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Recent Study of Some New Maleimide Copolymers and Their Electrolyte Study in Solvent

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Abstract: **This article describes the synthesis and characterization of N-(O-Nitro phenyl maleimide) polymer, obtained by the reaction of maleic anhydride with O-Nitroaniline respectively. Structural and thermal characterization of ONPMI and HONPMI and monomers were characterized with Fourier transform infrared (FTIR), ^{1}H-NMR.synthesis monomers copolymerization with methyl methacrylate (MMA) with various amounts of ONPMI with azobisisobutyronitrile as an initiator. Structural and molecular characterization of copolymers was performed with FTIR, 1H-NMR, elemental analysis, and gel permeation chromatography. The nitrogen percentage was used to calculate the copolymer composition. (number-average molecular weight) and3.3–101.8 3 103 (weight-average molecular weight), with polydispersity indexes in the range of 1.5–4.1. The molecular weight decreased with the increasing molar fraction of imide in the polymer backbone.**

Key words: Radical polymerization, AIBN,TGA, GPC, thermal properties

I. INTRODUCTION

The compounds having aniline or imide groups show high-performance stability and increased thermal stability, heat resistance and good mechanical properties[1]. Aromatic polyimides are one of the most important classes of high-performance polymers. Due to their thermal, electrical and high-temperature mechanical properties, aromatic polyimides have found many applications as high temperature insulators, coatings, adhesives and matrices for high-performance composites [2-6]. N-phenyl maleimide monomers with halogen substituent in the aromatic ring have been studied only in a few cases [7]. Anionic polymerization is a good method to obtain homopolymer [8-10]. The present paper reports the synthesis and free radical copolymerization of N-[O-Nitro phenyl] maleimide with methyl methacrylate (MMA). This copolymer has better thermal stability. Copolymer composition is determined by elemental analysis and thermal study was done with the help of TGA analysis. investigated the copolymerization of methyl methacrylate (MMA)with imide monomers, that is, maleimides or electron-withdrawing or electronreleasing substituents. The nature of the substituents as well as the position of the substituents had a large effect on the physical properties. In our previous studies,we found that the electron-withdrawing group had a large effect on the glass-transition temperature(Tg) as well as the copolymerization behavior. The aim of this work was to investigate systematically.in our study found that electron withdrawing groups showing nonelecrolyte behavior in solvent [11–23].

The aim of this work was to investigate systematically the effect of the Nitro group and its position benzene ring copolymerization behavior with MMA. This article describes the synthesis, characterization, and radical copolymerization of N-(O-Nitrophenylmaleimide) monomers of ONPMI with MMA In tetrahydrofuran (THF) as a solvent. Several copolymer samples were prepared by the variation of the molar fractions of the HONPMI and CONPMI in the initial feed to investigate the effects of the copolymer composition and structure on the thermal behavior. expected to produce copolymers with a great structures stiffness as well as higher thermal stabilities. The physical, spectral and thermal properties have been studied in order to characterize the homo and copolymer[24].

