

**COMPARATIVE THERMAL STUDY OF N-(4-METHOXYPHENYL)
MALEIMIDE WITH CINNAMIC ACID AND ACRYLAMIDE**Suresh Kumar Meena*¹Sanjeet singh²¹Department of Chemistry Government college, Kota, Rajasthan**ABSTRACT**

N-(4-Methoxyphenyl) Maleimide Copolymerized With Cinnamic Acid and Acrylamide under the identical condition and Free radical initiator AIBN and BPO were used. Purity and chemical composition were determined by Fourier transform infrared reflection spectroscopy and ¹H-NMR. Monomer of N-(4-Methoxyphenyl) Maleimide prepared by p-anisidine and maleicanhydride. Duration of the Chemical reaction we are used THF and DMF Solvent. Number average and weight average Molecular weight determined by Gel permeation chromatography. Polydispersity index determined by the ratio of number average and molecular weight and PDI range provide the structure of polymer in given solution. TGA Techniques were used for analysis of thermal stability. Degradation of the polymer was recorded in two steps. Intrinsic viscosity determined by Ubbelohde viscometer. Thermal degradation rate observed 10°C/minutes and degradation obtained in two steps for homopolymer and copolymer. Thermal degradation observed for homopolymer 220°C to 550°C and for copolymer obtained 200°C to 550°C.

Keywords:

Polymerization, Free radical, Methoxy group, DMF, GPC

INTRODUCTION

It is major interested to synthesis of new maleimide polymer and synthesized maleimide polymer have vast application in daily life and domestic applications, automotive, electronic parts, poly fiber sheets, medical and other fields due to its excellent optical properties, biocompatibility, safety equipments, weather resistance and stable mechanical properties have importance in drug delivered from one place to another [1]. Al though a lot of work have done but still needed for requirement to present scenario. *N*-substituted maleimide and other cyclic structure monomers [2-5]. due to the introduction of a rigid five-membered ring in the PMMA main chain, thereby significantly improving its heat resistance. However, under industrial conditions, the free radical bulk copolymerization of MMA and maleic anhydride (MAH) or *N*-substituted maleimide (*N*-PMI) is still difficult to achieve.[6-8]. maleic anhydride [9] methyl acrylate [10-11]. and chloroethylene [12]. At present time substituted *N*-Phenylmaleimide polymers have been recorded [13-23]. *N*-Substituted maleimide are interesting monomers for making transparent thermally stable polymeric materials [24-30]. In present article we are studied copolymerization of 4-Methoxy maleimide with Cinnamic acid and characterized by FTIR, ¹HNMR and thermal stability analysis by TGA technique.

Experimental

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].

