Synthesis and Characterization of N-(4-Nitrophenyl) Maleimide and Copolymerized with Cinnemic Acid

Suresh Kumar Meena[1] and Sanjeet singh[2]
Department of Chemistry Government college ,
Kota, Rajasthan

Abstract- **Copolymers containing N-(4-Nitro phenyl) maleimide (PNPMI) and Cinnemic Acid copolymerization under the identical conditions and different compositions have been prepared by radical copolymerization with different mole ratios. The free-radical-initiated copolymerization of PNPMI with Cinnemic acid carried out in THF and DMF solvent using free radical initiator as AIBN and BPO. Percentage yield were calculated at different time and different solvent variations. The monomers and copolymers were characterized by FTIR, ^{1}H-NMR spectral studies. The copolymer compositions were evaluated by nitrogen content in polymers. The molecular weights (Mw and Mn) and Polydispersity index of the polymers were determined by using gel permeation chromatography. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with an increase in the mole fraction of Structure in the copolymers. Thermal stability of polymer was determined by the TGA techniques. Shape of the polymer in given solution were determined by the Kuhan mark Sakwada Equations . Polymerization process observed by the Polydispersity index. Intrinsic viscosity determined by the using Ubbelohde viscometer. Solubility of the Homopolymer and copolymer determined in different solvent.**

Keywords-Polymerization, TGA, AIBN, BPO, DMF

I. INTRODUCTION

Design and synthesis of materials with novel properties is becoming an interestingly important aspect of polymer chemistry. Synthesis of polymers with controlled molecular architecture has been discussed due to the rising demands for the specialty polymers. Living polymerization is an essential technique for synthesizing polymers with controlled structure (narrow molecular weight distributions and controlled molecular weight). Living polymerization has largely been achieved using living anionic and group transfer .In today's time, it has been seen that where iron used to be used earlier, polymers are being used today, Today's time polymers have taken it. Where the usefulness of another polymer is increasing, its polymer pollution is also increasing, it is often seen that using iron is very difficult for everyone, we know that as well as using polymer is very difficult for us. itself is getting polluted but for this the Indian government should make a very important policy for the use of very important utilities so that it can be joined despite using it.
Poly(methyl methacrylate) (PMMA) sheets have a wide variety of applications due to its properties like light weight, excellent weather resistance, light transmittance, and good insulating properties [1,2]. But the low softening temperature limits their applications [3,4]. Methyl methacrylate (MMA) has been copolymerized with a variety of vinyl monomers to yield polymers with improved thermal stability, better impact strength and abrasion resistance [5–7].Extensive work has been done in our laboratories on the copolymerization of MMA with N-arylsubstituted maleimides and itaconimides and a significant increase in the glass transition temperature has been observed [8–9]. It is well known that *N*-substituted maleimide and styrene represent monomer pairs with a strong tendency toward radical alternating copolymerization moreover, after copolymerization, the thermal stability of polystyrene, which is widely used as a conventional plastic, will be greatly improved. So far, the copolymerization of *N*-butyl maleimide (NBMI) and styrene, *N*-4-hydroxy phenyl maleimide (NHPMI) and styrene has been reported in literature [10-13]. In your previous work we are synthesis of newly substituted N-Phenyl maleimide polymers which are showing excellent thermal stability [14,15]. Acidic comonomers such as acrylic acid (AA), methacrylic acid (MAA) and itaconic acid (IA) provide supplemental dye sites, modify the fibre morphology, increase the hydrophilicity and facilitate the cyclization of nitrile groups during thermo-oxidative stabilization of acrylic fibres prior to carbonization [16].
In this article we are prepared some new N-Phenylmaleimide monomers and copolymerized with Cinnemic acid and investigated their thermal stability.

II. EXPERIMENTAL

A. *Materials*

Maleicanhydride were recrystallized from acetone. Methylmethacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl2 for 6 hours and distilled [15]. 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

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

C. Methods

Preparation of N-(4-Nitorphenyl) maieimide (PNPMI): Nitroaniline (13.8 gm for 0.1mol) and 9.8 gm maleic anhydride were taken in 30 ml DMF. The solutions kept stirring 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. Yield was 70%, m.p. 145°C.

