Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

Thermal Study and Characterization of New Synthesis N-Benzylmaleimide and N- Phynyl Maleiide Polymers

Suresh Kumar Meena, Bharat Singh Meena, Manju Meena and B.L. Hiran
Department of Chemistry, Govt. College, Kota,
Rajasthan, India

***Abstract*- This article describes the synthesis of homopolymer and copolymer of N-Benzylmaleimide and N-Phenylmaleimide, synthesis monomers and copolymerized with MMA in THF solvent using AIBN as a free radical initiator. Prepared homopolymer and copolymer samples were characterized by FT-IR, ^{1}H-NMR, N- elemental analysis, solubility test, intrinsic viscosity. The thermal stability was determined by TGA techniques. Molecular weight of polymers was determined by GPC. Number average and weight average PDI determined by GPC.**

***Key words*- Radical polymerization, N-Benzyl maleimide, N-Phenylmaleimide, Characterization, thermal stability, Gel Permission Chromatography, Molecular weight.**

I. INTRODUCTION

Aromatic polymaleimides and their derivatives show higher excellent thermal stability due to maleimide unit present in their backbone. These provide the polymers with superior mechanical and thermal stability. Although maleimide undergoes homopolymerization with great difficulty, it copolymerized quite readily with a variety of vinyl monomers [1].

Generally aromatic polyimides have found many applications as like high temperature insulators, coating, adhesive and matrices for high- performance composites [2-4].

Most aromatic polyimides generated by the thermal solid phase imidization show insolubility, Infusibility, which make processing difficult. These undesirable properties limits the wider applications of the polyimides, are due to their chain rigidity as well as poor defined molecular architectures. Addition types of polyimides were developed mainly to overcome processing disadvantages [5-6].

Many authors have studied the N-Substituted maleimides and observed that maleimide polymers show excellent thermally stability [7-9]. At present there is a considerable interest not only in the synthesis of new type of polymers, but also in the modification of commodity polymers in order to improve their properties to meet requirements for new applications.

In this order to investigate the possibility of obtaining better polymers from N- substituted maleimides, here we report the homopolymer of N-Benzylmaleimide and N-phenyl maleimide, its copolymer with methyl methacrylate in THF solvent using AIBN as a free radical initiator. The polymer samples were characterized by IR, ^{1}H-NMR, solubility test and thermo gravimetric analysis.

II. EXPERIMENTAL

A. Materials

Maleic anhydride (SDH, AR) was recrystallized from chloroform, Ailine and benzyl amine were used after distilled. Azobisisobutyronitrile (AIBN, Wilson Laboratory) was recrystallized from methanol prior to use. Tetrahydrofuran (THF), N,N- Dimethylformaimde (DMF) were used after distillation [10].

B. Measurements

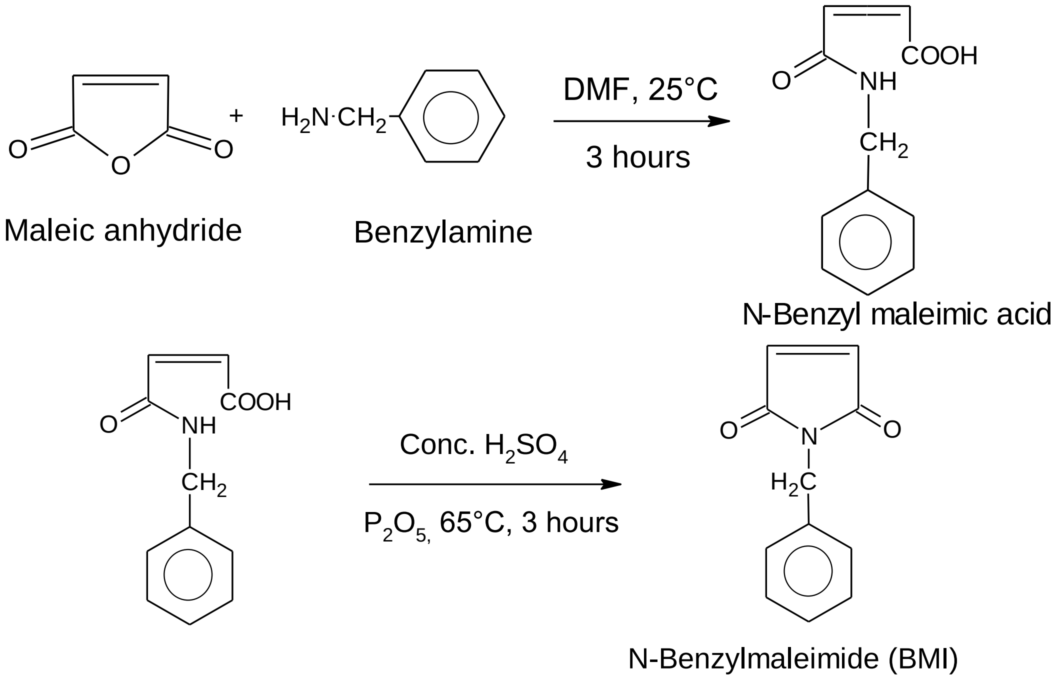
^{1}H-NMR spectra of homopolymer and copolymer samples were taken in DMSO-d$_6$ on a Bruker DPX-200/DPX-300 spectrometer at 300/400 MH$_Z$. FT-IR spectra of the polymer samples were recorded on a Perkin Elmer IR spectrometer using KBr pellet technique.

