

**THERMAL DEGRADATION STUDY OF N-(4-METHOXYPHENYL)
MALEIMIDE WITH ACRYLONITRILE*****¹Sanjeet Singh*****²Suresh Kumar Meena****¹Department of Chemistry, Physical and Polymer research laboratory
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Abstract

Newly prepared monomer of N-(4-Methoxyphenyl) maleimide copolymerized with Acrylonitrile. The polymers made under specific reaction conditions, Structural characterization of the copolymers including mechanistic studies was carried out using nuclear magnetic resonance spectroscopy, and their thermal properties were studied using thermogravimetric analysis. THF and DMF Solvent were used. The investigated polymer shows the highly solubility range of organic solvents. The molecular mass of the copolymers was determined by GPC. The glass transition temperature was measured and it was found to correlate well with the chemical structure, and increases with the increase of the maleimide content. Number average and weight average mass determined by gel permeation chromatography and PDI range provide the structure of polymer in given solution. Intrinsic viscosity determined by Ubbelohde viscometer. Thermal degradation rate observed 10°C/minutes and degradation obtained in two steps for homopolymer and copolymer.

Keywords:

Polymerization, Gel Permeation chromatography, Thermogravimetric.

Introduction

Polymers are widely used in technological applications in different fields, like as space shuttle, poly fibers, poly carbonated, specially heat resistant and especially the poly(n-alkyl methyl acrylate) which are used in nonlinear optics [1-2], holographic data handling, and energy storage [3-4]. The selected monomer belongs to the maleimide family which is known to impart improved thermal stability [5-9] well as enhanced electronic [10] and optical [11] properties when incorporated into the backbone of a copolymer. free radical copolymerization. The above studies show that NPMI derivatives and their copolymers play a positive role in improving the heat resistance of polymers. N-phenylmaleimide is a newly reactive monomer which has been widely used to prepare heat-resistant acrylic acid-butadiene-styrene resins. N-PMI and styrene dissolved in toluene-ethanol were copolymerized in the pore of PVC particles suspended in water-DMF-DMAC, and thus obtained heat-resistant and flame retardant PVC materials were characterized with scanning electron microscopy, elemental analysis, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry [12]. The research on the modification aiming at different defects of PMMA has been going on for decades, and the heat-resistant modification began in the 1980s. Compared with other methods like adding additives [13] the method of changing the molecule chain structure and introducing rigid groups can more effectively limit the movement of the polymer segment and can better improve the heat resistance of PMMA. Specifically, it can be achieved by increasing the intermolecular force [14], introducing large steric hindrance or rigid groups on the side chains [15], or introducing a rigid cyclic structure on the main chain [16-17]. MMA was copolymerized with Maleic anhydride [18-19]. N-substituted maleimide and other cyclic structure monomer [20-22]. due to the introduction of a rigid five-membered ring in the PMMA main chain, thereby significantly improving its heat resistance. In Present study we are investigating 4-Methoxyphenylmaleimide copolymerized with acrylonitrile and characterized by FTIR, ¹HNMR and Thermal stability were determined by TGA.

In recent years, the need of polymers and copolymers with more complex architecture for specific applications in science and industry led to the expansion of chemical modification of some commercially available polymers. This modification is an important method for obtaining new polymers with improved properties and therefore increases the scope of their applications [1]. Functional polymers having high glass transition temperatures (T_g) are attractive for the polymer industry because of strong economic rewards that may arise from their potential applications. For instance, poly(methyl methacrylate) (PMMA) is an amorphous, colorless thermoplastic possessing many excellent properties including light weight, optical clarity, good insulation, chemical resistance, scratch resistance, odorless, tasteless, and non-toxic [2–4]. PMMA or plexiglass, with a monomeric structure, contains both a hydrophilic (carbonyl) and a hydrophobic (methylene) group in each unit. PMMA has also application in other fields, such as aircraft glazing, signs, lighting, dentures, food-handling equipment, contact lenses, substitute for inorganic glass, coating applications, and so on [5–8].

Experimental

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.