N-(4-Nitrophenyl) Maleimide:Cyclodehydration of the 4-Nitromaleamic acid, an intermediate to maleimide was carried out by treating former with conc. H_2SO_4 and P_2O_5. The solution stirring 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

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

N-(4-Nitrophenyl) maleamide (PNPMI)
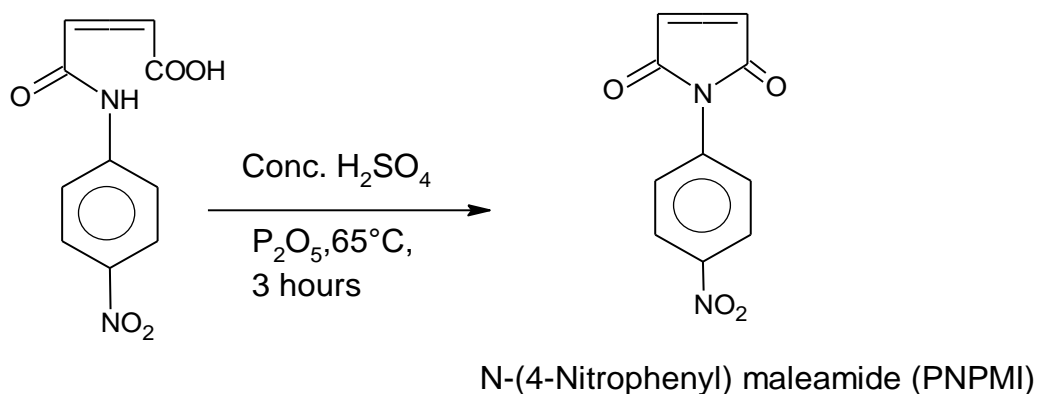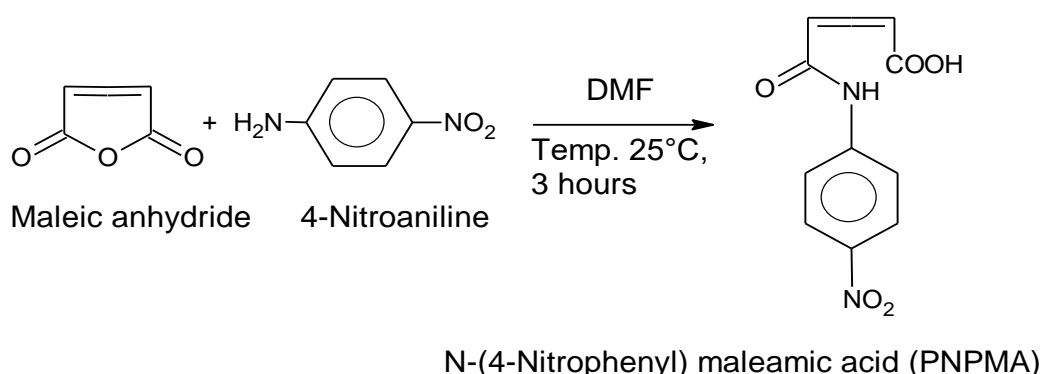
Homopolymerization of N-(4-Nitrophenyl) maleimide (PPNPMI)

4-Nitrophenylmaleimide (2.18 gm, 0.01 mol) were taken in 30 ml THF solvent in round bottom flask with reflux condenser. To this solution 20 mg AIBN was added and the reaction mixture was refluxed on heating mental at 65°C for 12, 24, 36 and 48 hours. Yield was obtained 32.33% for 24 hours. The synthesized polymer was isolated in excess quantity of methanol water mixture. It was dried under vacuum at 55°C.

SCHEME - 02
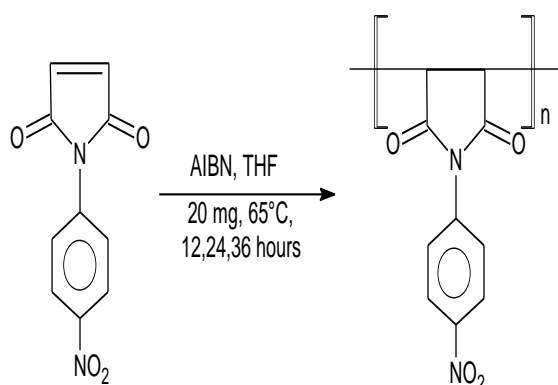
Copolymerization of N-(4-Nitrophenyl) maleimide with MMA (CPNPMI)

Equal amount of 4-Nitrophenylmaleimide and Cinnemic acid 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. Yield was 48.81%.

