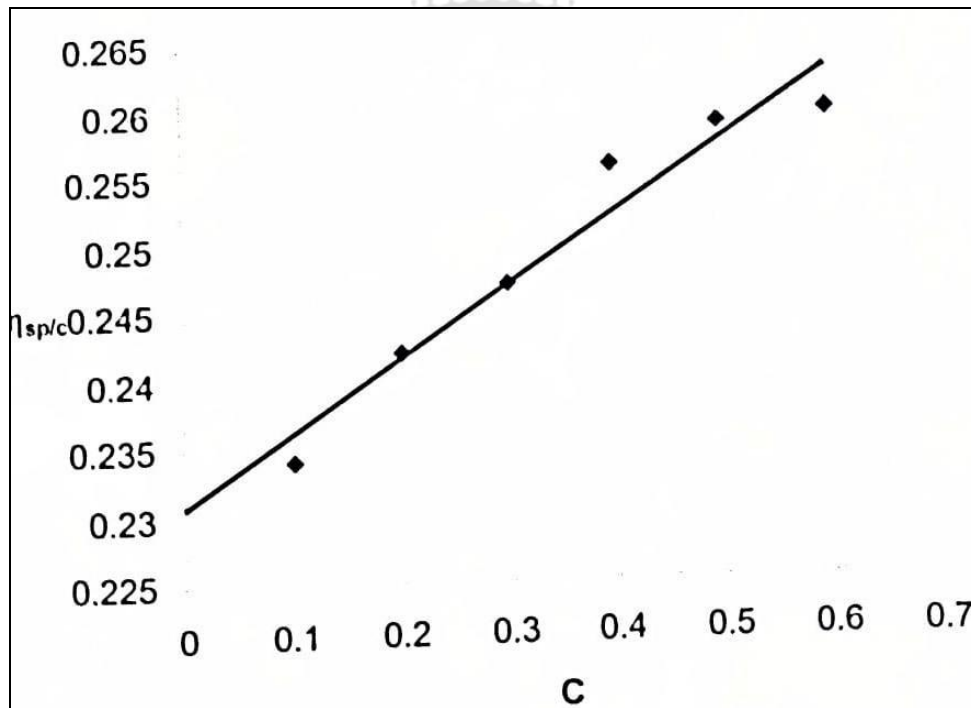


Fig. 4. for PAMCMA

Solubility behavior of Polymers

Synthesis polymers and their solubility determine by using different solvents and solubility of polymer depends nature of Solvents, temperature and pressure. In present article we are used a simple methods, firstly taking small amount of grounded powder and solvent in the test tube than insert the small (15-30mg) amount of finely polymer powder and shake it and observed. Results are summarized in table. 7.

Table 7. Relative solubility of homopolymer and copolymer are summarized

Solvents	PPAMI	PAMCMA
Chloroform	PartialSoluble	Soluble
THF	Soluble	Soluble
DMF	Soluble	Soluble
DMSO	Soluble	Soluble
Dioxane	Soluble	Soluble
Acetone	Soluble	Soluble
Ethyl acetate	Soluble	Soluble
Xylene	Partial Soluble	PSoluble
Toluene	Partial Soluble	PartialSoluble
Carbon tetrachloride	InsolubleSoluble	PartialSoluble
Cyclohexanone	InsolubleSoluble	Partial Soluble
Dichloromethane	Soluble	PSoluble
n-Hexane	Partial Soluble	I Soluble
Ethanol	Soluble	Soluble
Methanol	Soluble	Soluble
Benzene	Soluble	Partial Soluble

Thermal behavior of Homo and Copolymer

Synthesis homopolymer and copolymer and their thermal stability degradation are given in table.8 and table. 9 Thermal stability were determined by the TGA Techniques. Here Ti is initial

degradation and Tf is noted for final degradation at 500 °C. The TGA analysis of polymer completed by using PERKIN ELMERUSA PYRIS TGA-A Equipment. Degradation of the polymer were recording at 10 °C/ minute.