The intrinsic viscosity (η) measurements were carried out in DMF at 30ºC by Ubbelohde suspended level viscometer. Temperature was controlled by water thermostat. Weight average molecular weight and Number average molecular weight of the homopolymers & copolymers were determined by gel permeation chromatography technique using THF as a mobile phase and polystyrene as a standard [11, 12]. Thermogravimetric analysis was carried out in air at a heating rate of 10ºC/ minutes by means of a mettler TA-3000 system.

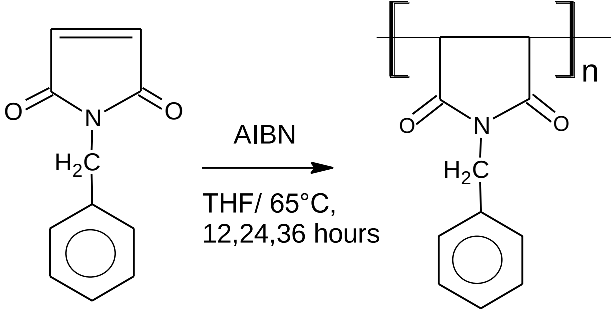
C. Methods

Preparation of N-Benzylmaleimide (NBMA): N-Benzylmaleamic acid:- Benzylamine (10.88ml, 0.1mol) and Maleicanhydride (9.8gm, 0.1mol) were taken in 30ml DMF solvent. The solution stirred for three hours at room temperature. Solution poured in cool water and obtained white solid precipitated. The product was filtered, dried and recrystallized from ethyl alcohol to obtained pure form of NBMA. Yield 90%M.P.98ºC.

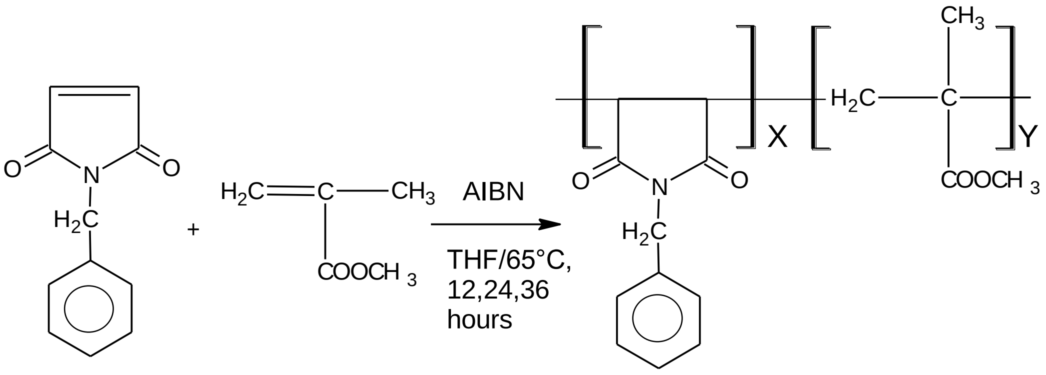
N-Benzylmaleimide (NBMI):-N-Benzylmaleamic acid was taken in DMF solvent and treated with conc. H_2SO_4 and P_2O_5.The solution kept for stirring three hours at 65ºC. Solution poured in cool water or ice water to obtain the white colour precipitated of NBMI.The precipitate was filtered and dried. NBMI was recrystallized from ethyl alcohol solvent. The yield was 70%, M.P. 99-100 ºC. The purity and structure of the monomer was determined by elemental analysis, IR, ^{1}H-NMR study. FT-IR: 3075(aromatic-H stretch), 1775, 1709(symmetric and asymmetric stretch of C=O in a five member imide ring), 1586, 1509, 1466 (C=C, aromatic), 1329, 1309(C-N stretch) and 952, 908 (CH=CH), ^{1}H-NMR (400MH$_Z$,TMS, DMSOd$_6$, δ, ppm): 7.15 (s, CH=CH), 5.6(CH$_2$), 7.52, 7.78 ppm(m) aromatic protons.