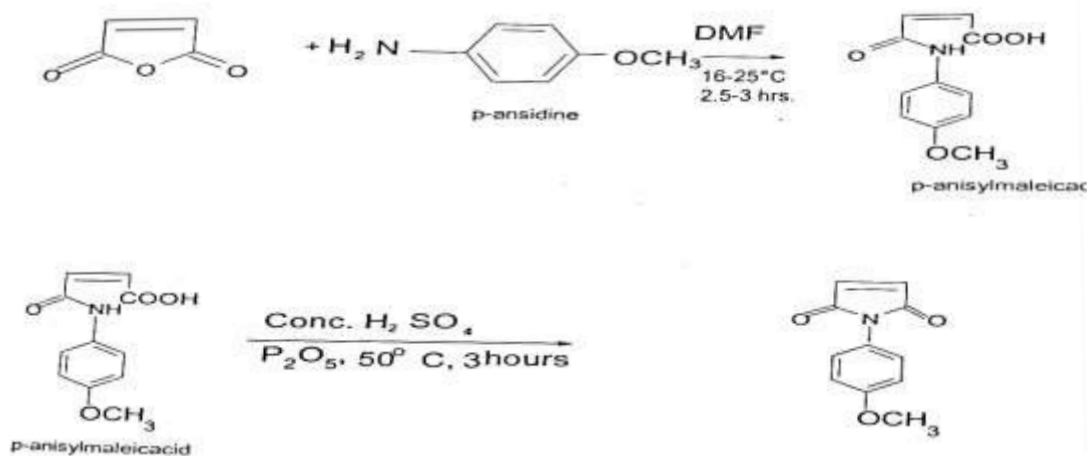
Measurements

$^1\text{H-NMR}$ 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 pouring in crushed ice. Green solid precipitate was obtained, than 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.

SCHEME-I

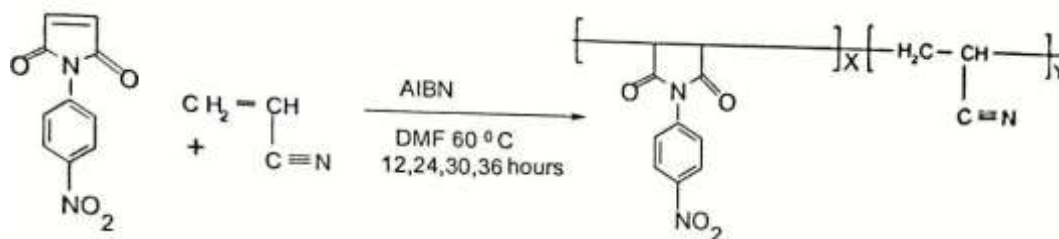


p-anisylmaleimide

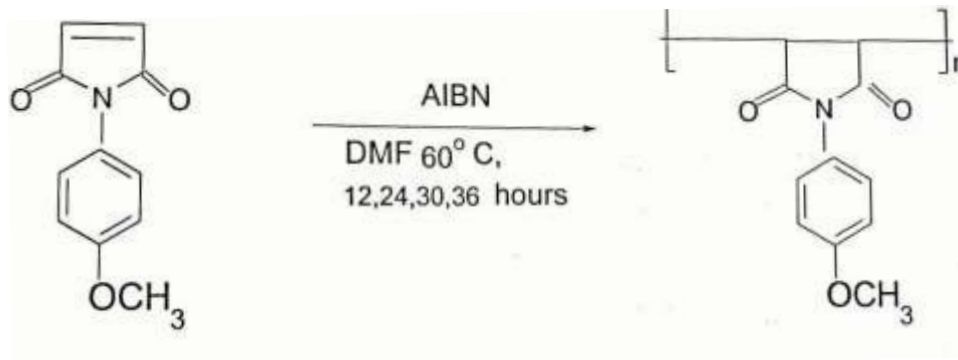
Copolymerization of N-(4-Methoxyphenyl) maleimide with Acrylonitrile

Equal amount of N-(4-Methoxyphenyl) maleimide and Acrylonitrile 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-2



SCHEME-3



Results and Discussion

HPAMI

Synthesis structure of HPAMI was intuit 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 at δ $7.23\text{--}7.35$ ppm corresponds to the four aromatic protons. Two protons in --CH--CH-- group have appeared at δ $4.02\text{--}3.05$ ppm. $^1\text{H-NMR}$ of HPAMI monomer shows chemical shift δ at 7.15 (s) ppm characteristic of --CH=CH-- group [24-26].