II EXPERIMENTAL

A. Materials

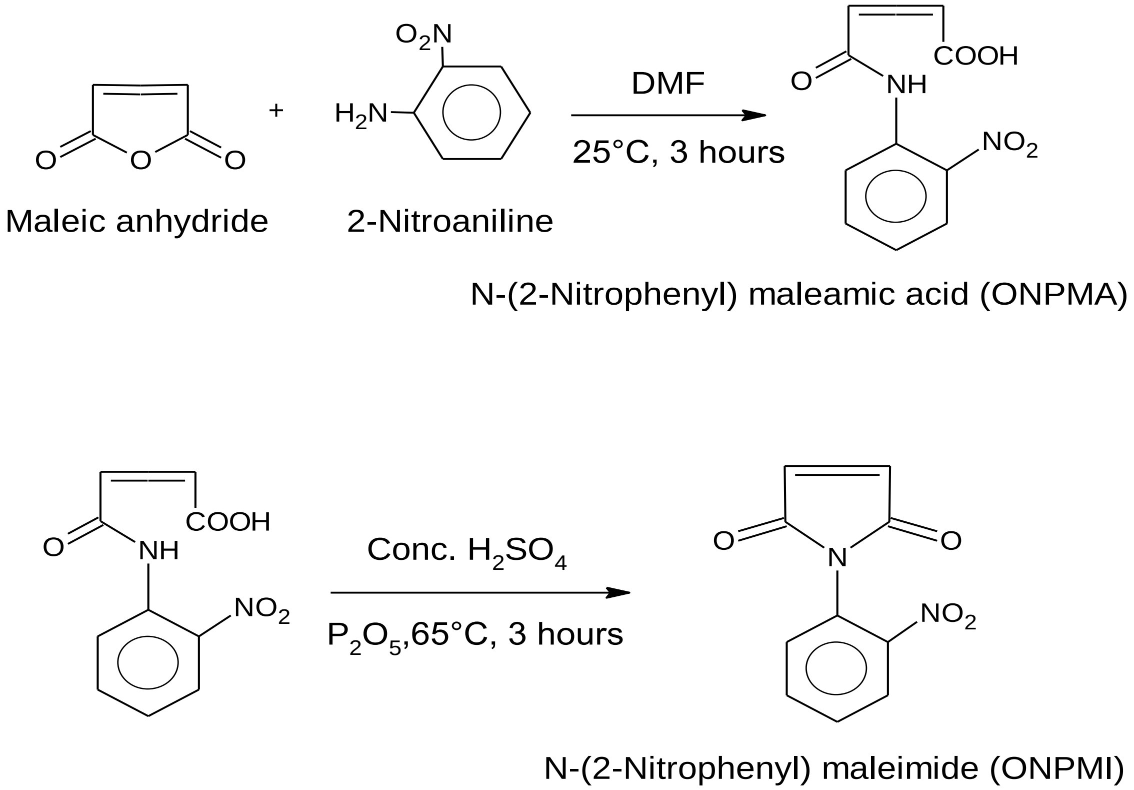
Maleic anhydride were recrystallized from acetone. Methylmethacrylate (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl2 for 6 h and distilled [24]**.** The head and tail fractions were discarded. AIBN (2,2_-azobis–isobutironitrile (spectorchem.)) 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

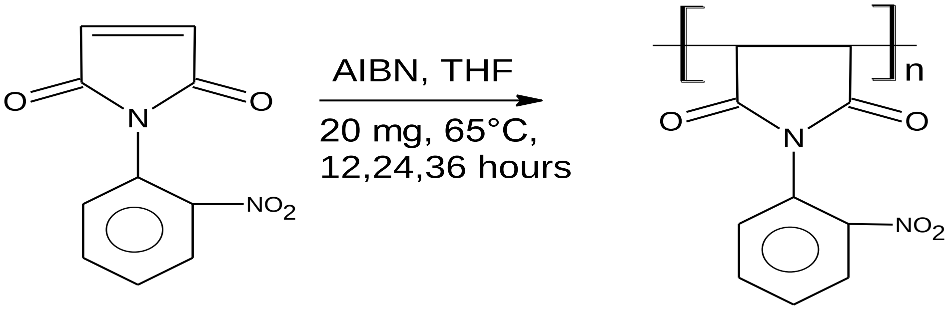
Preparation of N-(2-Nitorphenyl) maleamic acid**:**Nitroaniline (13.8 gm for 0.1mol) and 9.8 gm maleic anhydride were taken in 30ml DMF. The solutions kept stirring for three hours at 25°C. The reaction mixture was poured in crushed ice. Yellow solid precipitate was obtained, then filtered and dried under vacuum. It was recrystallized from methanol to obtained pure N-(2-Nitrophenyl) maleamic acid. Yield was 70%, m.p. 145°C.N-(2-Nitrophenyl) Maleimide:Cyclodehydration of the 2-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-(2-Nitrophenyl) maleimide was recrystallized from ethyl alcohol solvent. The yield was 65%, m.p. 120°C. synthesis monomer characterized by FT-IR spectraThe major characteristic FT-IR spectra with characteristic absorption frequencies 3105 (aromatic and alkene C–H stretch), 1716, 1790, (symmetric and asymmetric stretch of C=O in a five-member imide ring 1528, 1354 (symmetric and asymmetric stretch of NO_2 group), 1606(C=C, alkene) 1586,1491,1454 (C=C, aromatic) ,1150 (C–N stretch) , 957(CH=CH), 834 (1,2 disubstituted of benzene), as shown in these are consider with the structure of ONPMI [25-27] **.**^{1}H-NMR , 400 MH$_z$, ref. TMS, solvent DMSO-d$_6$, δ,ppm) (a) two methine (CH=CH) protons at δ 6.93 (s) ppm and (b) one phenyl protons at δ7.29-8.20(m).synthesis ONPMI shown in sceme-1.