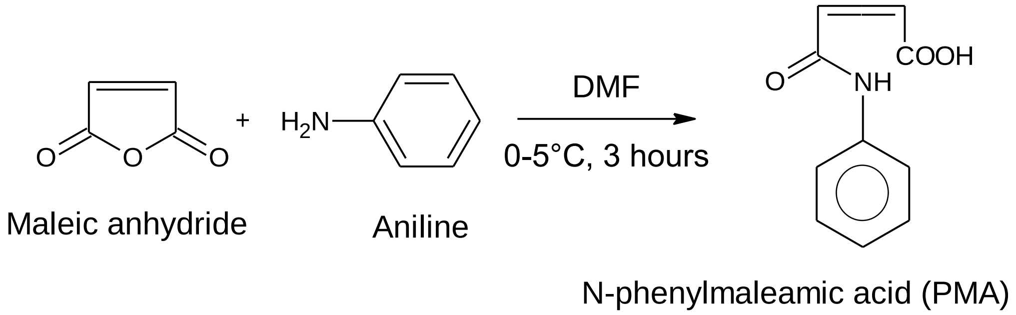
Synthesis of Homopolymer: - Synthesis of homopolymer of N-Benzylmaleimide was carried out in THF solvent using AIBN as a free radical initiator at 65°C. The reaction mixture was refluxed for 48 hours. The prepared polymer was isolated in excess quantity of methanol water mixture. The crude polymer was purified by dissolving in THF and reprecipitating from a methanol water mixture. The precipitated polymer PBM was washed with methanol several times and dried at 60°C under vacuum. The homopolymer was synthesized keeping on different time of polymerization and percentage yields are given in Table 1.

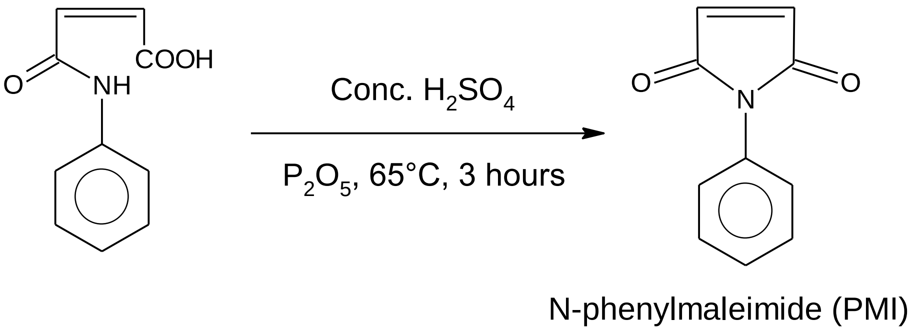


Synthesis of Copolymer:- In equimolar amount of NBMI and MMA, solvent THF were taken and free radical initiator AIBN was taken in round bottom flask fitted with reflux condenser at 65°C on 48 hours. The copolymer CBMM was isolated by methanol water mixture. The crude form of polymer was purified by dissolving in THF and reprecipitate from a methanol water mixture. The precipitated copolymer were washed with methanol several times and dried at 60°C under vacuum. The nine copolymer samples using different feed ratio of comonomers were synthesized and physical properties are described in Table 3. The copolymers were synthesized in different time and yields are given in Table 1. Reaction schemes is given below:



Synthesis of N-Phenyl Maleimide Monomer (PMI): N-Phenylmaleimide was synthesized from maleic anhydride and aniline in two steps.



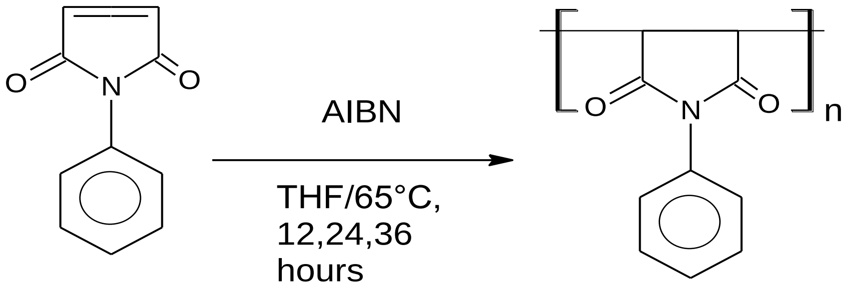


(i) **Preparation of N- Phenylmaleamic Acids:** Aniline (9.1 ml, 0.1 mol) and maleic anhydride (9.8 gm, 0.1 mol) were taken in 50 ml DMF solvent, in flat round bottom flask. The reaction mixture was cooled externally by ice water. Maleic anhydride reacted, exothermically with aniline. The reaction mixture kept stirring for three hours at room temperature. The solution was added to crushed ice or cooled water. The white solid N- Phenylmaleamic acid was filtered and dried. It was recrystallized from ethanol to obtained pure N- phenylmaleamic acid, yield 95%, m.p. = 202-203^{o}C.