PAMCAN

FTIR Figure 1 Shows, $2937, 3279$ (CH=CH), 2241 (CN), $1711, 1750$ (C=O), 1513 (--CH-- Stretching of imide) 1461.9 (C-H band, --CH_2), 1393 (C-N, Stretching of maleimide), 1170 (C-O-C), $1030, 1251$ (Ar-O-C), 830 (p-OCH₃) and 668 cm^{-1} (out of plane C-H band of benzene ring), and 650 (aromatic ring C=C band). $^1\text{H-NMR}$ of PAMCAN In Figure 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 Acrylamide, δ values obtained in 2.8 to 3.6 ppm, appeared due to [--CH--CH--]_n protons and --OCH_3 protons [24-26].

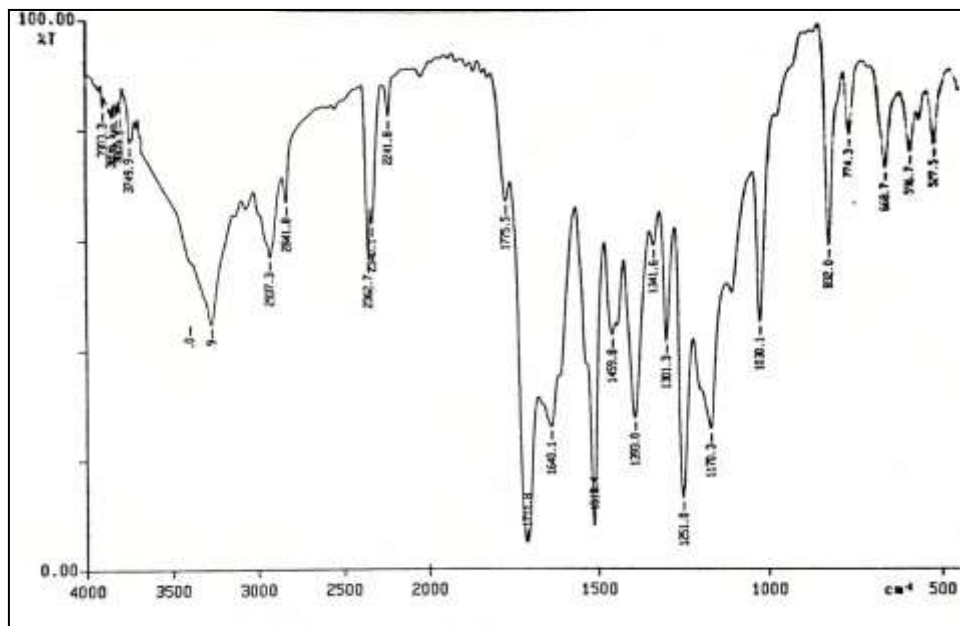
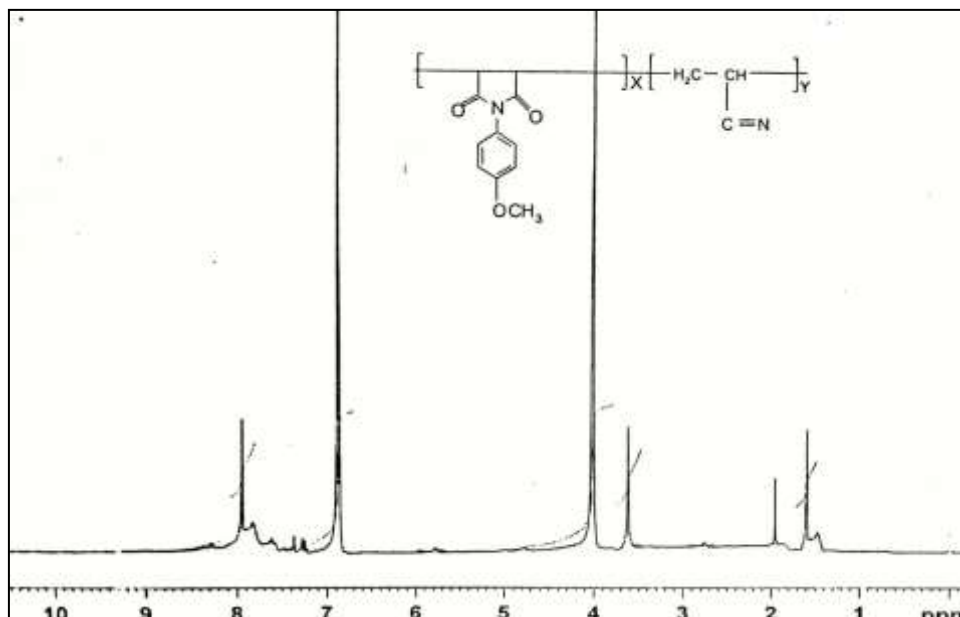