SCHEME-1

Homopolymerization of N-(2-Nitrophenyl) maleimide (HONPMI):

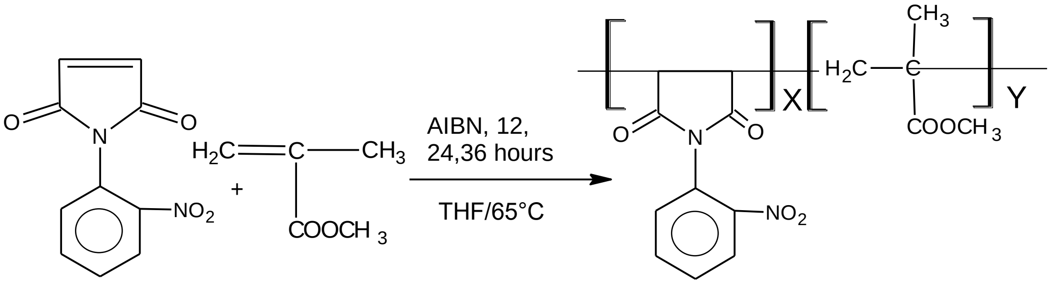
Polymerization of N-(2-Nitrophenyl) maleimide was carried out in THF solvent. Using radical initiator AIBN 65°C. 2-Nitrophenylmaleimide (2.18 gm), 0.01 mol and THF in 30ml were placed in round bottom flask with reflux condenser. To this solution 20mg AIBN was added and the reaction mixture was refluxed on heating mental at 65°C. For 12, 24, 36 and 48 hours. Very less polymer was formed if the reaction was carried out up to 12 hours. Yield was obtained 26.45% for 24 hours. The synthesized polymer was isolated in excess quantity of methanol water mixture. It was dried under vacuum at 60°C.



SCHEME-2

Copolymerization of N-(2-Nitrophenyl) maleimide with MMA (CONPMI)

2-Nitrophenylmaleimide (2.18 gm, 0.01 mol) and MMA (1.06 ml, 0.01 mol) in 30 ml THF solvent was taken in a round bottom flask. The copolymerization reaction was carried out at 65°C for 24 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 obtained 42.90%. copolymerization reaction given in scheme-3.



SCHEME-3

FT-IR and ^{1}H-NMR Spectral analysis of Homopolymer and copolymer:

In Fig.1, the major characteristic absorption bands (in cm^{-1}) are observed at 3150–2951 (Aromatic, C-H stretch, CH_3, and CH_2 in MMA), 1721, 1770 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1602, 1535 (C=C stretch, aromatic), 1487, 1444 (C-H band, $–CH_2$), 1352 (due to overlapping of C-N stretch and C-H band of $–CH_3$ group), 1299, 1190, 1150 (asymmetric and symmetric C-O-C stretch, 831 (1,2-disubstituted benzene) and 781, 741 cm^{-1} (out of plane C-H band of benzene ring, and 699 (out of plane (aromatic ring C=C band). These characteristic bands confirm that units of both the monomers. ONPMI and MMA are present in the copolymer samples. The absence of characteristic band of vinyl group at 957 cm^{-1} indicates the polymer formation via vinyl group.

The FT-IR spectrum of HONPMI is shown in Fig. 2. The major characteristic absorption IR frequencies (in cm^{-1}) 2935 (C-H stretch, alkane), 1785, 1721 (symmetric and asymmetric stretching of C=O in a five member imide ring, 1661, 1608, 1587, 1437 (C=C stretch, aromatic), 1502, 1386 (symmetric and asymmetric, Ar-NO_2 group), 1257 (asymmetric C-O-C stretch), 1189, 1102 (symmetric C-O-C stretch), 851 (1, 2 disubstituted benzene) 620 (out of plane aromatic ring C=C bend) are consistent with the structure of HONPMI [24].

Fig. 3 shows the ^{1}H–NMR spectra for CONPMI, the chemical shift δ for four aromatic protons is observed at 7.29–8.20 ppm. for 2H (–CH–CH–) and $–OCH_3$ signals at δ 3.60–3.79 ppm and $–CH_3$ signals at 0.85–1.23 ppm, 2H for ($–CH_2–$) observed at 1.83–2.49 ppm.

In Fig. 4 the chemical shift δ for HONPMI is observed at 7.50–7.90 ppm is assigned to four proton (m). 2H in –CH–CH– group have appeared at 3.50–3.90 ppm. ^{1}H–NMR of HONPMI monomer shows chemical shift δ at 6.93 (s) ppm characteristic of –CH=CH– group. The disappearance of this peak in HONPMI shows that the radical polymerizations proceed through the double bond [28-30].