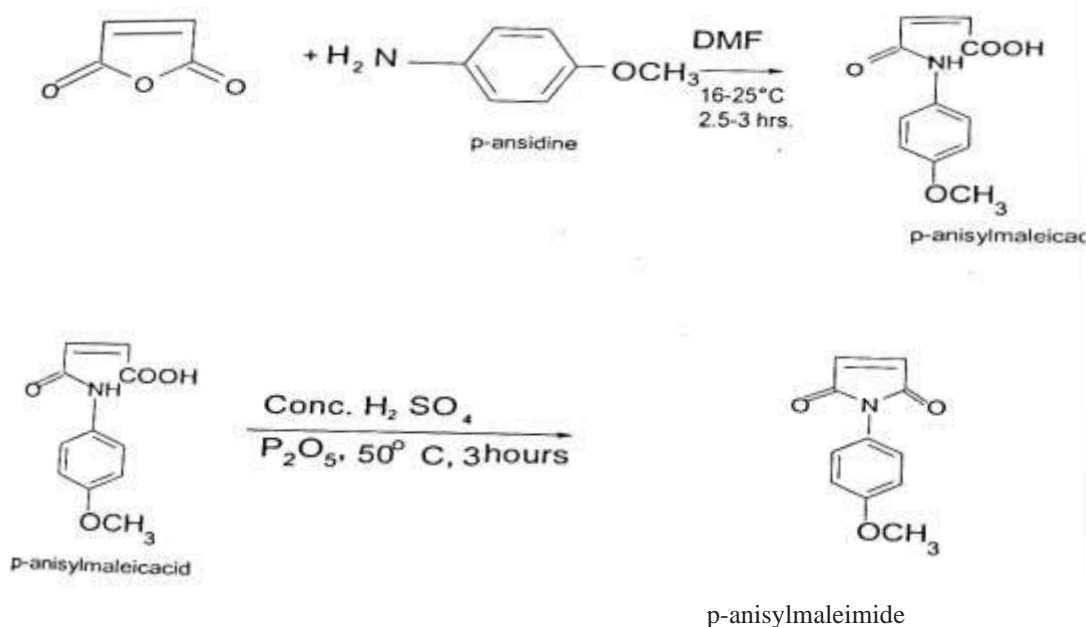
Measurements

¹H-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

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. Green 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.

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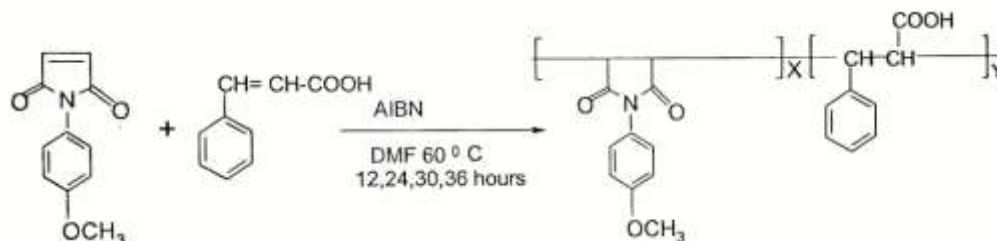


Copolymerization of N-(4-Methoxyphenyl) maleimide with Cinnemic acid

Equal amount of N-(4-Methoxyphenyl) maleimide and Cinnemic acid 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.

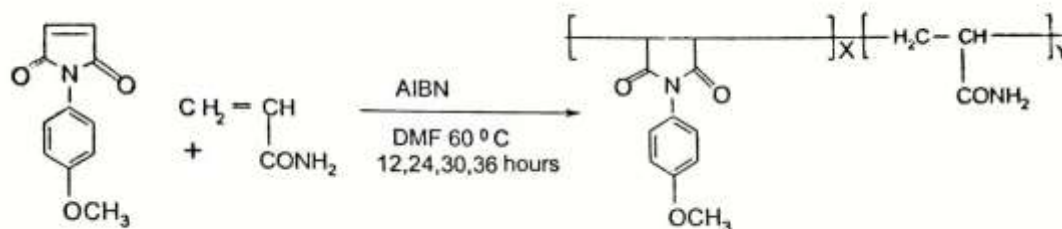
SCHEME-2



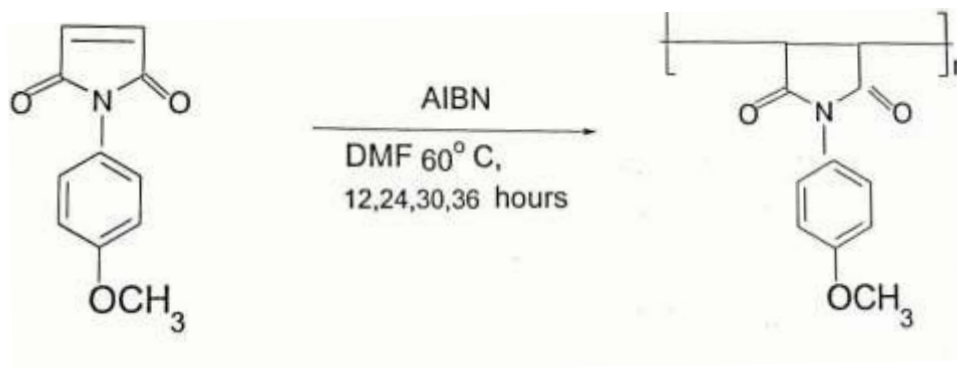
Copolymerization of N-(4-Methoxyphenyl) maleimide with Acrylamide

0.1 mole of N-(4-Methoxyphenyl) maleimide and 0.1 mole of Acrylamide have taken in 30 ml THF solvent in a round bottom flask with fitted reflux condenser 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 desiccators.