Figure 1: FTIR Spectra of PAMCAN

Figure 2 : ^1H NMR Spectra of PAMCAN

Effect of time with percentage Yield and solvent initiator system

Percentage yield and physical state of polymers are summarized in table 1 to table 3, Obtained percentage yield from the table are indicated that AIBN system give more yield as compare to BPO solvent systems. No yield obtained below 12 hours. Solvent and free radical system is more important for any industrial purpose. Results are summarized 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 HPAPMI 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
PAMCAN	DMF	61.8	60.2	Light brown
	THF	59.0	58.2	Light Yellow

Intrinsic viscosity and molecular mass

Intrinsic viscosity of the synthesis polymer determined by the Ubbelohde viscometer. The relationship between viscosity and molecular weight can be explained as follows. Flowing of large chain polymers is difficult due to entanglement and friction between the chains. That makes the solution thicker and these exhibit higher viscosities. The intrinsic viscosity, η as function of average molecular weight, M is represented by Mark Houwink Sakurada equation $[\eta] = KM^\alpha$, where K and α are empirically determined constants for a given polymer solvent temperature system. The distribution of molecular weights in a heterogeneous polymer is that $M_z > M_w > M_v > M_n$. This can be easily applied in Figure molecular weight but such relation always not same [23].

Table 4: Shows the Molecular weight of polymers.

Copolymer	M_w	Log M_w	$H \times 10^3$	Log $\eta \times 10^3$
PPAMI	2376	3.3758	28	1.4472
PAMCAN	7625	3.8822	213	2.3284

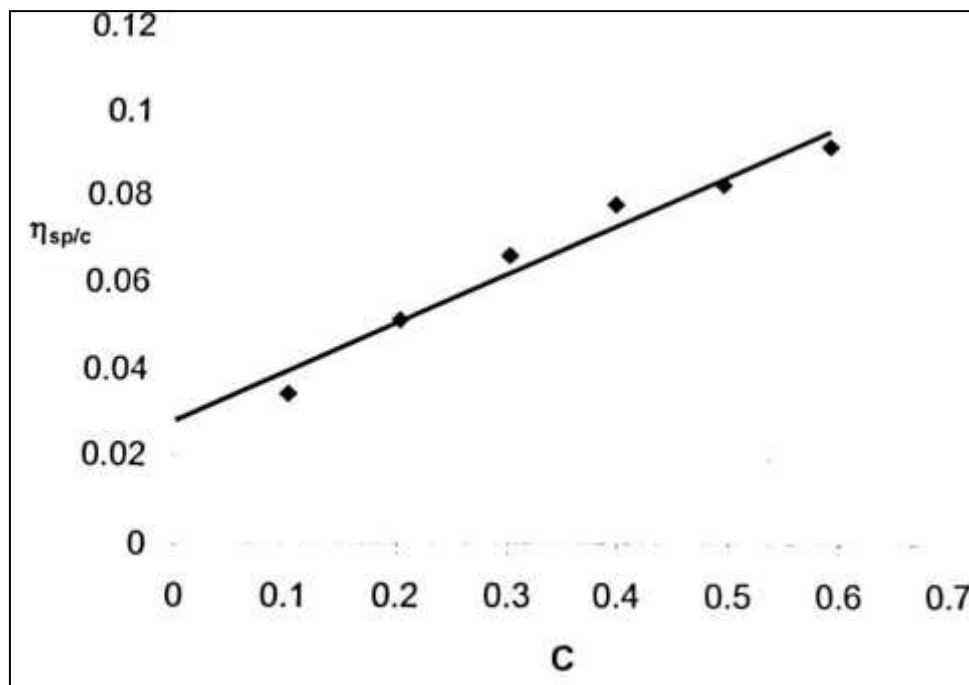
Table 5: Typical data of Viscosity measurements of HPAPMI summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
HPAMI	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 PAMCAN summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PAMCAN	0.1	1.0222	0.0222	0.222	0.213
	0.2	1.0474	0.0474	0.237	
	0.3	1.0723	0.0723	0.241	
	0.4	1.1036	0.1036	0.259	
	0.5	1.1345	0.1346	0.269	
	0.6	1.1638	0.1638	0.273	