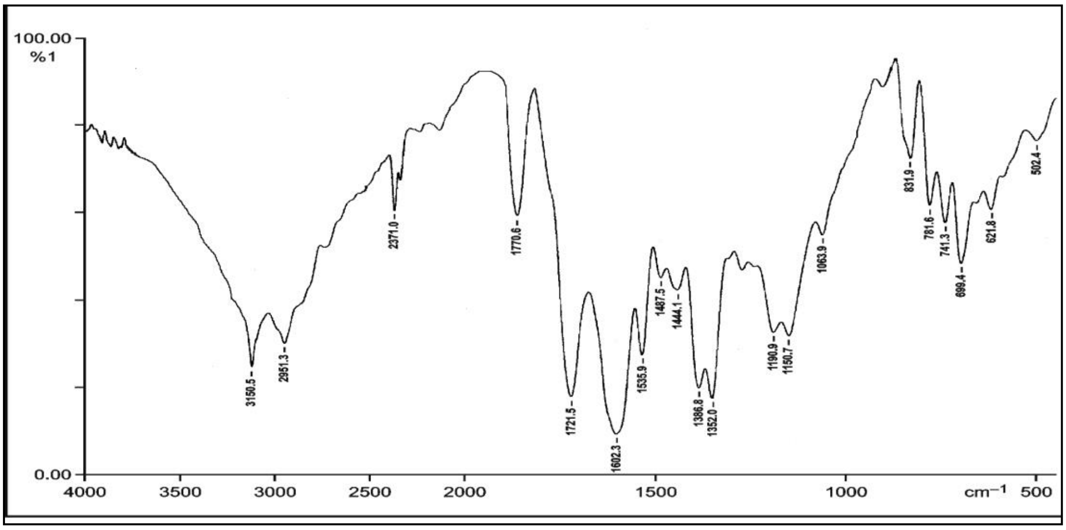


Fig.1 FT-IR Spectra of CONPMI

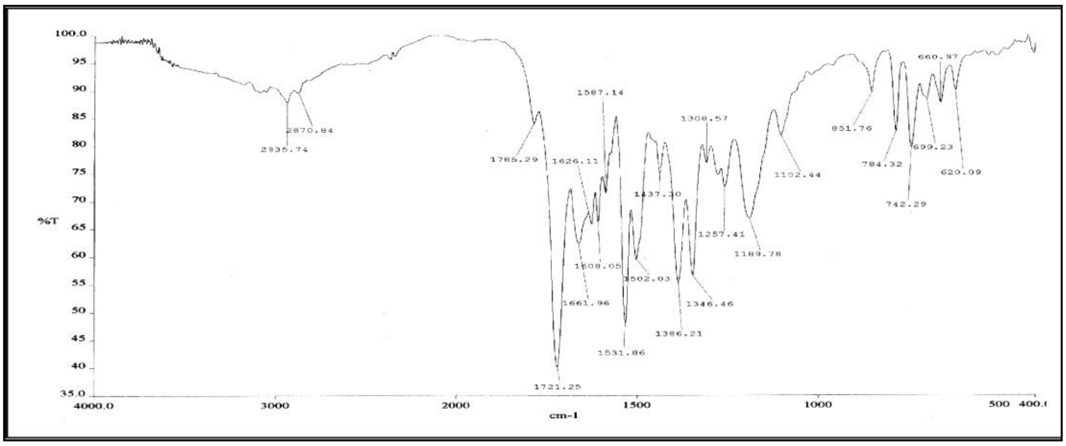


Fig. 2 FT-IR Spectra of HONPMI

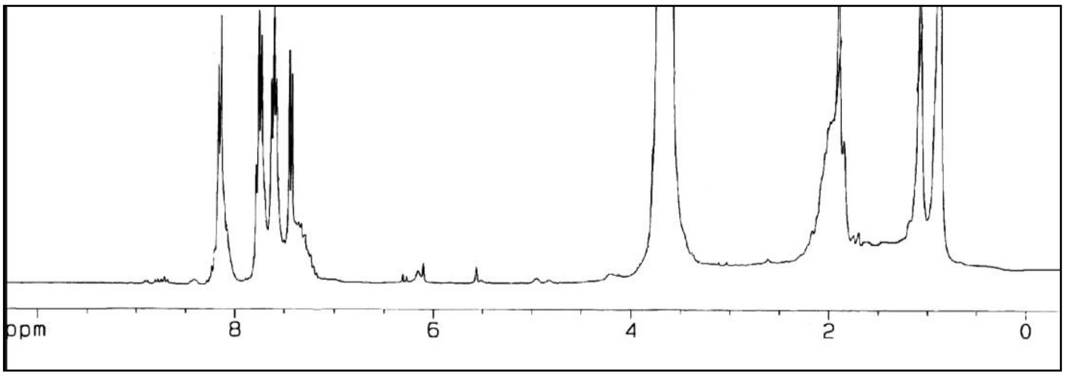


Fig. 3 ^{1}HNMR of CONPMI

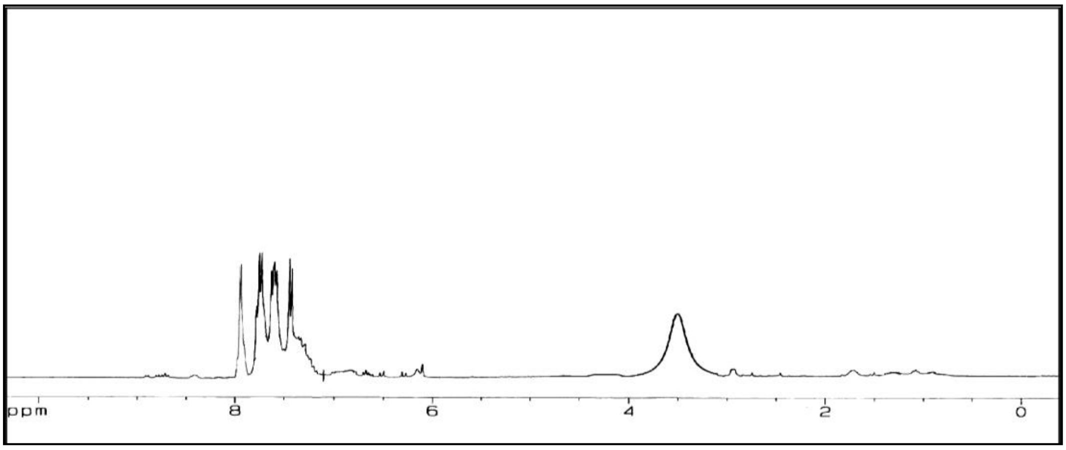


Fig. 4 ^{1}-HNMR of HONPMI

Results and Discussion:

Effect of Polymer Concentration on Viscosity and electrolyte study: Graph plotted in between (η) reduced viscosity and concentration with a positive slope. The results of the viscosity measurement show linear relationship