SCHEME-3



SCHEME-4



Results And Discussion**PAMCCA**

FTIR spectra of PAMCCA In Figure 1, 2936,3064 (CH=CH), 1776, 1713 (C=O), 1513 (-CH-Stretching of imide) 1461.9 (C-H band, -CH₂), 1390 (C-N, Stretching of maleimide), 1169 (C-O-C), 1512 -CH-stretching,1029,1251(Ar-O-C),830 (p-OCH₃) and 664 cm⁻¹ (out of plane C-H band of benzene ring), and 650 (aromatic ring C=C band). ¹H-NMR of PAMCCA In Figure 2, δ values from 6.9 to 8.0 due to present of phenyl ring protons and a signal of showing δ at 4.0 present of Acrylamide, δ values obtained in 3.3 to 3.8 ppm, appeared due to [-CH-CH-]n protons and -OCH₃ protons [28-29].

PAMCAA

FTIR spectra of PAMCAA In Figure 3, 2938,3190 (CH=CH), 3448 (-CONH₂),1709, 1720 (C=O), 1513 (-CH-Stretching of imide) 1461.9 (C-H band, -CH₂), 1394 (C-N, Stretching of maleimide), 1172 (C-O-C), 1513 -CH-stretching,1029,1251(Ar-O-C),832 (p-OCH₃) and 668 cm⁻¹ (aromatic ring C=C band). ¹H-NMR of PAMCAA In Figure 4, δ values from 6.9 to 8.0 due to present of phenyl ring protons and a signal of showing δ at 4.0 present of Acrylamide, δ values obtained in 3.3 to 3.7 ppm, appeared due to [-CH-CH-]n protons and -OCH₃ protons [28-29].

HPAMI

Prepared structure of HPAMI was ascertained by IR and ¹H-NMR spectra, 2932,2832 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 -CH-CH- group have appeared at δ 4.02–3.05 ppm. ¹H-NMR of HPAMI monomer shows chemical shift δ at 7.15 (s) ppm characteristic of -CH=CH- group [26-28].