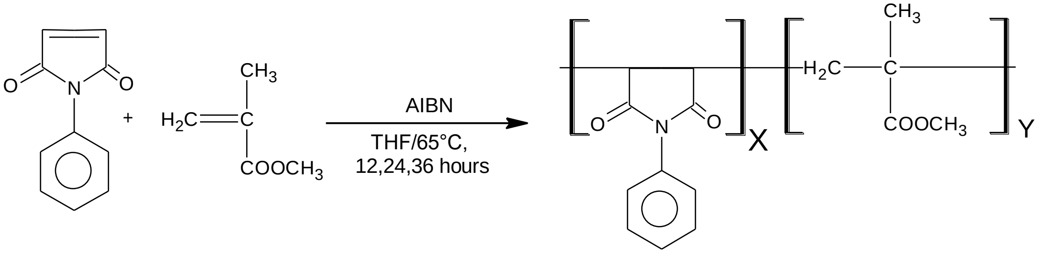
(ii) **Cyclization of N-phenylmaleamic Acid:** N-phenylmaleamic acid 19.1 gm (0.1 mol) and 50 ml DMF were taken in flat round bottom flask. A solution of 5.0 gm of P_2O_5, 10 ml DMF of 3 ml H_2SO_4 was added dropwise over a 30-minute period to above solution. The reaction mixture kept stirring for 3 hours at 65°C. The reaction mixture poured in crushed ice and yellow colour precipitate was obtained and filtered by the Buckner funnel. The product was washed with 10% sodium bicarbonate solution followed by cooled water and finally dried. Yellow needle shape crystals obtained by recrystallization from ethyl alcohol. Yield 80%, M.P. 98-99˚C. Synthesis monomer were characterized by FT-IR,H-NMR spectra, characteristic absorption frequencies 3094 (aromatic and alkene C-H stretch), 1708 and 1787 (symmetric and asymmetric stretch of C=O in a five-member imide ring 1575, 1507,1454 (C=C, aromatic) 1330, 1311 (C-N stretch),948,908 (CH=CH), 832 (monosubstituted benzene), and 696 (cis-CH=CH) as shown in figure are consistent with the structure of N-phenylmaleimide.^{1}H-NMR (Fig. 3.1B) 400 MHz, ref. TMS, solvent DMSO-d_6, δ, ppm) of NPMI shows two methine (CH=CH) protons at δ7.23 (S) ppm[6]. (b) multiplets aromatic protons at δ7.48-7.78 ppm .

Synthesis of Homopolymer and copolymer

Homopolymerization of N-Phenylmaleimide (HPMI): Homopolymerization of N-Phenylmaleimide was carried out in THF solvent using free fradical initiator AIBN, temperature 65°C. N-Phenylmaleimide (1.73 gm, 0.01 mol) and THF 30 ml were taken in flat 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. If the reaction was carried out up to 12 hours, very less polymer was formed. Yield was obtained 35.26% for 24 hours. The prepared polymer was isolated in excess quantity of methanol- water mixture. It was dried under vacuum at 55°C.



Copolymerization of N-Phenylmaleimide with Methylmethacrylate (CPMI): N-Phenylmaleimide (1.73 gm, 0.01 mol) and methyl methacrylate (1.06 ml, 0.01 mol) in 70 ml THF solvent were taken in flat 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 samples 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. The yield was 34.42%.



D. FT-IR SPECTRA FOR HOMOPOLYMERS

HPMI: The FT-IR spectra of HPMI is shown in Fig. 3.1C. The major characteristic absorption IR frequencies (in cm^{-1}) 2937–3058 (C–H stretch, alkene), 1778, 1709 (symmetric and asymmetric stretching of C=O in a five member imide ring)[19], 1538, 1600, 1668, 1442 (C=C stretch, aromatic), 1387 (Ar-N stretch), 1289, 1259, 1199 (asymmetric C-O-C stretch), 1098, 1026 (symmetric C-O-C stretch), 894 (monosubstituted benzene)[19], and 693 (out of plane aromatic ring, C=C bend)[19] are consisted with the structure of HPMI.

HPMI: In Fig. 3.1G, the chemical shift for HPMI is observed at 7.42–7.08 (m), the multiplet in the range at 7.42–7.08 ppm corresponds the five aromatic protons[21,22]. 2H in –CH–CH–group have appeared δ 3.40–4.02 ppm. The small peaks observed at δ 1.24–2.13 ppm are due to terminal methyl protons of AIBN moiety. ^{1}H–NMR of HPMI shows chemical shift δ at 7.23 (s) ppm characteristic of –CH=CH– group. The disappearance of this in polymer HPMI shows that the radical polymerizations proceed via an opening of the double bond (vinyl polymerization) [21,22,23].