SCHEME-3
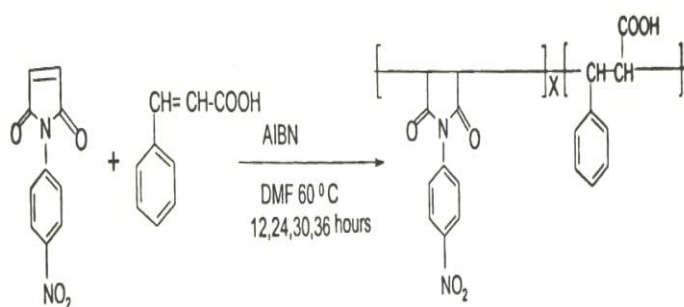
III. RESULTS AND DISCUSSION

PNPMI

FT-IR spectra (Fig.1, in cm^{-1}) with characteristic absorption frequencies 3091.3,2980.8 (aromatic and alkene C-H stretch), 1797 and 1708 (symmetric and asymmetric stretching of C=O in a five member imide ring.[15,16] 1634(CH=CH, alkene), 1564 1456 (C=C, aromatic) [17,18].1335,1504 (symmetric and asymmetric stretch of –

NO$_2$) [19]. 967 (CH=CH) [20]. 856(1,4 disubstituted benzene) these are consistent with the structure of PNPMI. ^{1}H-NMR spectra (Fig. 2, 400 MH$_z$ TMS, DMSO-d$_6$, δ, ppm) of PNPMI shows two methine (CH=CH) protons at δ 6.82 (s) ppm; two aromatic protons (o-group in phenyl ring) at δ7.13-7.15 (d) ppm; two aromatic proton (m-group in phenyl ring) at δ7.63-7.64 (d) ppm .

PPNPMI

In Fig. 3, for PPNPMI, the specific characteristic absorption bands observed are at 3088 (C-H aromatic), 2981 (C-H stretch alkene), 1778, 1715 (symmetric and asymmetric stretching of C=O group) 1614, 1651, 1563, 1444, 1596 (C=C stretch aromatic), 1504, 1331 (symmetric and asymmetric, Ar-NO$_2$ group), 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) are consistent with the structure of PPNPMI. In Fig.4, the ^{1}H–NMR spectrum of PPNPMI is observed at δ 7.50–8.08 (d). 2H in –CH–CH– group have appeared at 3.5–4.0 ppm. ^{1}H–NMR of PPNPMI monomer shows chemical shift δ at 6.82 (s) ppm characteristic of CH=CH group. The disappearance of this in polymer PPNPMI shows that the radical polymerization proceed through the double bond [21-24].

PNPMCCA

In fig. 5, 3064,2936 (Aromatic,C-H), 2679.6 (-COOH),1713, 1776 (C=O), 1560 (C=C stretch, aromatic),1560(-NO2 group) 1461.9 (C-H band, –CH$_2$), 1390 (due to overlapping of C-N), 1251.3 (Ar-O-C-), 1560 (-NO2) 830.7 (1,2-disubstituted benzene) and 772.6, 772.2 cm^{-1} (out of plane C-H band of benzene ring, and 664 (out of plane (aromatic ring C=C band). ^{1}H-NMR of PNPMCCA data showing In Fig. 6, δ values from 7.5 to 8.1 due to present of phenyl ring and a signal of showing δ at 4.0 it means present of the unit, signal δ values obtained in 3.2 to 3.5 appearance of polymerization precede via single bond.
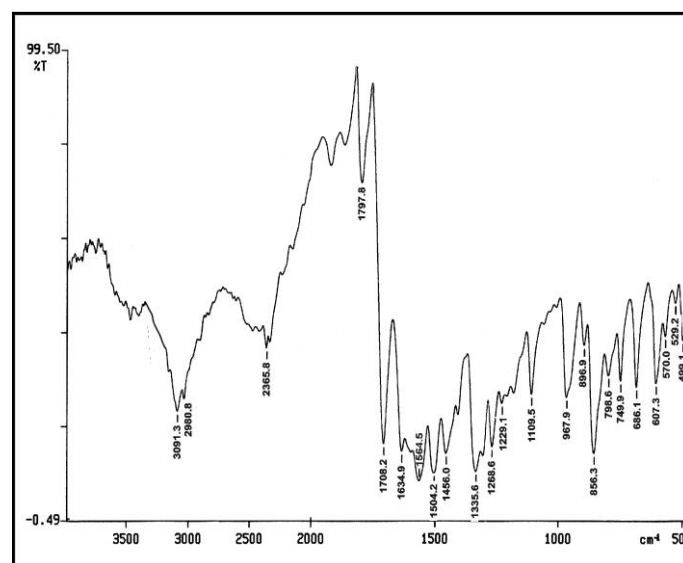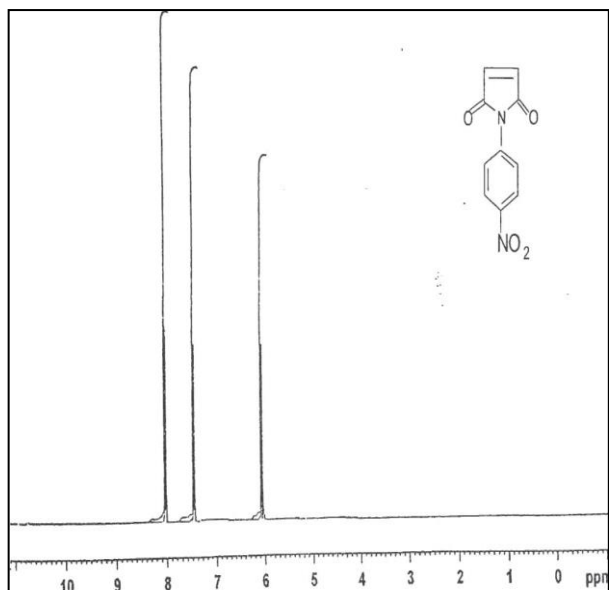