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

**Figure 3: for HPAMI**

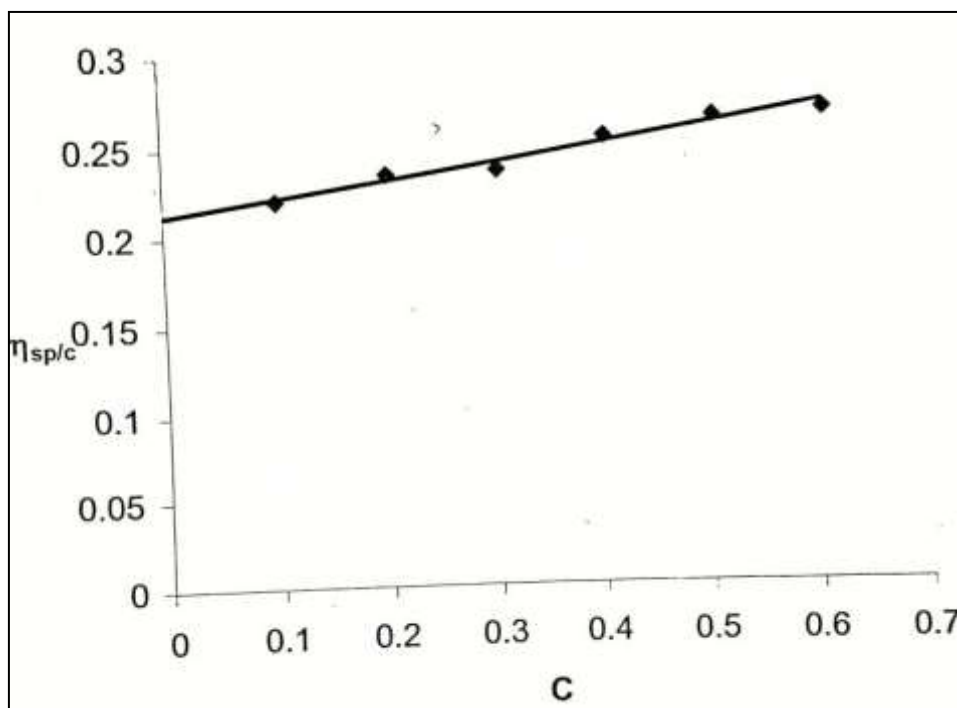


Figure 4 :for PAMCAN

Solubility behavior of Polymers

Solubility behavior of polymer investigated in different solvents and solubility results of the polymers are summarized in table 6.

Table 7: Relative solubility of homopolymer and copolymer are summarized

Solvents	HPAMI	PAMCAN
Chloroform	P Soluble	Soluble
THF	Soluble	Soluble
DMF	Soluble	Soluble
DMSO	Soluble	Soluble
Dioxane	Soluble	Soluble
Acetone	Soluble	Soluble
Ethyl acetate	Soluble	Soluble
Xylene	P Soluble	P Soluble
Toluene	P Soluble	P Soluble
Carbon tetrachloride	I Soluble	P Soluble
Cyclohexanone	I Soluble	Partial Soluble
Dichloromethane	Soluble	P Soluble
n-Hexane	P Soluble	I Soluble
Ethanol	Soluble	Soluble
Methanol	Soluble	Soluble
Benzene	Soluble	P Soluble

Thermal behavior of Homo and Copolymer

The TGA analysis of polymer studied by using PERKIN ELMER USA PYRIS TGA-A Equipment. Degradation rate of the polymer were stabilize at 10 °C/ minute . Thermal degradation found in two steps and results are summarized in table 8 and table 9 and thermal stability of the polymer shows by the thermal curve are shows in figure 8 and 9.