HBMI

CPMI: The FT-IR spectra of NPMI copolymer are shown in Fig. 3.1D. The major characteristic absorption bands (in cm^{-1}) are observed at 2999-2889 (C-H stretch, CH_3, and CH_2 in MMA), 1780, 1715 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1596, 1500 (C=C stretch, aromatic), 1436 (C-H bend $–CH_2$), 1385–1354 (due to overlapping of C-N stretch and C-H bend of $–CH_3$ group), 752 cm^{-1} (out of plane C-H band of mono substituted benzene ring) and 648–621 (out of plane aromatic ring C=C bend). These characteristic bands confirm that units of both the monomers: PMI and MMA are present in the copolymer samples. The absence of characteristic band of vinyl group at 948 cm^{-1} indicates the polymer formation via vinyl group[5].

^{1}H–NMR SPECTRAL ANALYSIS FOR COPOLYMERS

CPMI: Fig. 3.1E shows the ^{1}H–NMR (spectra 400 MH_z, TMS, DMSO-d_6) of copolymer, CPMI shows the chemical shift δ for five aromatic protons is observed at 7.00–7.42 ppm. The δ observed at 3.4–3.68 ppm corresponds to over lapping of 2H–(CH–CH–) in the polymer main chain and 3H ($–OCH_3$) of MMA segment. For 3H ($–CH_3$) around 0.85–1.134 ppm and 2H of methylene group is appeared at 1.6-2.2 ppm.

III. RESULTS AND DISCUSSION

A. Effect of time on yield

The homopolymerization and copolymerization were carried out in THF solvent at varying time of polymerization. The effect of percentage yield with time is given in Table-1&2.tables reveals that the yield of polymers was increased with increasing time.

Table-1: Polymer code, yield, physical state and colour of homopolymers.

Polymer code	Time (hrs)	Yield %	State	Colour
PBM	12 24 36 48	19.17 25.64 27.48 39.45	Solid Solid Solid Solid	White White White White

Table-2: Polymer code, yield, physical state and colour of copolymers.

Polymer code	Time (hrs)	Yield%	State	Colour
CBMM	12 24 36 48	24.25 39.91 47.25 53.45	Solid Solid Solid Solid	White White White White

Table 3: Copolymers of BMI with MMA (time 12 hrs. initiator AIBN).

Polymer Code CBMM	Feed mol ratios NBMI:MMA	Yield %	State	Colour
CBMM 1	1:9	35.9	Viscous liquid	White
CBMM 2	2:8	34.4	Viscous liquid	White
CBMM 3	3:7	37.1	Solid powder	White
CBMM 4	4:6	38.6	Solid powder	White
CBMM 5	5:5	39.0	Solid powder	White
CBMM 6	6:4	40.0	Solid powder	White
CBMM 7	7:3	41.1	Solid powder	White
CBMM 8	8:2	42.0	Solid powder	White
CBMM 9	9:1	45.0	Solid Powder	White

B. Solubility behaviour

The solubility of investigated homo and copolymer samples is given in Table 4. The investigated homo and copolymaleimides show excellent solubility in THF, DMF, DMSO, $CHCl_3$, dichloromethane, acetone and cyclohexanone.

Table 4: Relative solubility of monomer, homopolymer and copolymer at 30°C.

Solvents	NBMI	CBMM	PBM
THF	S	S	S
DMF	S	S	S
DMSO	S	S	S
Dioxane	S	S	S
Acetone	S	S	S
Chloroform	S	S	S
Ethyl acetate	S	S	S
Benzene	S	S	IS
Toluene	S	PS	IS
CCl_4	PS	IS	IS
CH_2Cl_2	PS	S	S
Ethanol	S	S	S
Methanol	S	S	IS
N-Hexane	IS	PS	IS
Cyclohexanone	PS	PS	IS
Xylene	S	PS	IS
1-Butanol	IS	IS	PS
2-Butanol	IS	IS	PS

C. Physical properties

Some of the physical properties of polymers were investigated. Intrinsic viscosity[η] of polymers is measure of hydrodynamic volume and depends on the molecular weight as well as on the size of the polymer coil in a given solution. The values of intrinsic viscosity [η] were carried out in DMF solution at 30°C, using an Ubbelohde viscometer. The value of intrinsic viscosity of homopolymer and copolymer are summarized in table 5. Table reveals that the viscosities of homopolymer are less than as comparative copolymer. The molecular weight of homo and copolymers were determined by GPC and weight average molecular weight is given in Table 5. The chromatogram of polymers is given below and indicates that molecular weight of homopolymer is less than that of copolymer.