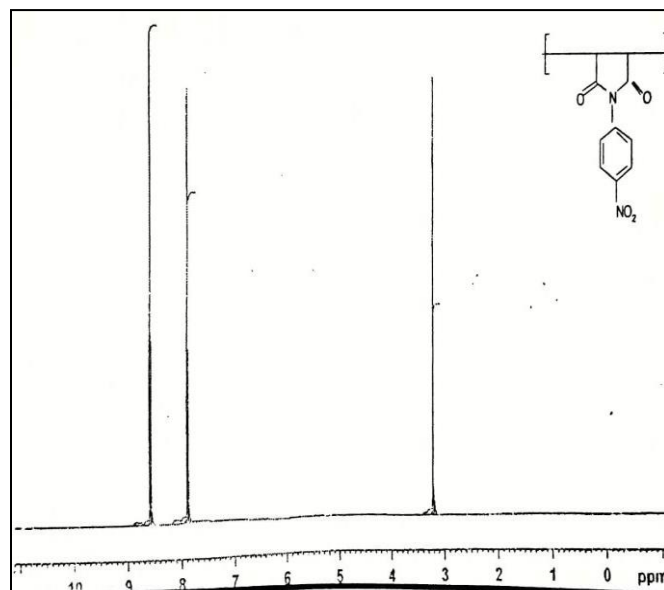
Figure 1. FTIR for PNPMI

Figure 2. ¹H-NMR of PNPMI
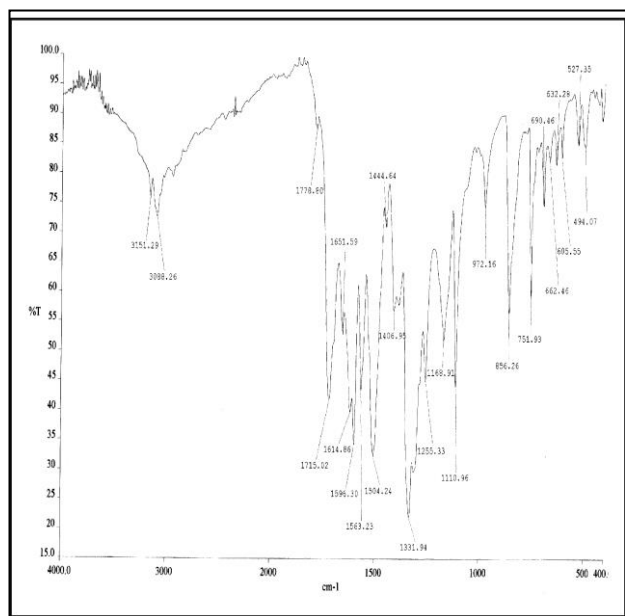

Figure 4. ¹H-NMR of PPNPMI
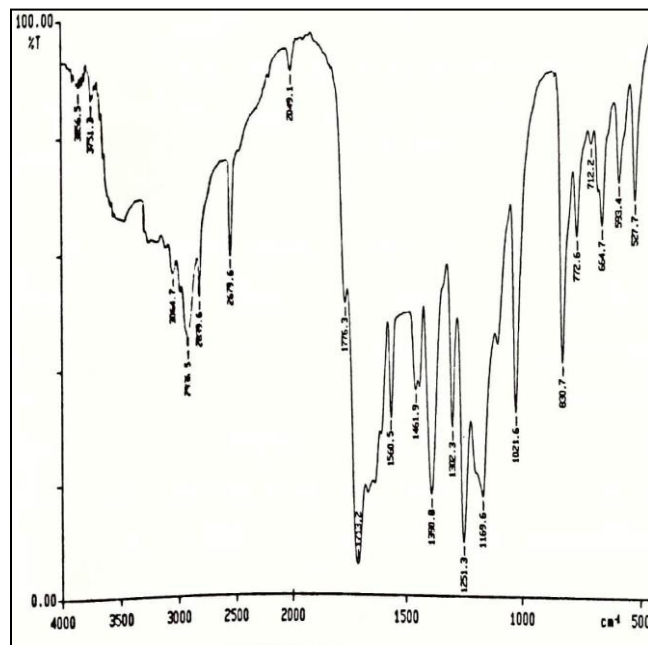

Figure 3. FTIR of PPNPMI
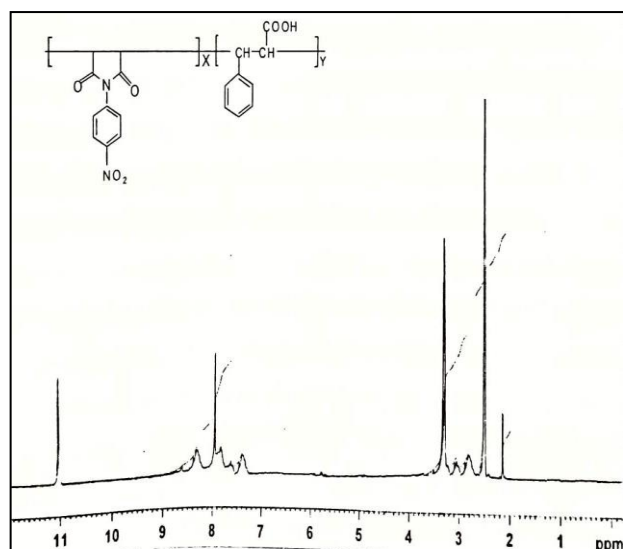

Figure 5. FTIR of PNPMCCA

Figure 6. ^{1}H-NMR OF PNPMCCA

A. Effect of time on yield

Prepared monomer copolymerized with Cinnemic Acid with at different time hours and percentage yield was given in table.1, it is seems that no any percentage yield or polymer formation found around the 12 hours, only percentage yield obtained upper to 12 time hours.

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

Polymer Code	12Hr.	24Hr.	30Hr.	36Hrs.	Colour
PPNPMI	18.78	33.23	38.12	40.78	Yellow
PNPMCCA	38.9	40.3	41.8	44.2	Yellow

B. Effect of solvent and Initiator system

Synthesis homopolymer and copolymer were carried out in different THF and DMF solvent System and effect of the solvent on percentage yield was calculated and result are summarized in the table.2.

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

Polymer Code	Solvent	AIBN	BPO	Colour
PPNPMI	THF	35.32	29.77	Yellow
	DMF	40.72	36.29	Yellow
	1,4 DIOXANE	34.21	31.72	Light yellow

From table .2 indicate that percentage yield was in AIBN-DMF system is more suitable as comparative BPO- DMF solvent system .AIBN-DMF system gives to more yield.

C. Relation in between intrinsic viscosity and molar mass

Molecular weight of synthesis compounds determined by the Gel permission Chromatography and relation find out in between molar mass and intrinsic viscosity, Intrinsic

viscosity determined by Ubbelohde suspended viscometer. For commercial purposes, the molar mass is usually characterized from measurement of the viscosity of dilute solutions. It has been shown that, for dilute solutions, the relation between the viscosity and the molar mass (in this case the "viscosity average" molar mass) may be given by the relationship $[\eta] = K M^a$, where K and a are constants,

M is the molar mass, $[\eta]$ is the intrinsic viscosity or limiting viscosity number.