in all cases. This clearly indicates non-electrolyte behavior of all the polymers solution under study. This could be understood from the fact that the Benzene and NO_2 groups have a very low dissociation constant and such groups in non-aqueous media may not dissociate appreciably to show any polyelectrolyte behavior. As size of monomer increases intrinsic viscosity increases. Fig. 5 and Fig. 6 are showing of intrinsic viscosity of HONPMI and CONPMI.

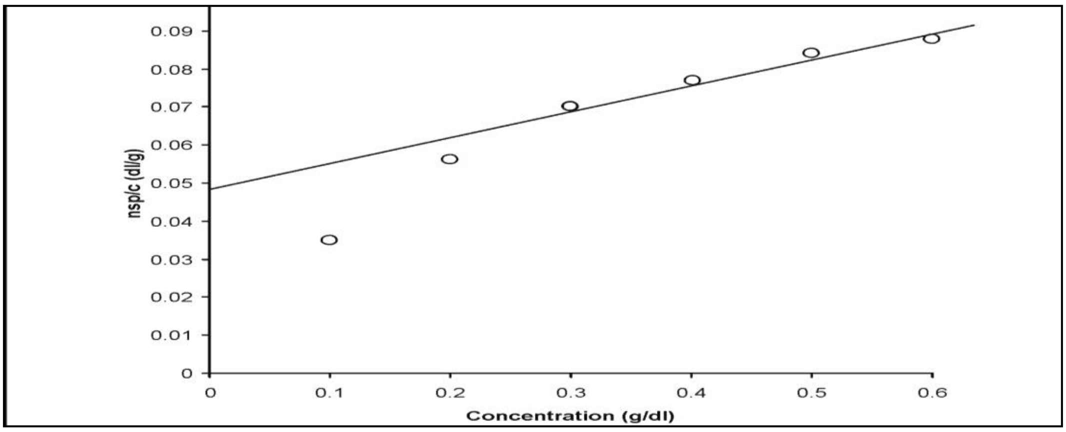


Fig. 5 Intrinsic viscosity of HONPMI.