Table 5: The physical properties of Homopolymer and copolymers

Polymer code	Solvent	Temp.	[η]	Mw
HBMI	DMF	30°C	0.031	5675
CBMI	DMF	30°C	0.062	25581

D. Spectral characterizations

The FT-IR spectrum and ^{1}H-NMR spectrum (300MHz in DMSO- d_6) of PBM are shown in Figure 1 and 2. The absence of a sharp band at 952cm^{-1} and chemical shift δ at 7.15 ppm due to CH=CH in a monomer having a vinyl group, such as monomer NBMI, indicates the formation of polymer via vinyl group polymerization[13, 14]

The presence of absorption bands at 1784 and 1714 cm^{-1} due to symmetric and asymmetric stretching of C=O in the five member imide ring indicates that the imide ring remained intact in the polymerization. The imide group is also confirmed from the bands observed at 1466(Ar- N stretch), 1372(C-N stretch), 1195 (C-N-C) and 772 cm^{-1}.

The FT-IR spectrum and ^{1}H-NMR spectrum (300MHz in DMSO- d_6) of PBM are shown in Figure 3 and 4. The δ observed at 7.15 ppm due to CH=CH in the monomer has shifted to 3.4-4.1 ppm in the polymer, as a result of the formation of a semi flexible poly (substituted methine) -[CH-CH]$_n$- group[15]. The broad peak at 7.0 –8.1 ppm corresponds to 5 Ar-H.

The major characteristic absorption bands are observed at 1779, 1714 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1597, 1512 (aromatic) and 1191 (C-O-C of ester). These characteristic bands confirm that units of both the monomers NBMI and MMA are present in the copolymer samples. The ^{1}H NMR spectra of the copolymer showed the following chemical shifts. The δ at 7.1-7.84 ppm of aromatic hydrogen.. The δ observed at 4.87 ppm is 2H in –CH_2 of benzyl segment. The δ observed at 3.4-3.9 ppm corresponds to overlapping of 2H -(CH-CH)- in the polymer main chain and 3H ($-OCH_3$) of MMA segment. The δ in the range 0.84-2.4 ppm is of 2H of methylene group and 3H of $-CH_3$.

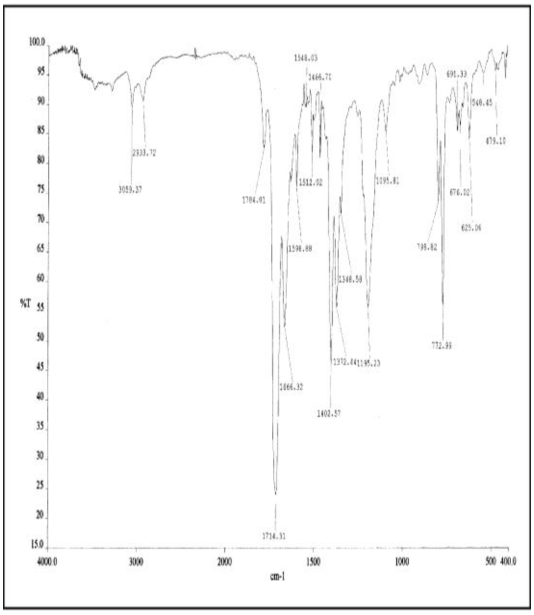


Figure 1: FT-IR Spectra of PBM.

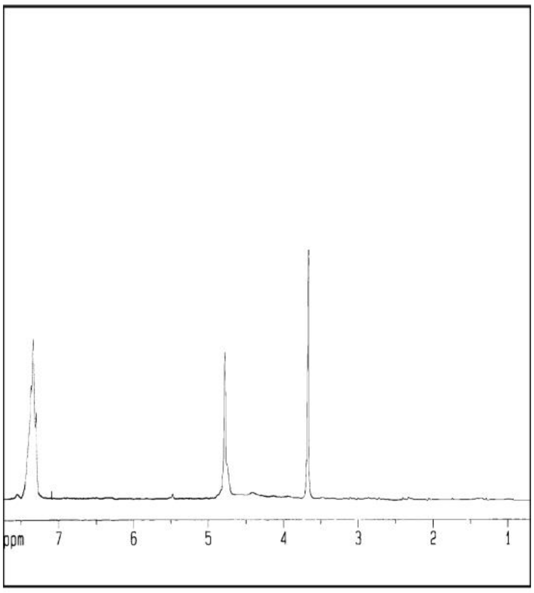


Figure 2: 1H-NMR Spectra of PBM.