This is obtained by plotting $(\eta - \eta_0)/\eta_0 c$ against concentration c and noting its extrapolated value at infinite dilution. In this case, η is the viscosity of the polymer solution and η_0 the viscosity of the pure solvent. Intrinsic viscosity obtained by (fig.7,8) Hugging plots reduced viscosity verses concentration .

Table: 3 Shows the number molecular weight and Intrinsic viscosity of PPNPMI and PNPMCCA

Polymer Code	Number Average(Mn)	Weight Average(Mw)	Polydispersity (Mw/Mn)	Start Mw	Intrinsic Viscosity
PPNPMI	456	519	1.138	2779	0.0423
PNPMCCA	680	1832	2.573	2660	0.238

Table: 4 Typical data of Viscosity measurements of PPNPMI summarized in DMF at 30°C

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

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

Polymer code	Conc.(c) g/dl	η_{rel}	η_{sp}	η_{red}	Intrinsic viscosity
PNPMCCA	0.1	1.0244	0.0244	0.244	
	0.2	1.0508	0.0508	0.254	0.238
	0.3	1.0789	0.0789	0.263	
	0.4	1.1068	0.1068	0.267	
	0.5	1.1380	0.1380	0.276	
	0.6	1.1692	0.1692	0.282	

From comparison of the table 4 and 5 are showing that intrinsic viscosity of Copolymer having more than of Homopolymer it is due to present of both are unit in the structure of copolymer and molecular weight of copolymer is more than as compare to homopolymer.
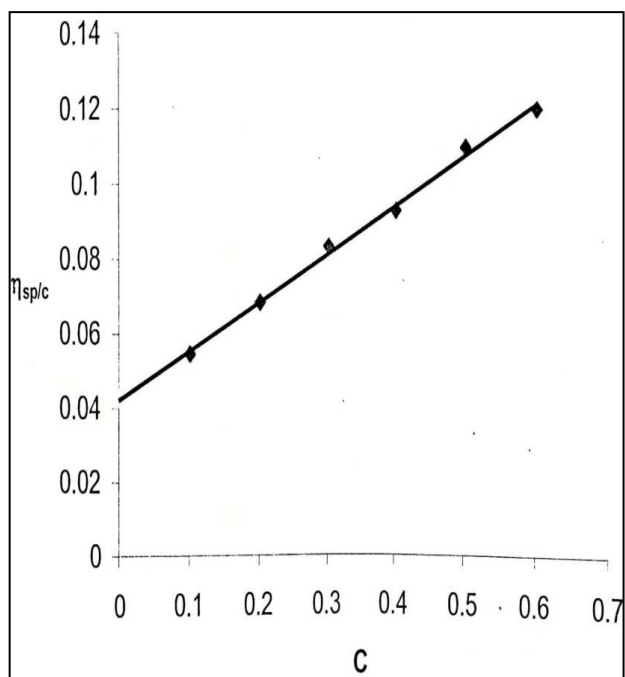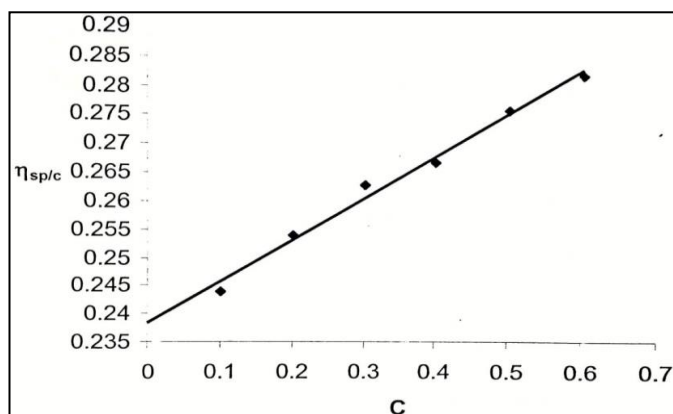

