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Novel Study of N-(4-Methoxyphenyl) Maleimide and Copolymerized with Ethylacrylate



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ABSTRACT

P-Anisidinmaleimide were prepared under the identical condition and presence of p-anisidine and maleicanhydride. THF and DMF Solvent were used. Prepared p-anisidinmaleimide copolymerized with Ethylacrylate. Free radical initiator AIBN and BPO were used duration of the chemical reactions. The chemical composition of polymers were identified by Fourier transform infrared reflection spectroscopy and ¹H-NMR and molecular weight determined by Gel permeation chromatography. The thermal stability and degradation of the copolymer were recorded by TGA Techniques. Synthesis polymer and their shape in given solution identified by Kuhan- mark-Howink Sakwada equation. Intrinsic viscosity determined by Ubbelohde viscometer. Thermal degradation rate observed 10°C/minutes and degradation obtained in two steps for homopolymer and copolymer.



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INTRODUCTION

N-phenylmaleimide (NPMI) and its copolymers have been studied extensively [1-4] and maleimide product due to their thermal stability, widely used in home appliances, automobiles, and the electronics industry [5-7]. The presence of a five-membered ring of 1,2-vinyl double substitution is a key feature that not only determines the heat resistance, but can also be exploited for further polymerization via free radical copolymerization; examples of comonomers include styrene [8-10], maleic anhydride [11], methyl acrylate [12-13], and chloroethylene [14]. At present time substituted N-phenylmaleimide polymers have been recorded [15-25]. N-Substituted maleimides are interesting monomers for making transparent thermally stable polymeric materials [26-32]. Although a lot of work has been studied but still there has been major interest in the synthesis of new maleimide polymer. In present work we are taken 4-methoxy phenyl maleimide monomer copolymerized with Ethylacrylate and evaluation of thermal stability by TGA techniques and characterized by $^1\text{H-NMR}$.

EXPERIMENTAL

MATERIALS

Methylacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl_2 for 6 hours and distilled. The head and tail fractions were discarded. AIBN (2,2'-azobis-isobutyronitrile (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

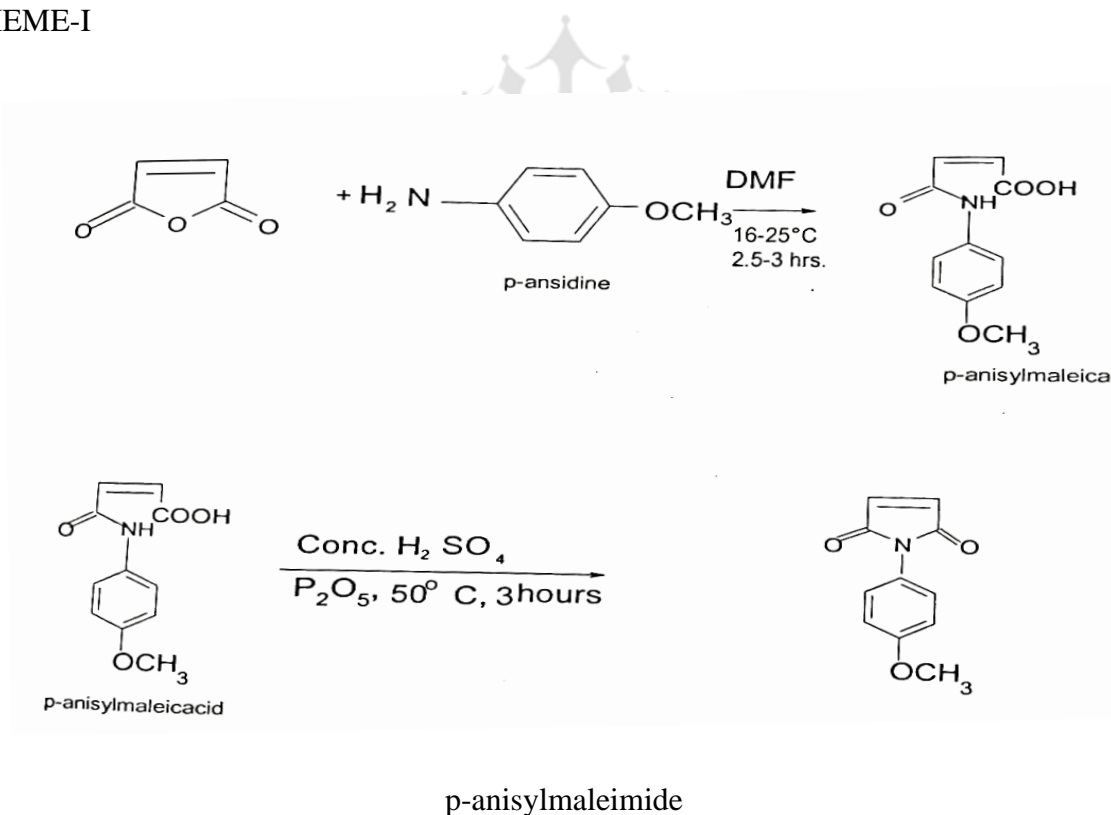
$^1\text{H-NMR}$ spectra of monomer and polymer samples were taken in DMSO-d_6 on a Bruker DPX-200/DPX-300 spectrometer at 200/300 MHz. The internal reference used was TMS. FT-IR spectra of the monomer and polymer sample were recorded on a Shimadzu 8201 PC (4000-400 cm^{-1}) FT-IR spectrometer, using 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 pour 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. H₂SO₄ and P₂O₅ 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. Characterized by ¹HNMR (fig.1), 3.4 ppm to 4.0 ppm for -OCH₃ proton, 3.0 ppm 5.0 ppm for -CH=CH-, 7.0-9.0 PPM for Aromatic protons, these are data confirmed of PAMI structure.