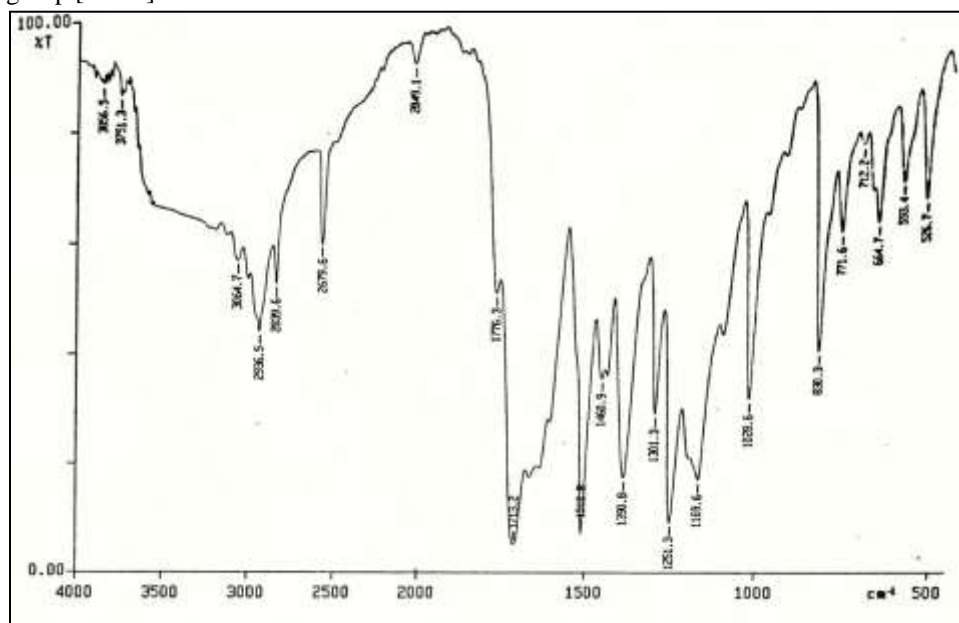


Figure 1: FTIR Spectra of PAMCCA

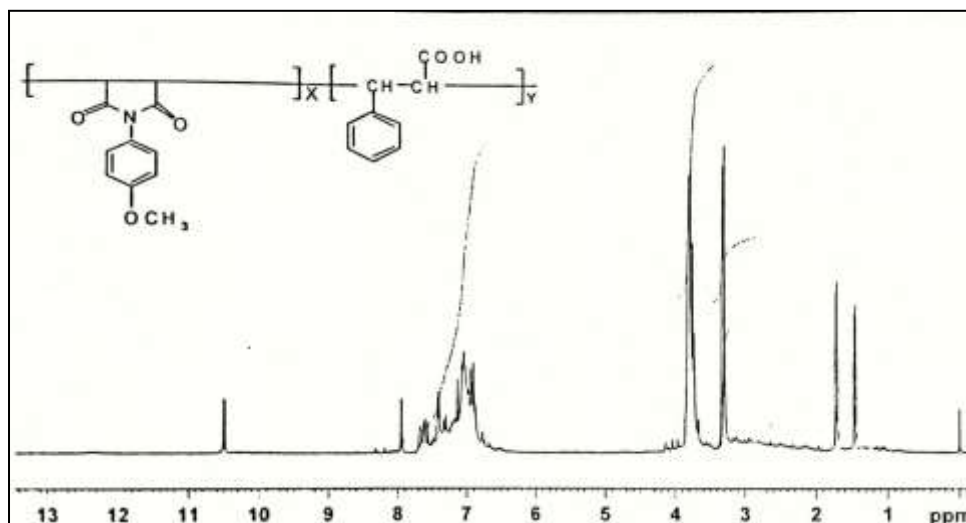


Figure 2 : ¹H NMR Spectra of PAMCA

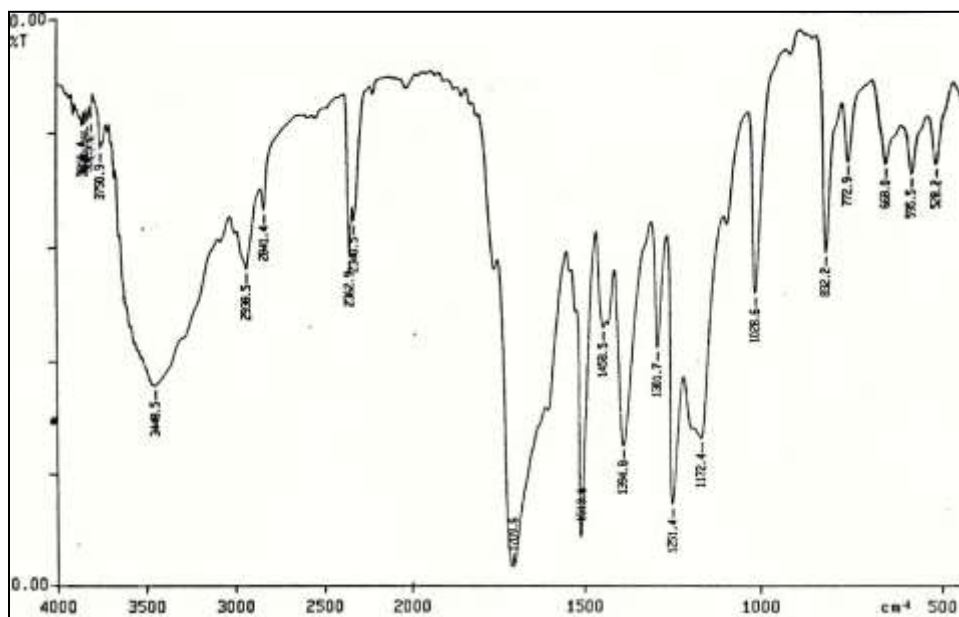


Figure 3 : FTIR Spectra of PAMCA

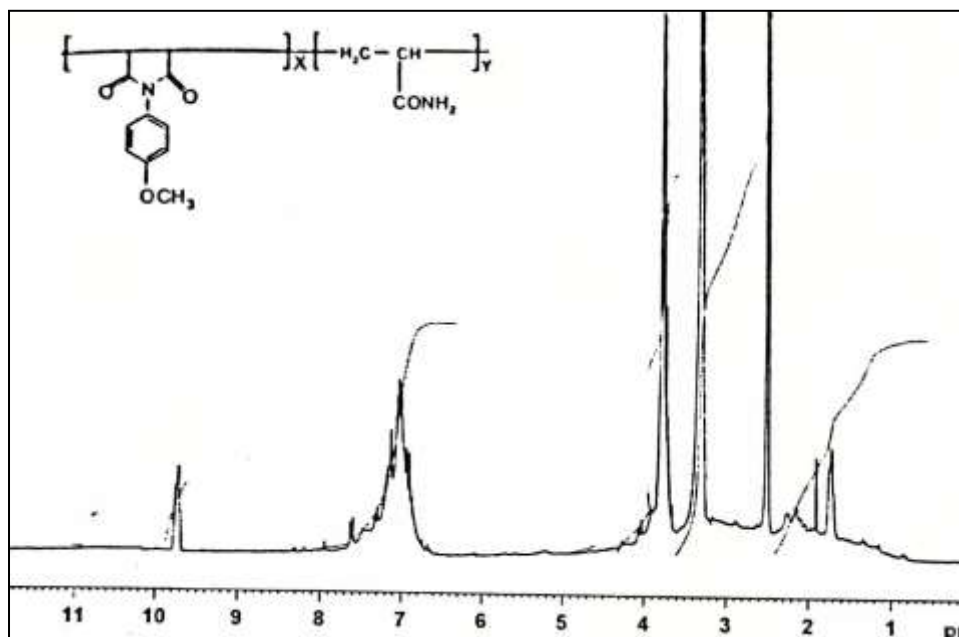


Figure 4 : ^1H NMR Spectra of PAMCAA

Effect of time on Yield and solvent initiator systems

Synthesis of Homopolymer and copolymer and their obtained percentage yield and physical state are summarized in table 1 to table 3, From comparison of the tables, conclude that AIBN system give more yield as compare to BPO solvent systems and study of the system, with time found that percentage yield increases with time hours. No yield obtained below 12 hours. Solvent and free radical system is more important for any industrial purpose. Obtained 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
PAMCCA	DMF	61.8	60.2	Light brown
	THF	59.0	58.2	Light Yellow
PAMCAA	DMF	62.3	62.0	Light brown
	THF	60.8	59.8	Light Yellow

Viscosity measurements

Synthesis polymer and their intrinsic viscosity observed from the plotted graph between concentration verses reduced viscosity. Results are summarized in table 4 and table 5. Viscosity measured by the Ubbelohde viscometer.

Table 4: Typical data of Viscosity measurements of HPAMI 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 5: Typical data of Viscosity measurements of PAMCCA summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PAMCCA	0.1	1.0208	0.0208	0.208	0.202
	0.2	1.0428	0.0428	0.214	
	0.3	1.0672	0.0672	0.224	
	0.4	1.0908	0.0908	0.227	
	0.5	1.1185	0.1185	0.237	
	0.6	1.1440	0.1440	0.240	

Table 6: Typical data of Viscosity measurements of PAMCAA summarized in DMF at 30°C

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PAMCAA	0.1	1.0225	0.0225	0.225	0.220
	0.2	1.0458	0.0458	0.229	
	0.3	1.0702	0.0702	0.234	
	0.4	1.0960	0.0960	0.240	
	0.5	1.1120	0.1120	0.244	
	0.6	1.1488	0.1488	0.248	