Fig. 7. for PPNPMI

Figure. 8 for PNPMCCA

D. Solubility Behavior of Polymers

The solubility of monomers and polymers were observed by finely grounded polymer powder which was placed into test tube and two to three ml solvent was added and stirred at 30C. same procedure repeat for each sample. Solvent was taken were as follows: THF,DMF,DMSO,Benzene.Methylacetate,,1,4Dioxane,Xylene,dichloromethane,2Butanol,cyclohexanon,water,methanol and carbon tetrachloride. Solubility of any polymeric materials depends upon the composition. Solubility of homopolymer is less than copolymer although same

condition is not found regular. Solubility of homopolymer and copolymer summarized in table

Table. 6: Relative solubility of homopolymer and copolymer are summarized

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

E. Thermal behavior

Synthesis homopolymer and copolymer and their Thermal stability were determined by Perkin Elmer USA Pyris TGA-A Techniques and thermal degradation rate of homopolymer and copolymer are summarized in table.. and Thermograms of synthesis PPNPMI and CPNPMI are shown in Fig.9 and 10. Initial temperature Ti and Final temperature Tf range shown in Table 7 and 8 shows decomposition rate, integral procedural decomposition temperatures and The results of percentage weight loss suffered from $100\,^{o}$C to $550\,^{o}$C .

Table 7 :Thermal degradation of Homopolymer and copolymer samples

Polymer Code	Degrdation step	Ti ^{o}C	Tmax ^{o}C	Tf ^{o}C	Residue at 500 ^{o}C
PPNPMI	I	240	340	370	20.88
	II	370	410	550	
PNPMCCA	I	225	275	342	17.09
	II	342	448	560	

Table 8:.Percentage weight loss of Homopolymer and copolymer at various temperature.

Polymer Code	200 ^{o}C	300 ^{o}C	400 ^{o}C	500 ^{o}C	550 ^{o}C
PPNPMI	-0.8	-20.8	-72.8	-79.1	-79.2
PNPMCCA	-0.21	-62.14	-79.83	-82.91	-82.72

From the table 7 and 8 gives the comparative study because percentage degradation in homopolymer shows very less, while percentage degradation in copolymer shows very high it is due to homopolymer having only one unit while copolymer having two units and percentage degradation of the thermal curves are shows in fig.9 and 10.
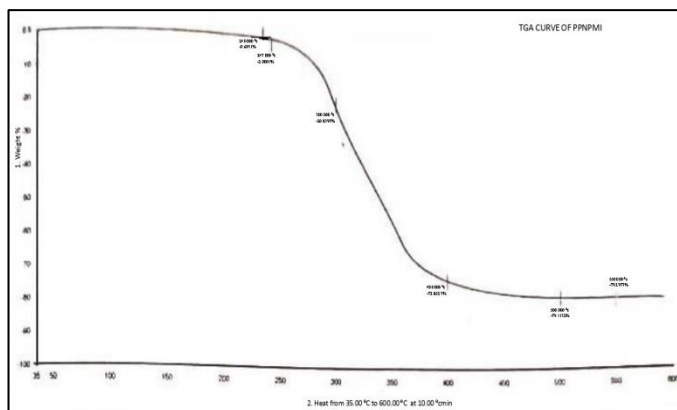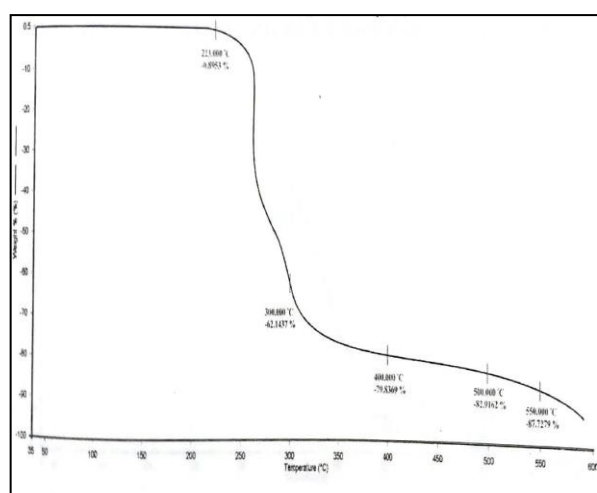
Figure: 9 , Thermogram curve of PPNPMI

Figure: 10 Thermogram curve for PNPMCAA

IV. CONCLUSION

Thermal stability of the homopolymer shows in excellent stability, while copolymer shows the less stability to because of homopolymer having single unit and copolymer having both are unit. 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. Polymerization process through the free radical polymerization reactions, this is approved by the Polydispersity index Molecular weight of copolymer is 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.

V. ACKNOWLEDGEMENT

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