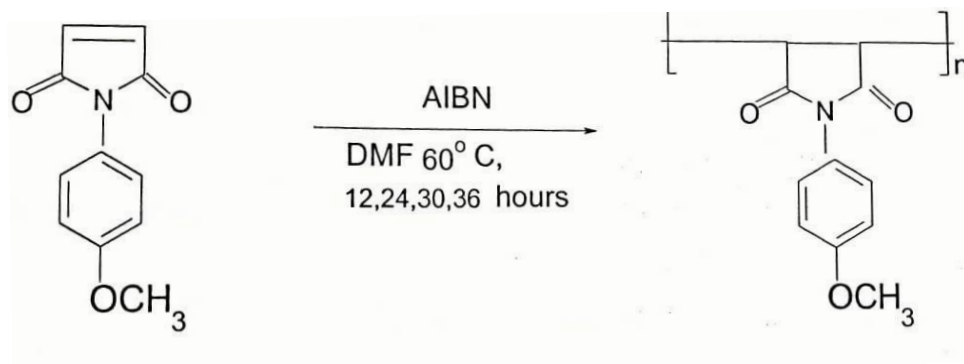
SCHEME-I



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

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 mental 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 dedicator free from moisture.

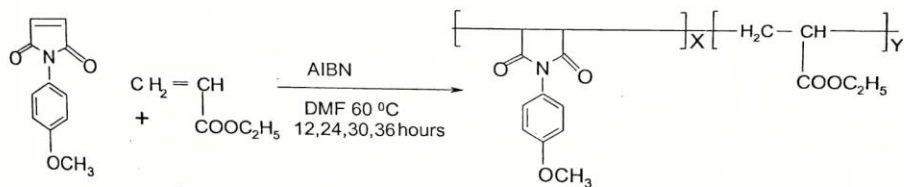
SCHEME - 02



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

Equal amount of N-(4-Methoxyphenyl) maleimide and Ethylacrylate in 30 ml THF solvent were taken in a round bottom flask. The reaction medium 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

HPAMI

Prepared structure of HPAMI was ascertained by IR and $^1\text{H-NMR}$ spectra, $2932, 2832\text{ cm}^{-1}$ (aromatic C-H stretching), $1772, 1713$ (C=O group), 1463 cm^{-1} represent (C=C) ring stretching. $1512, 1390$ (asymmetric and symmetric group). $1251, 1221$ (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 (Figure 1) at δ 7.23–7.35 ppm corresponds to the four aromatic protons. Two protons in $-\text{CH}-\text{CH}-$ group have appeared at δ 4.02–3.05 ppm. $^1\text{H-NMR}$ of HPAMI monomer shows chemical shift δ at 7.15 (s) ppm characteristic of $-\text{CH}=\text{CH}-$ group [26-28].