Table 8. Thermal degradation of Homopolymer and copolymer samples

Polymer Code	Degradation step	Ti °C	Tmax °C	Tf °C	Residue at 500 °C
PPAMI	I	220	290	315	8.55
	II	315	328	550	
PAMCMA	I	196	350	415	22.02
	II	415	460	575	

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

Polymer Code	200 °C	300 °C	400 °C	500 °C	550 °C
PPAMI	-1.2	-34.8	-86.8	-91.5	-94.7
PAMCMA	-0.81	-20.00	-57.69	-77.98	-86.20

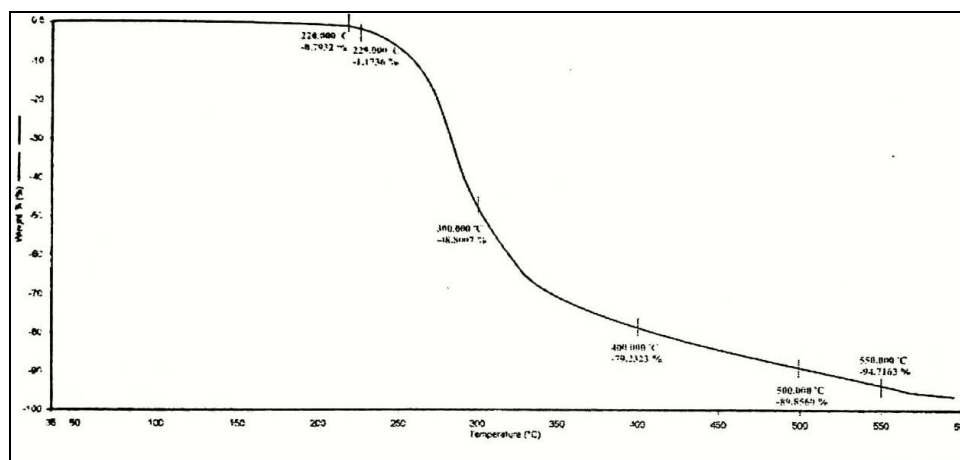


Fig. 5 TGA curve for PPAMI

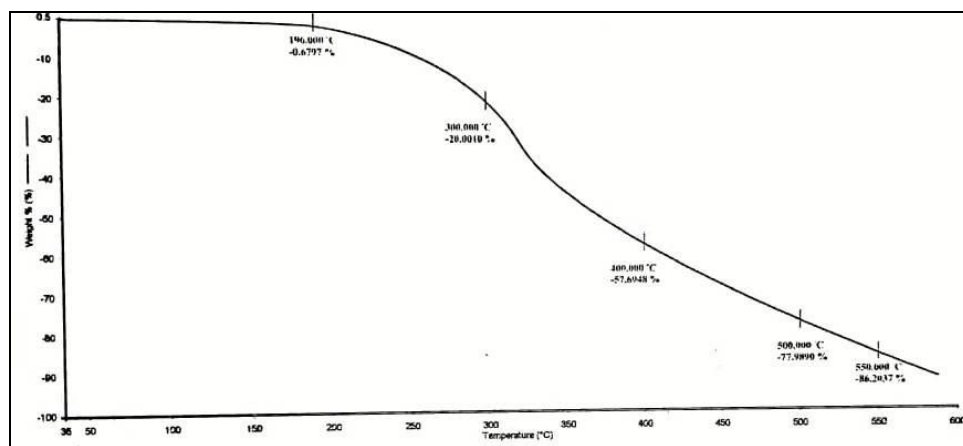


Fig. 6 TGA curve for PAMCMA

CONCLUSION

Synthesis polymer shows the excellent thermal stability. Thermal degradation of the polymer observed in two step degradation. Solubility of the polymer determined by a simple procedure and excellent solubility shows by the synthesis polymer in THF, DMF, DMSO, Chloroform, Ethyl acetate and solubility of the polymers is very essential and important for industries purpose. solubility of any polymeric materials depends on temperature, pressure and composition. Polymerization reactions completed via radical polymerization it is approved by the Polydispersity index. PDI index observed in range 1.4 to 10. Weight average and number average molecular weight determined by the Gel permeation chromatography. Synthesis of polymer in given solution having rigid rods shape while homopolymer present in unperturbed shape.

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