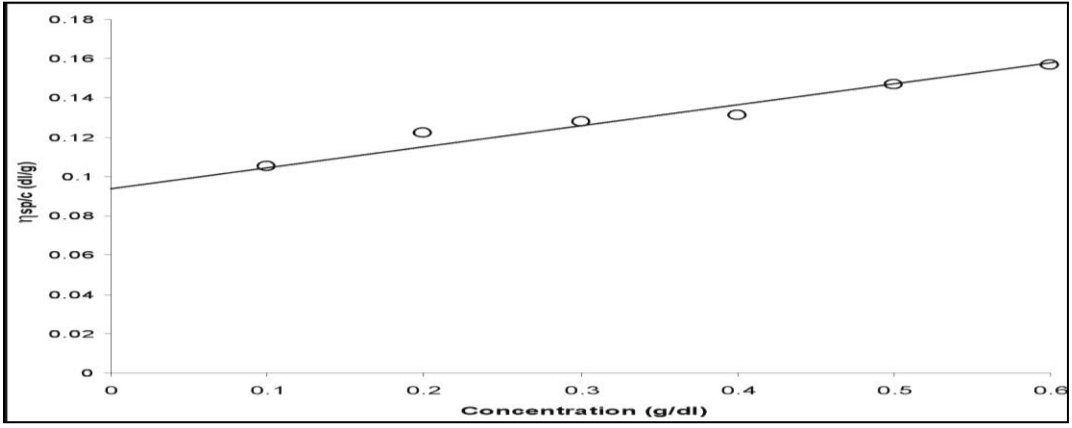


Fig. 6 Intrinsic viscosity of CONPMI

Viscosity-Molecular Weight Relationship

The dependence of intrinsic viscosity [η] on molar mass of polymer chain is given by the empirical Kuhn-Mark-Howink Sakwada equation as

$[\eta] = K_\eta M^\alpha$

$\log [\eta] = \log K_\eta + \alpha \log M$

The exponent α value is dependent on the shape of the polymer molecules and segment distribution. It is generally predicted by theory that the value of $\alpha = 0$ for spheres, $\alpha = 0.5$ when the polymer chain acquires unperturbed dimensions $\alpha = 0.764$ for perturbed coils and $\alpha = 2$ for rigid rods. The system in which α is close to 0.5 can be regarded to exist in θ conditions, (when the polymer coil has no interaction with the solvent molecule, it acquires unperturbed dimensions). Plot of log [η] versus log Mw gives straight line. In the present study when only homopolymers are taken $\alpha \approx 0.48741$. It shows homopolymers in unperturbed dimensions. In case of copolymers $\alpha \approx 1.4921$. Hence molecules shows are in shape of rigid rods. log value are shown in the Table. 1.

Table. 1: Log value of HONPMI and CONPMI.

Polymer	**Mw**	**Log Mw**	**$\eta \times 10^3$ dl/gm**	**Log $\eta \times 10^3$**
HONPMI	18984	4.2784	48	1.6812
CONPMI	39908	4.6011	92	1.9638

Effect of time on yield formation:

The homopolymerization and copolymerization carried out in THF Solvent at different time hours and obtained data revealed that the percentage yields are increased with time hours (Table 2) and copolymers of ONPMI with MMA (Time 12 hrs. initiator AIBN) is shown in Table 3.

Table 2: % yield at various time hours.

Polymer code	Time hrs	Yield %	State	Color
HONPMI	12	16.17	Solid	Yellow
	24	26.45	Solid	Yellow
	36	28.46	Solid	Yellow
	48	39.42	Solid	Yellow
CONPMI	12	17.25	Solid	Yellow
	24	42..90	Solid	Yellow
	36	52.50	Solid	Yellow
	48	54.55	Solid	Yellow