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	
PAMCAN	I	208	358	415	14.33
	II	415	470	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
HPAMI	-1.2	-34.8	-86.8	-91.5	-94.70
PAMCAN	-1.01	-16.92	-64.82	-85.67	-91.28

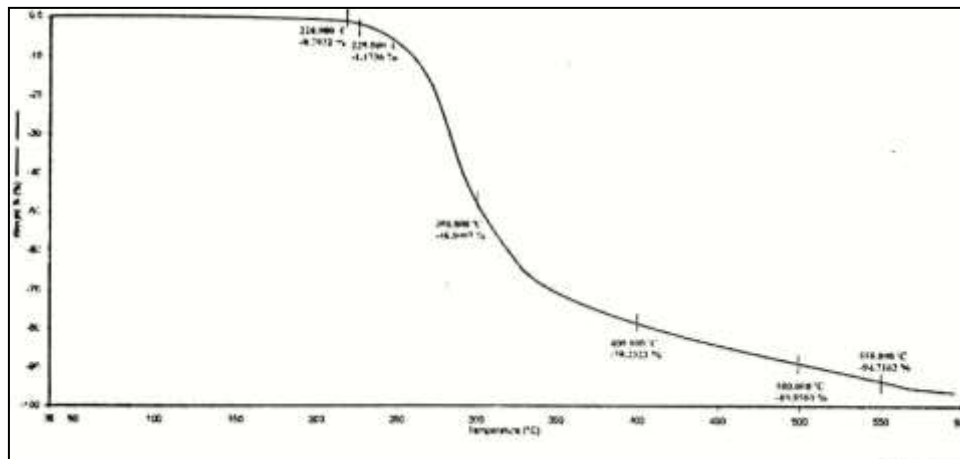


Figure 5: TGA curve for HPAMI

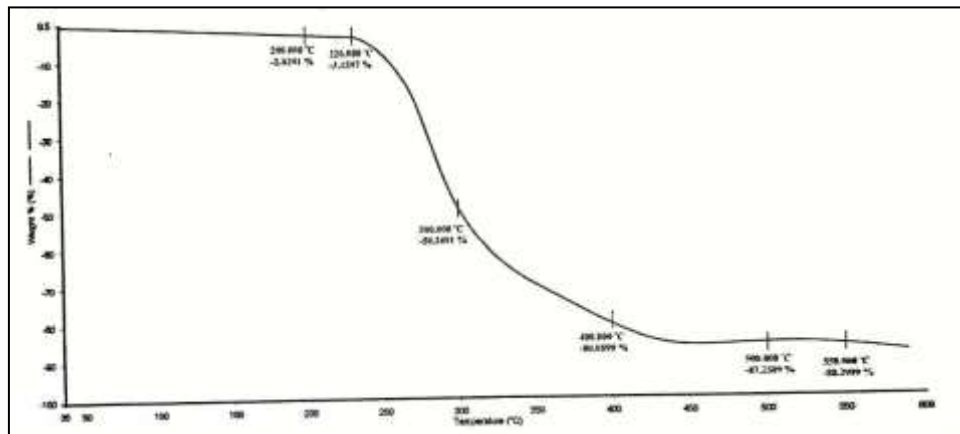


Figure 6 : TGA curve for PAMCAN

CONCLUSION

The effect of substituted vinyl monomers on thermal stability has been studied by copolymerization with Acrylonitrile, from the thermal stability curve we are obtained that HPAPMI shows higher thermal stability than PAMCAN. Solubility of Polymer covered large range of organic solvent like as THF,DMF,DMSO, Acetone ,Ethyl acetate, Chloroform and solubility of any polymeric material depends on temperature, pressure and chemical composition. Polydispersity and Number average and weight average molecular weight determine by the Gel permeation chromatography. Polymerization reaction proceeds through the free radical polymerization it is approved by the Polydispersity index.

Conflicts of Interest

“The author declared that there is no conflict of interest regarding the publication of this paper.”

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