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Free Radical Copolymer Synthesis, Characterization and Antibacterial properties of 4-Cl (phenyl) maleimide with EA

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ABSTRACT

Free radical copolymerization of 4-Cl (phenyl) maleimide (N-PCPMI) with ethyl acrylate (EA) was performed at 70°C using THF as a solvent and BPO as a free radical initiator. Copolymer is characterized by nitrogen percentage intrinsic viscosity, solubility test, FT-IR, ^1H NMR spectral analysis. Variations based on solvent, free radical initiator, time was also studied. The intrinsic viscosity of C-PCPMI II in DMF solution was 0.170 dL/g. Thermogravimetric analysis (TGA) characterizes the thermal stability of the copolymer. The initial decomposition temperature of C-PCPMI II was 270 ^oC. The gel permeation chromatography (GPC) determines the molecular weight and polydispersity index (PDI) as 8050 and 1.5191. The antimicrobial activities of monomer and the copolymer were also investigated against various microorganisms.

Keywords: Free radical copolymerization, spectral analysis, thermal stability, GPC, antimicrobial activity.

INTRODUCTION

Free radical polymerization is used for the preparation of thermally stable polymers. Aromatic polyimides polymers possessing imide group chain are considered to have thermo-oxidative stabilities [1-2], heat and chemical resistant properties. Such, polymers have high thermal degradation temperature [3]. Aromatic polyimides polymers are considered to have high thermo-oxidative stabilities, chemical resistance and good electrical properties. And, widely used for wide range of applications [4-5]. Thus, various disadvantages, like insolubility, infusibility due to condensation type polyimides can easily be overcome by addition type polyimides [6]. Such polymers have high thermal degradation temperature and are polymerized free radically to provide good structural stiffness [7-10].

Our study on copolymerization of 4-Cl (phenyl) maleimide with Ethylacrylate (EA) could give satisfying results, explaining its thermal stability. TGA and GPC techniques were carried out to

study the thermal stability behaviour and molecular weight determination of prepared copolymers.

The presence of chlorine has been suggested to give an antimicrobial activity to the copolymers. The polymers showing such properties are suitably applicable to films, packaging materials, foodstuffs, sanitary applications and many others [11-13]. Such copolymers have been used to screen their antimicrobial activity against microorganisms such as bacteria (*Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*) and fungi (*Aspergillus niger*, *Alternaria solani*).

MATERIAL AND METHODS

Materials

4-Chloro (phenyl) maleimide (SRL, Mumbai) was used as received. Maleic anhydride (SRL, Mumbai) recrystallized from acetone. Methylmethacrylate (MMA) and Ethylacrylate (EA) (SRL, Mumbai) were stirred for 10 minutes at 30 ± 0.1 °C with 5% NaOH to eliminate hydroquinone inhibitor [18]. It was then dried over anhydrous calcium chloride for 8 hours. The head and tail fractions were discarded before using the acrylate monomers. Benzoyl peroxide (BPO) (CDH, Mumbai) was used as received. 2, 2-azobis-isobutyronitrile (AIBN) (spetrochemical, Mumbai) was recrystallized twice from methanol before use. Phosphorus pentoxide and concentrated H_2SO_4 (SRL, Mumbai) were used as received. N, N-Dimethylformamide (DMF), Tetrahydrofuran (THF), Dimethyl sulfoxide (DMSO), Acetone, 1, 4-dioxane used were of analytical grade and used as received.

Measurements

^{1}H NMR spectra of monomer and copolymer samples were recorded on a Bruker DPX-300 spectrometer at 300 MHz with $CDCl_3$ as a solvent. The internal reference used was TMS. FT-IR-spectra of monomer and copolymer samples were recorded on Perkin-Elmer model RXI (4000-450 cm^{-1}) FT-IR spectrophotometer by using KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.1 °C, using on Ubbelohde suspended level viscometer. Elemental analysis was made on Carlo-Erba Model NA 500 series analyzer. The number average molecular weight and polydispersity index of the copolymer was obtained using a water gel permeation chromatography (GPC) with 13082008 mix bead THF (30 to 1000 sec). Thermograms were obtained on a Mettler TA-3000 system at the scanning rate of 20°/min from 50 ^{o}C to 900 ^{o}C in air.