PAMCEA

FTIR spectra of PAMCEA In Figure 2, $3278, 3077$ (CH=CH), $1778, 1712$ (C=O), 1513 (-CH-Stretching of imide) 1461.9 (C-H band, $-\text{CH}_2$), 1391 (C-N, Stretching of maleimide), 1170 (C-O-C), 1513 -CH-stretching, $1029, 1252$ (Ar-O-C), 831 (1,2-disubstituted benzene) and 666 cm^{-1} (out of plane C-H band of benzene ring), and 650 (aromatic ring C=C band). $^1\text{H-NMR}$ of PAMCEA In Figure 3, 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 E A, δ values obtained in 3.5 to 3.8 ppm, appeared due to $[-\text{CH}-\text{CH}-]_n$ protons and $-\text{OCH}_3$ protons [28-29].

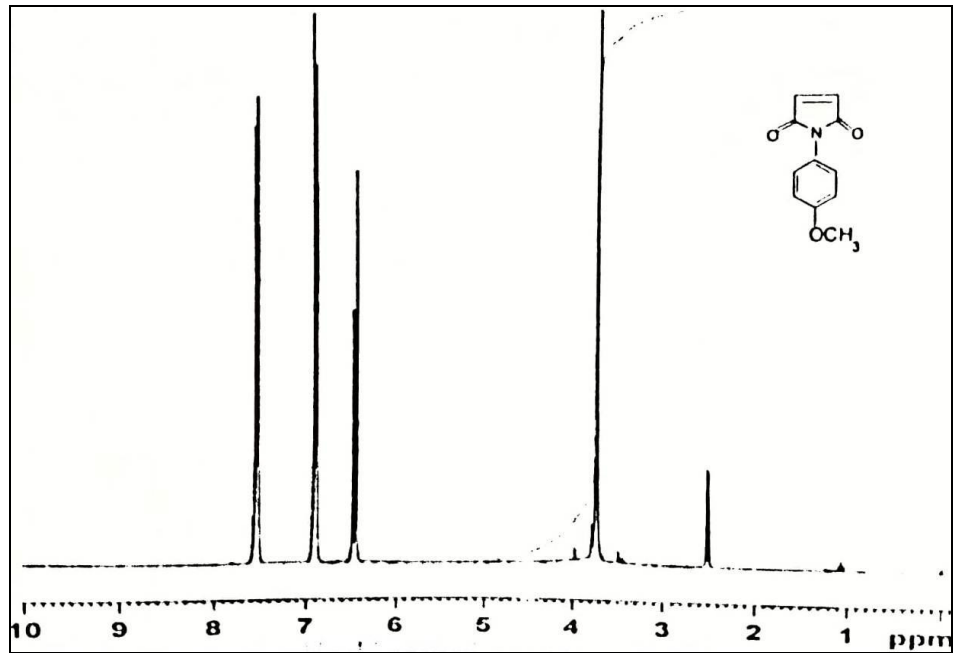


Figure 1: ¹H-NMR Spectra of PAMI

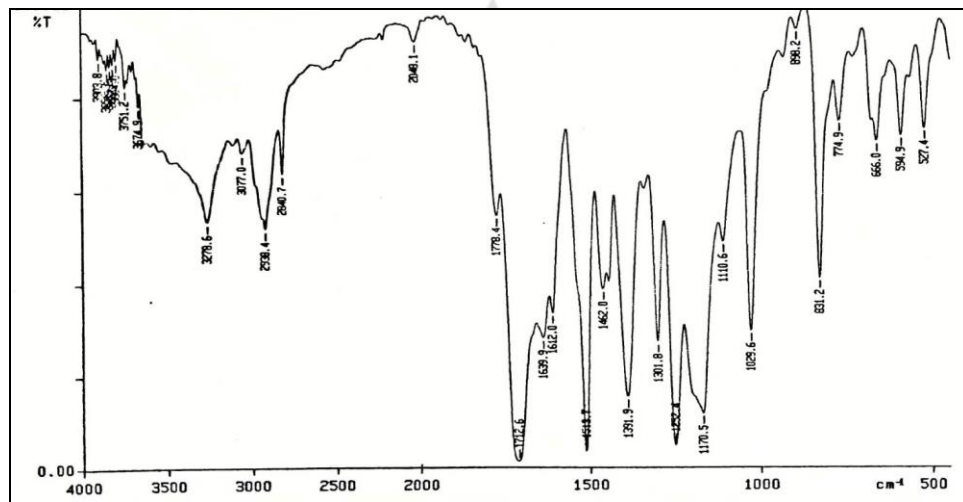


Figure 2: FTIR Spectra of PAMCEA

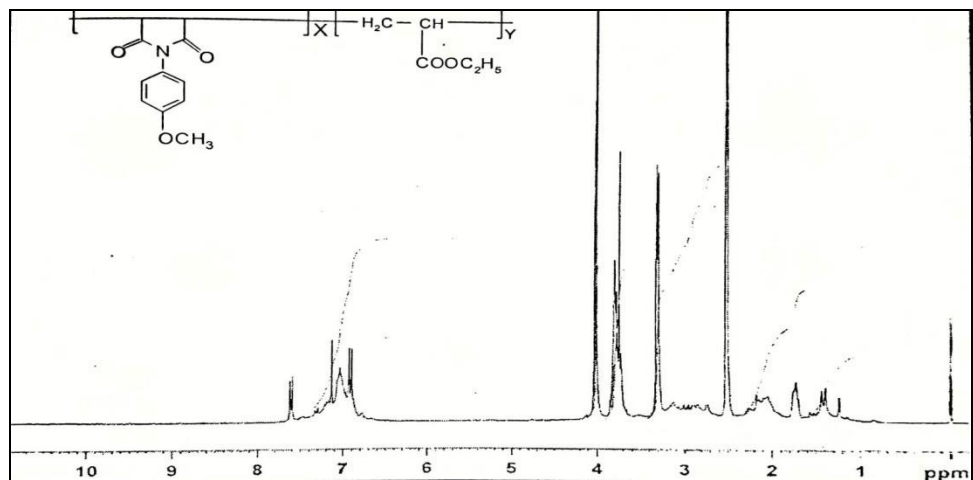


Figure 3: ¹H NMR Spectra of PAMCEA

Effect of time on Yield and solvent initiator systems

Synthesis monomer were copolymerized with different time hours and obtained percent yield were given in table 1.

Table 1: Percentage Yield of Homopolymer of HPAMI given in table with respect to time.

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

Table 2: Percentage Yield of PAPMI in different free radical solvent system given in table

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

Table 3: Shows the result of percentage yield in DMF-AIBN and DMF-BPO Solvent system

Polymer Code	Solvent	AIBN	BPO	Colour
PAMCEA	DMF	69.0	68.0	Brown
	THF	67.20	67.4	Light green

Result of percentage yield are compile in table 2 and 3. They are shows AIBN-DMF system is more suitable as compare of BPO-DMF solvent system. I

Intrinsic viscosity and molar mass

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

Polymer code	Mw	Log Mw	$\eta \times 10^3$ dl/gm	Log $\eta \times 10^3$	Intrinsic viscosity
HPAMI	2376	3.3758	28	1.4472	0.028
PAMCEA	25322	4.4035	232	2.3955	0.232

It is observed that intrinsic viscosity of copolymer shows more than Homopolymer, it concludes that copolymer having both are unit while Homopolymer have only single unit in their backbone.