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

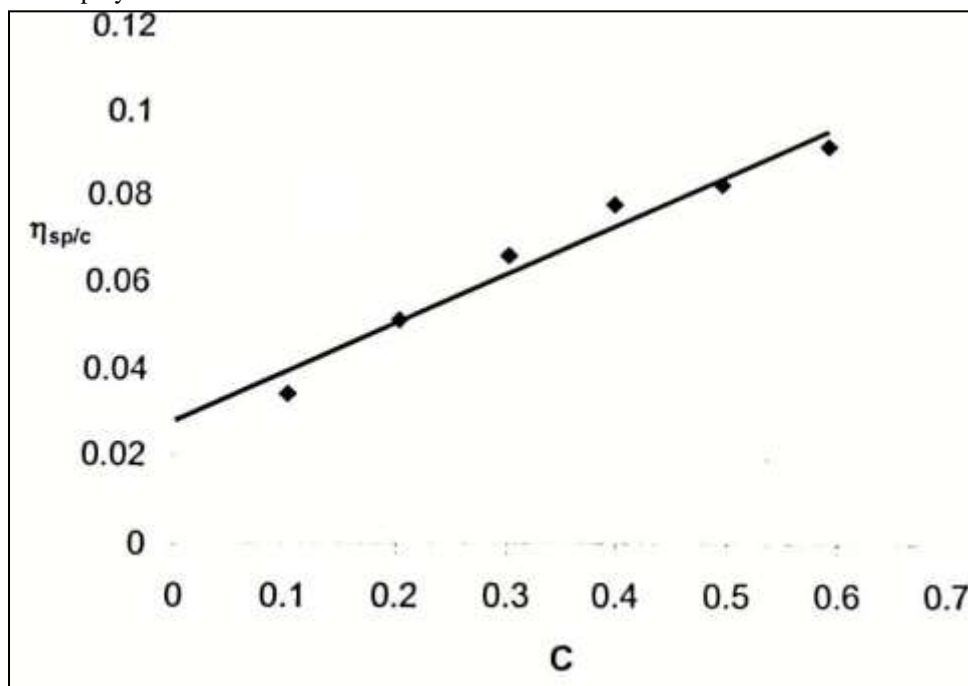


Figure 5: for HPAMI

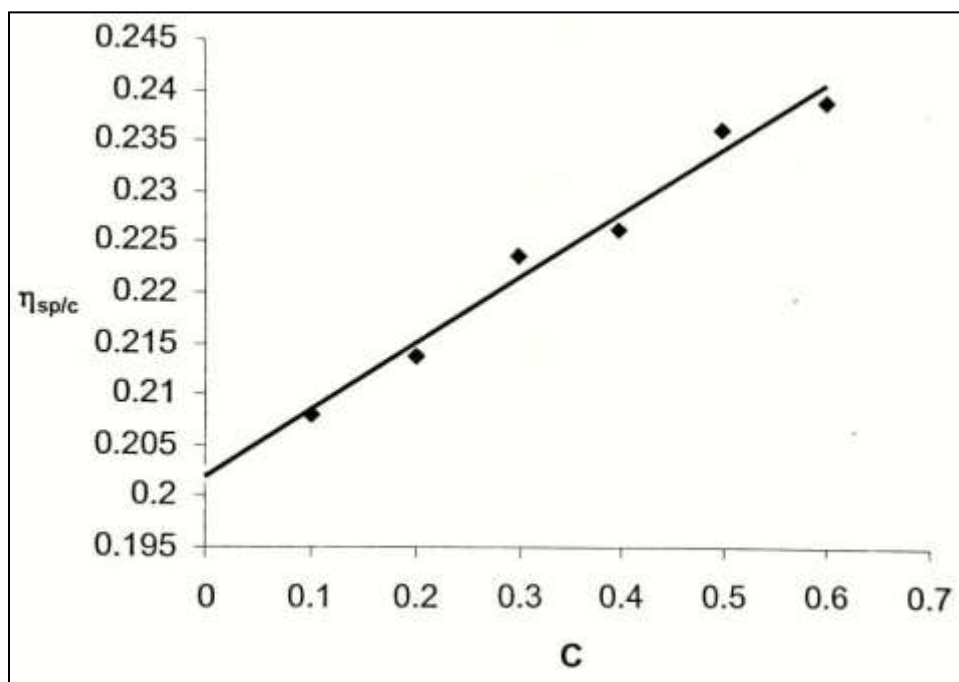


Figure 6 :for PAMCCA

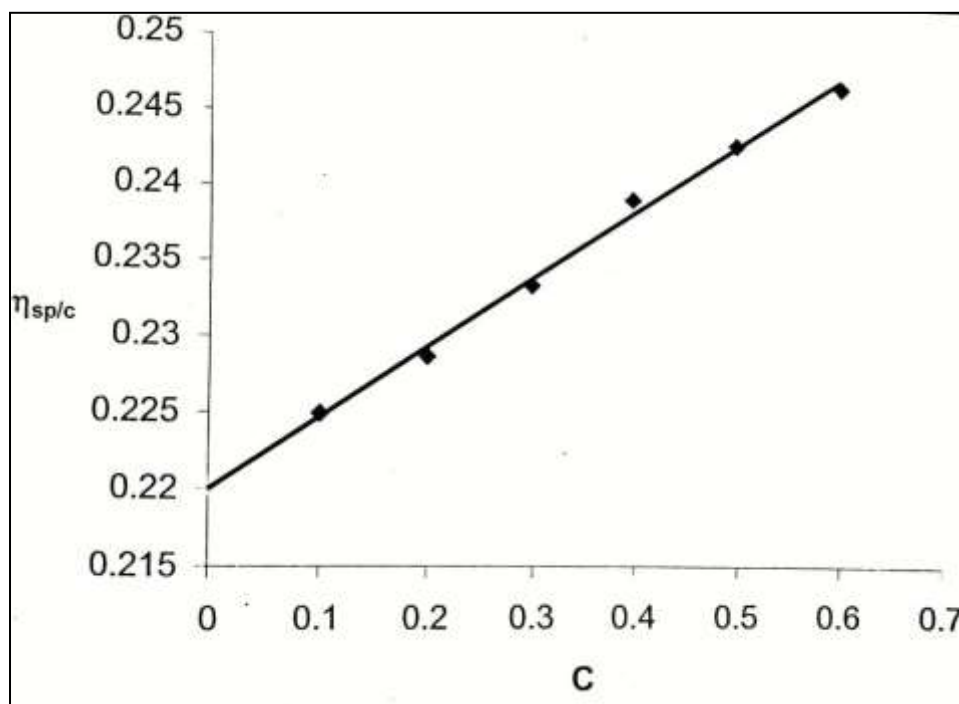


Figure 7 :for PAMCAA

Solubility behavior of Polymers

Solubility behavior of polymer investigated in different solvents and solubility results of the polymers are summarized in table 7.

Table 7: Relative solubility of homopolymer and copolymer are summarized

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

Thermal behavior of Homo and Copolymer

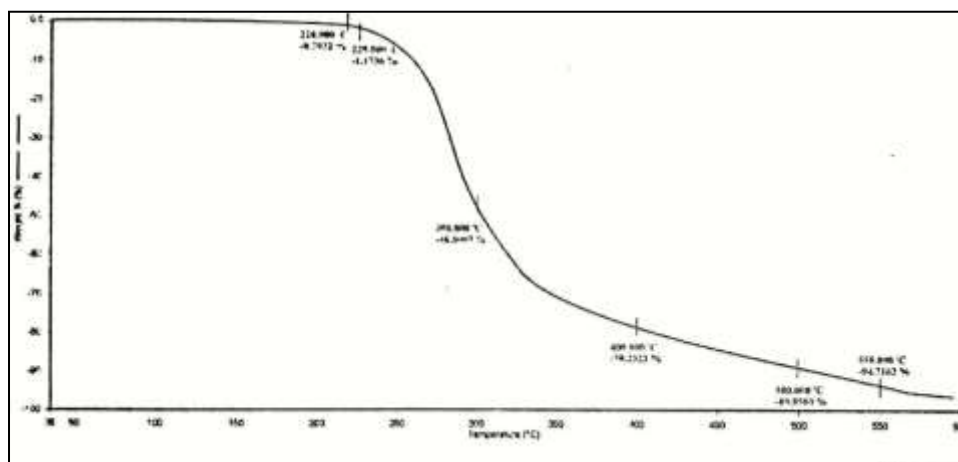
The thermal behavior of the homopolymer and copolymers has been studied by TGA. The loss in weight due to pyrolysis of the polymeric material with increase in temperature forms a TGA curve[31]. The TGA analysis of polymer completed by using PERKIN ELMER USA PYRIS TGA-A Equipment. Degradation of the polymer were recording at 10°C/ minute . 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	
PAMCCA	I	206	315	358	22.02
	II	358	518	570	
PAMCAA	I	200	275	342	6.85
	II	342	420	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
PAMCCA	-3.01	-35.86	-68.10	-72.89	-83.87
PAMCCA	-1.43	-67.81	-89.89	-93.15	-96.10