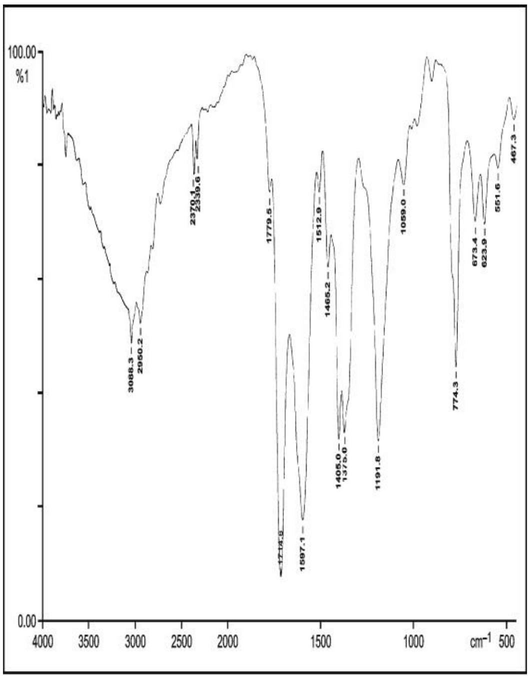


Figure 3: FT-IR Spectra of CBMM

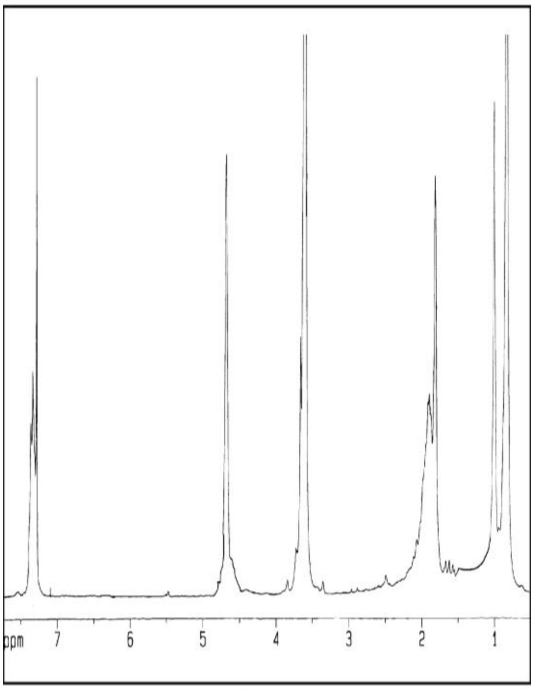


Figure 4: 1H-NMR Spectra of CBMM

E. Thermal properties

The thermal behaviour of the synthesized homopolymer and copolymers were investigated by TGA. The TGA curve of PBM and CBMM are shown in Figure 5 and 6. The initial decomposition temperature, temperature for maximum weight loss and final decomposition temperature of homopolymer and copolymers are summarized in Table 6. The results of percentage weight loss suffered from 100°C-600°C at 100 intervals are furnished in Table7.

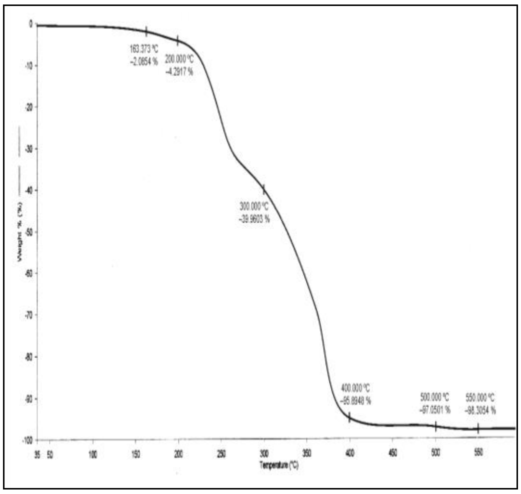


Figure 5 TGA Curve of PBM

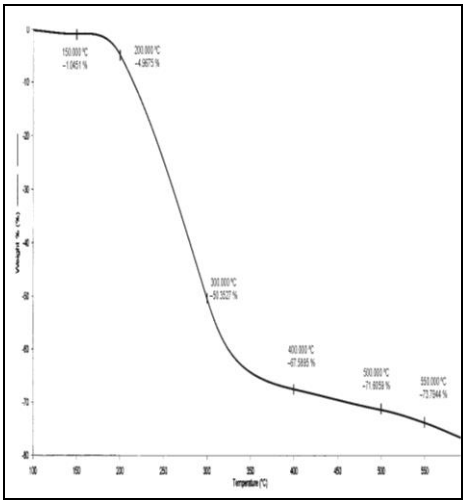


Figure 6: TGA Curve of CBMM

Table 6: Thermal behaviour of homopolymaleimides and copolymaleimides

Polymer code	Ti	Tmax	Tf	Residue at, 550°C
PBM	200	400	550	26.21
CBMM	190	300	550	3.70

The TGA results indicate that the homopolymaleimides are more stable as compare to copolymaleimides. This is because in homopolymers, only single maleimides unit involved while in copolymers both units are involved in backbone. The TGA results showed that the decomposition temperature increased with the increasing the content of substituted N-benzylmaleimide.