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 PAMCEA summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PAMCMA	0.1	1.0249	0.0249	0.249	0.232
	0.2	1.0518	0.0518	0.259	
	0.3	1.0789	0.0789	0.263	
	0.4	1.1152	0.1152	0.288	
	0.5	1.1510	0.1510	0.302	
	0.6	1.1866	0.1866	0.311	

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

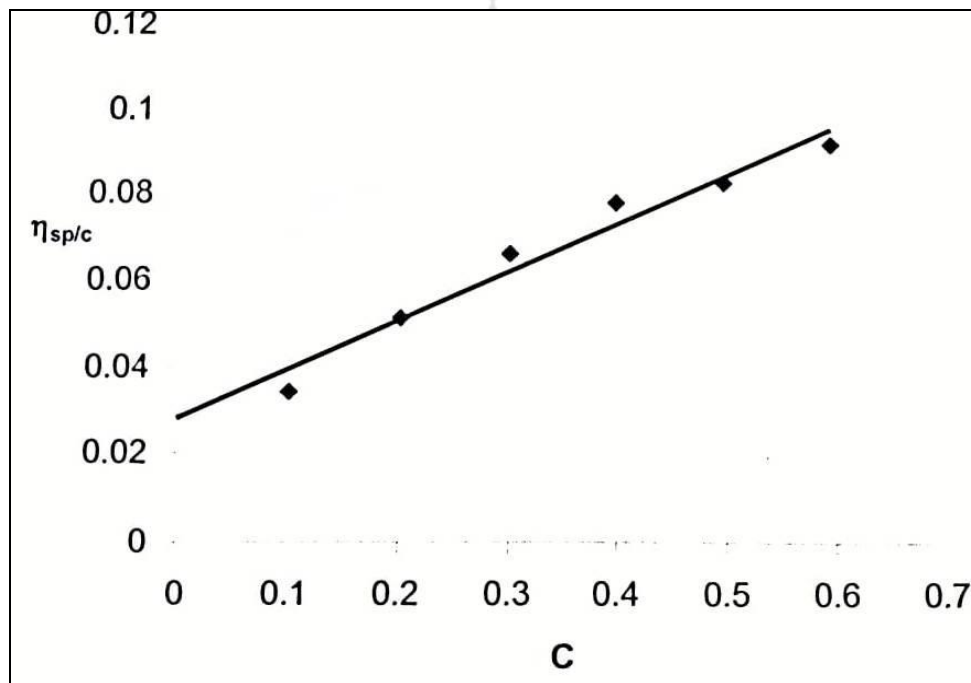


Figure 4: for HPAMI

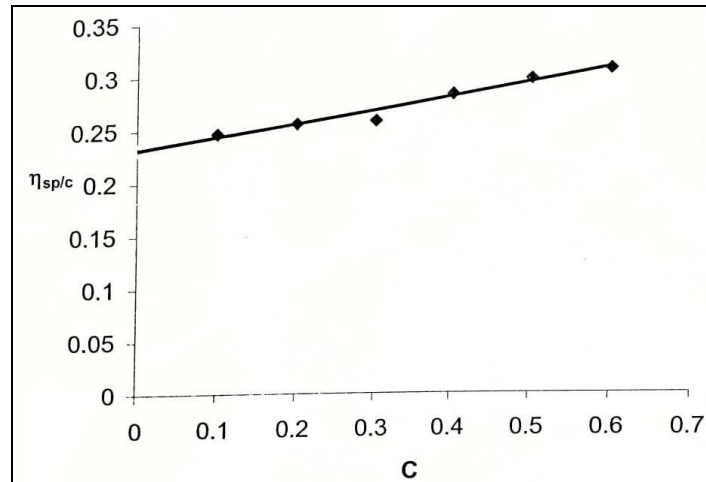


Figure 5: for PAMCEA

Solubility behavior of Polymers

Synthesis of Homopolymer and copolymer and their solubility are summarized in table 7.

Table 7: Relative solubility of homopolymer and copolymer are summarized

Solvents	HPAMI	PAMCEA
Chloroform	Partial Soluble	Partial 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	Partial Soluble
Carbon tetrachloride	Insoluble Soluble	Partial Soluble
Cyclohexanone	Insoluble Soluble	Partial Soluble
Dichloromethane	Soluble	P Soluble
n-Hexane	Partial Soluble	I Soluble
Ethanol	Soluble	Soluble
Methanol	Soluble	Soluble
Benzene	Soluble	Partial Soluble

Thermal behavior of Homo and Copolymer

Thermal stability degradation of polymer is given in table 8 and table 9, The TGA analysis of polymer completed by using PERKIN ELMER USA 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
HPAMI	I	220	290	315	8.55
	II	315	328	550	
PAMCEA	I	190	310	360	17.66
	II	360	438	560	