Table 3: Feed mol ratios ONPMI:MMA

CONPMIMMA	Feed mol ratios ONPMI:MMA	Yield%	State	Colour
CONPMIMMA1	1:9	38.2	Viscous liquid	Light yellow
CONPMIMMA2	2:8	38.3	Viscous liquid	Light yellow
CONPMIMMA3	3:7	40.3	Viscous liquid	Light yellow
CONPMIMMA4	4:6	41.1	Solid powder	Light yellow
CONPMIMMA5	5:5	42.9	Solid powder	Light yellow
CONPMIMMA6	6:4	41.3	Solid powder	Light yellow
CONPMIMMA7	7:3	44.2	Solid powder	Light yellow
CONPMIMMA8	8:2	46.3	Solid powder	Light yellow
CONPMIMMA9	9:1	48.9	Solid powder	Light yellow

Solubility Behavior:

The solubility of a polymeric material depends upon the molecular weight of polymer, nature of the solvent and the temperature of the system. The solubility or insolubility of polymer in a particular solvent and its dependence on temperature can provide more information about the polymer solvent interaction. Further, the knowledge of solubility of polymer is essential for the polymer processing industries as well as separating homopolymer from copolymer samples formed during polymerization [30-34]. The solubilities of the present homopolymer and copolymer samples in variety of solvents at 30ºC were examined. Behaviour of polymer solubilities were summarized in Table 5.

Table 5: Relative solubility of Homo and Copolymers

Solvents	HONPMI	CONPMI	COLOUR
THF	Soluble	Soluble	Yellow
DMF	Soluble	Soluble	Yellow
DMSO	Soluble	Soluble	Yellow
Dioxane	Soluble	Soluble	Yellow
Acetone	Soluble	Soluble	Yellow
Chloroform	Soluble	Soluble	Yellow
Methyl acetate	Soluble	Soluble	Yellow
Ethyl acetate	Soluble	Soluble	Yellow
Benzene	Soluble	Soluble	Yellow
Toluene	Soluble	Soluble	Yellow
CCl_4	Soluble	Soluble	Yellow

Physical properties:

Synthesis homo and copolymers and their Thermal analysis measured by TGA techniques and their decomposition were showing by the TGA Curve. TGA curve of HONPMI and CONPMI are shown in Fig. 6 and Fig. 7, respectively. The initial decomposition of the, decomposition rate was very slow. The weight loss of copolymer and homopolymer are summarized in Table 6 and after analysis that decomposition of homopolymer is less than copolymers. It is due to homopolymer have only one backbone in the chain of the polymers, while copolymers having two or more than two in copolymer back bone.

Table 6: Decomposition of HONPMI and CONPMI.

Polymer code	Ti	Tmax	T final
HONPMI	210°C -1.4881%	400°C -86.1683%	550°C -91.1736%
CONPMI	185°C -1.349%	400°C -68.59%	500°C -72.6160%

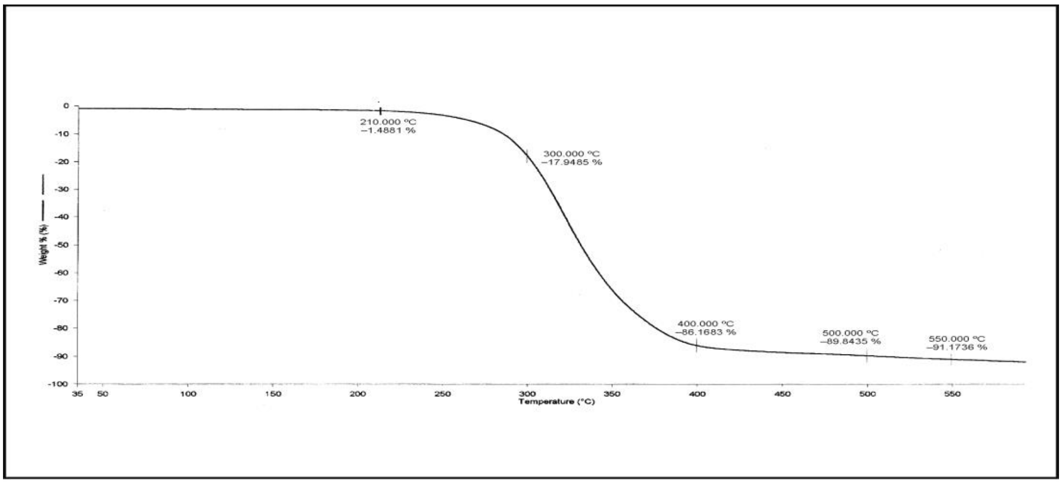


Fig. 6 TGA curve of HONPMI.