**Figure 8: TGA curve for HPAMI**

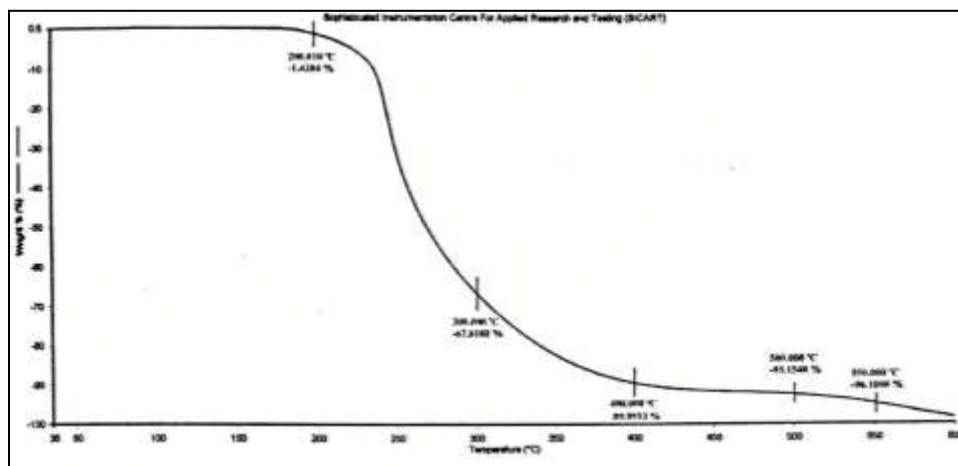


Figure 9 : TGA curve for PAMCAA

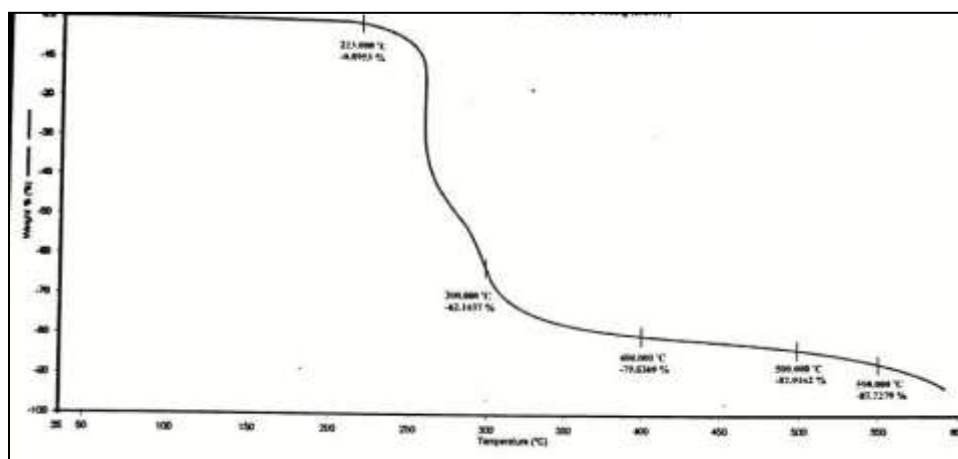


Figure 7: TGA curve for PAMCCA

CONCLUSION

The effect of substituted vinyl monomers on thermal stability has been studied by copolymerization with cinnamic acid and Acrylamide and from the thermal stability curve we are obtained that PAMCCA shows higher thermal stability than PAMCAA. This is due to nature of present vinyl groups. In case of Cinnamic acid due to presence of benzene ring π electrons are more delocalized due to resonance and -I Effect of C_6H_5 , phenyl group stabilizes this compound more, comparison to Acrylamide ($-CONH_2$) group. synthesis polymer shows the excellent solubility in given solvent like as THF, DMF, DMSO, Acetone, Ethyl acetate, Chloroform and solubility of any polymeric material depends on temperature, pressure and chemical composition. Number average and weight average molecular weight determine by the Gel permeation chromatography. Polymerization reaction proceed through the free radical polymerization it is approved by the Polydispersity index.

ACKNOWLEDGEMENT

We are thankful to CDRI Luck now and SICART Vallabh-Vidhyanagar for analysis work. Authors Shiv Narayan Paliwal and Suresh Kumar Meena is thankful to UGC (RGNF), DST FIST ,New Delhi or financial assistance, I am also thanks My Sincerely Prof. Harishanker Sharma, he is giving me valuable support for solved my problems.

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