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

Polymer Code	200 °C	300 °C	400 °C	500 °C	550 °C
HPAMI	-1.2	-34.8	-86.8	-91.5	-94.7
PAMCEA	-0.72	-36.18	-74.12	-82.34	-89.38

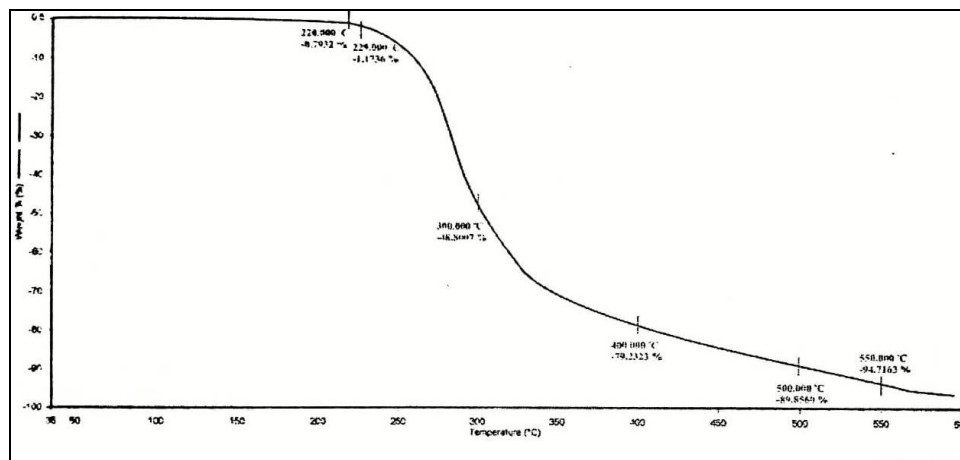


Figure 6: TGA curve for HPAMI

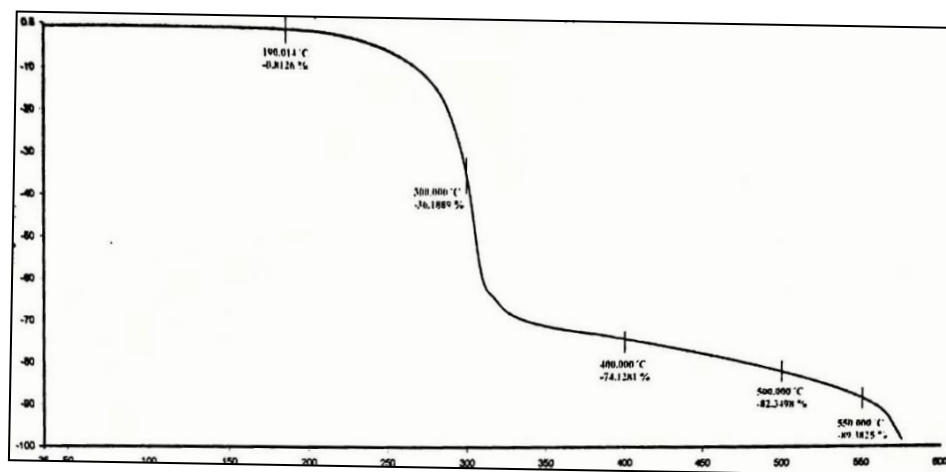


Figure 7: TGA curve for PAMCEA

CONCLUSION

Experimentally we will note that prepared polymer shows the excellent thermal stability. it is observed that degradation of the polymer pound in two step degradation. Synthesis polymer shows the excellent solubility in THF, DMF, DMSO, Chloroform, Ethyl acetate. intrinsic viscosity determined by the Ubbelohde viscometer and linear relation observed in between concentration and molecular weight. From the Polydispersity index we will get to knowledge, Polymerization reactions completed via radical polymerization it is approved by the Polydispersity index. PDI index observed in range 1.5 to 10. Weight average and number average molecular weight determined by the Gel permeation chromatography. In the present study homopolymer are taken $\alpha=0.48741$, it means they are in unperturbed dimension and copolymer have $\alpha=1.4921$ hence molecules shows are in shape of rigid rods.

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