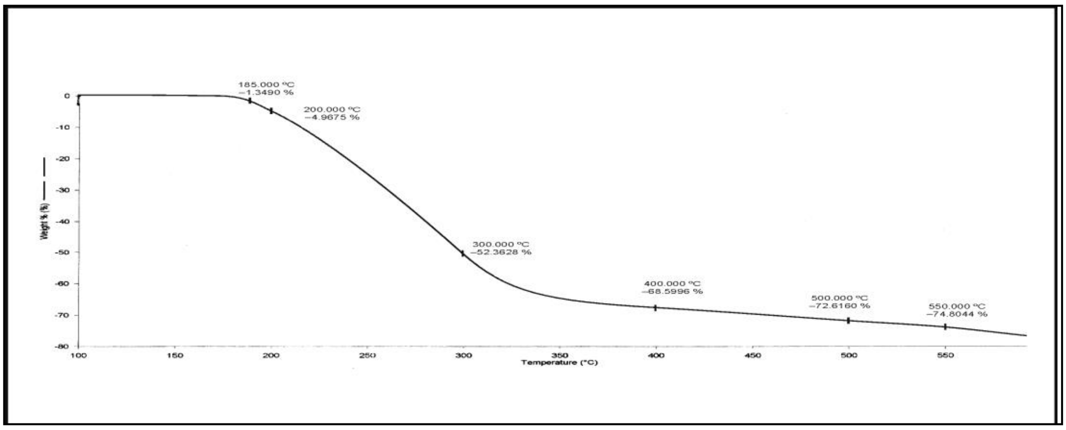


Fig. 7 TGA curve of CONPMI.

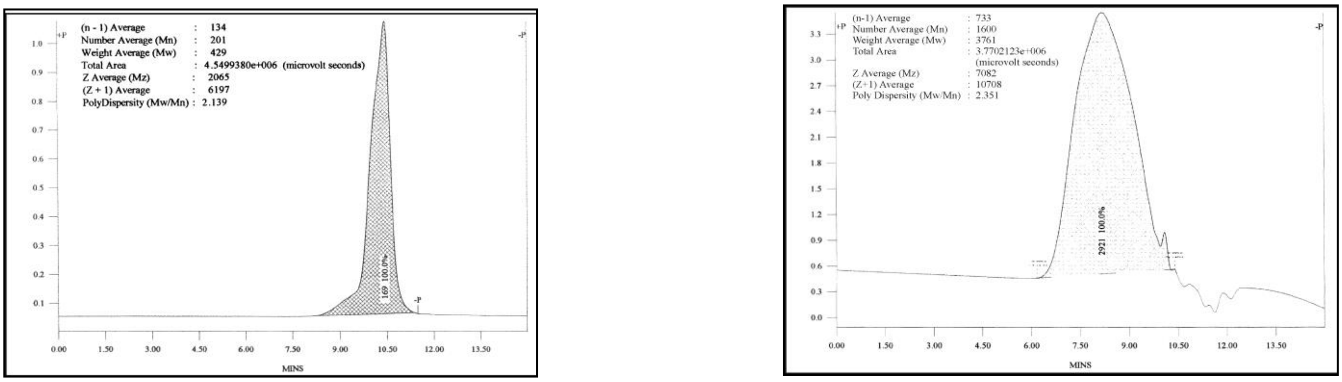
Relation in molecular weight and PDI:

Prepared homopolymer and copolymer and number average and weight average molecular weight was determine by Gel permission chromatography and find out that value of polydispersity index are given in Table 7. PDI values showing that polymerization proceed via free radical polymerization.

Table 7: indicate the molecular weight and weight average molecular weight and PDI values.

Polymer code	Number average	Weight average	Polydispersity Index	Start Mw	End Mw
HONPMI	201	429	2.13	18984	22
CONPMI	1600	3761	2.35	39908	171

From the table is clearly indicates PDI values range in between 1.0 to 10 is obtained that the polymerization via free radical proceed. Polygraph of HONPMI and CONPMI are given in Fig. 8 (a & b).



(a) **(b)**

Fig. 8 Polygraph of HONPMI and CONPMI.

CONCLUSION:

Synthesis homo and copolymerization HONPMI and CONPMI showing excellent thermal stability and polymers characterized by FT-IR and ^{1}H-NMR .from the polydispersity index .results are observed that polymerization through the free radical polymerization. Synthesis HOMO and Copolymer showing excellent solubility in THF,DMF,DMSO,CCl4,Chloroform,dichloromethane,Acetone,Cyclohaxene and their physical properties investigated by intrinsic viscosity, Molecular weight and number average weight find out by GPC system.

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