Table 7: Percentage weight loss of homo and copolymer at various temperatures from the TGA.

Polymer code	200	300	400	500	550
PBM	4.29	39.96	95.89	96.05	96.30
CBMM	4.96	50.35	67.59	71.60	73.79

IV. CONCLUSION

Synthesis, through free radically, homo polymer of NBMI and copolymer of NBMI with MMA has been investigated. The investigated homo and copolymaleimides show excellent solubility in THF, DMF, DMSO, $CHCl_3$, dichloromethane, acetone and Cyclohexanone. The characterization of homo and copolymer were carried out through intrinsic viscosity, molecular weight distribution, elemental analysis, FT-IR and ^{1}H-NMR spectral analysis. Homopolymer shows excellent thermal stability then copolymer but other properties are improved in copolymerization.

V. ACKNOWLEDGEMENT

We are thankful to CDRI Luck now and SICART Vallabh-Vidhyanagar for analysis work. Authors Shiv Narayan Paliwal and Suresh Meena is thankful to UGC(RGNSF), New Delhi for financial assistance.

VI. REFERENCES

[1] Mittal KL, Ed. Polyimides: Synthesis, Characterization and Applications, Chs.1and 8, vols.1&2, Plenum New York, 1984.
[2] Feger CJ, Khojasteh MM, McGrath JE, Eds. Polyimides: Materials, Chemistry characterization, Elsevier Science B.V., Chapter 1, Amsterdam, 1989.
[3] Lipinski JH, Moore RS, Eds., Polymeric Materials for Electronic Packaging and Interconnection; ACS Symposium Series 407; Am.Chem. Soc; Ch.5 Washington, DC. 1989.
[4] Kim YJ, Glass TE, Lyle GD, McGrath JE, Kinetic and mechanistic investigations of the formation of polyimides under homogenous conditions, Macromolecules, 26, 1344-1358, 1993.
[5] Cubbon RCP, The free radical and anionic polymerization of some N-Substituted maleimides, Polymer, 6, 419-426, 1965.
[6] Sadhir RK, Smith JDB, Laser Initiated Copolymerization of N-vinyl pyrilidone with Maleic anhydride and MMA, Journal of Polymer Science: Polymer Chemisty Ed. 30, 589-595, 1992.
[7] Xulin J, Ping X, Wanli L, Deyue Y, Atom transfer radical copolymerization of styrene and N- Cyclohexyl maleimide, J Polymer Sci Part A : Polym. Chem, 38, 1203-1209, 2000.
[8] Miller CW, Johnson ES, Hoyle CE, Vishvanathan K, Valente EJ, Evaluation of N-aromatic maleimide as free radical photo initiators: A photo physical and photo polymerization characterization, J Phys Chem B, 105, 2707-2717, 2001.
[9] Kim JY, Kim TH, Synthesis of N-(Phenyl) maleimide- based photopolymer and its application to photo- aligning of LC molecules, Polymer, 53, 83-89, 2002.
[10] JengRJ, Changa CC, Chena CP, Chenb CT, Changa WC, Thermally stable crosslinked NLO materials based on maleimides, Polymer, 44,143-155, 2003.
[11] Burget D, Mallein C, fouassier JP, Visible light induced polymerization of maleimide –vinyl and maleimide -allyl ether based systems, Polymer, 44,7671-7678, 2008.
[12] Riddick JA, Bunger WB, Sakano TK, Organic Solvents Physical Properties And Methods of Purification, Wiley interscience, New York, 1986.
[13] Oswal SL, Rao AV, Viscosities and molecular interaction in binary mixtures of tryethyl, trypropyl, and trybutylamine in cyclohexene and benzene, Ind J Chem Soci A, 24,1024-1028, 1985.
[14] Nair CPR, Copolymerization of 4-maleimidobenzoicacid with alkyl acrylates. Kinetic penultimate unit effect and copolymer characteristics, Macromolecules, 26, 47-57, 1993.
[15] Doi T, Akimoto A, Oki Y, and Otsu T, Alternating copolymerization of N-(alkyl-substituted phenyl) maleimides with isobutene and thermal properties of resulting copolymers, J Polym SciPart A: Polymer Chem, 34, 2499-2505, 1996.