Methods

Preparation of 4-Chloro (phenyl) maleimide monomer (N-PCPMI) (described below and shown in scheme-1)

4-Chloro (phenyl) maleimide was prepared in two steps from maleic anhydride and P-Chloroaniline.

Step 1: Synthesis of 4-Chloro (phenyl) maleiamic acid (N-PCPMA)

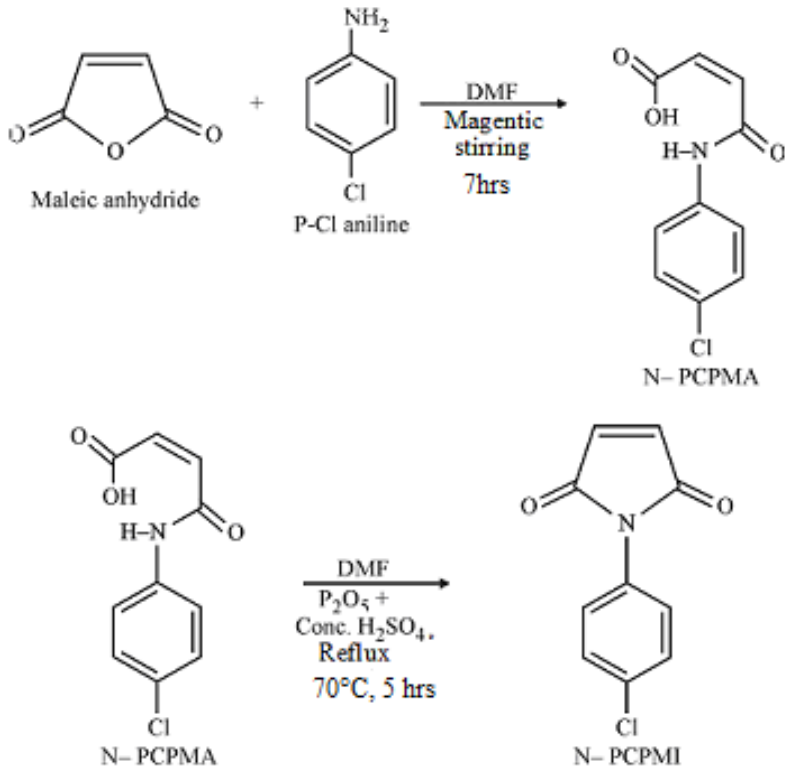
For 0.1 mol, 12.7 g of 4-Chloroaniline was dissolved in 40 mL DMF in a flat bottom flask. This solution was added in a well-stirred solution of 9.8 g of maleic anhydride (0.1 moles) in 40 mL DMF in flat bottom flask. It was then stirred for 7 hours at room temperature. The reaction mixture was poured into a beaker containing crushed ice-cooled water. The solid white mass obtained is filtered and dried (yield 85%, M.P. 155 ^{o}C).

Step 2: Synthesis of 4-Chloro (phenyl) maleimide (N-PCPMI)

The N-PCPMI obtained was taken in a flat bottom flask containing 80 mL DMF solution. To this, added 6 g P_2O_5 following 1to 2 drops of concentrated H_2SO_4 into it. After this, the solution was stirred at 65-70 ^oC for 5 hours. The mixture was then poured into a crushed ice water to precipitate out the crude N-PCPMI. It was filtered and washed with sodium bi-carbonate solution to remove any unreacted N-PCPMA residue. The remaining residue left behind was of crude N-PCPAMI, which was filtered and dried in vacuum for 8 to 9 hours. On drying, it was recrystallized twice with 95% ethanol.

Yellow crystals of N-PCPMI were obtained. It has a yield of 75% and melting point 104 ^oC. The purity of the obtained monomer was checked by FT-IR and ^1H NMR and elemental analysis.

Diagrammatic representation of the synthesis process of 4-Chloro (phenyl) maleimide (N-PCPMI) given in scheme 1.



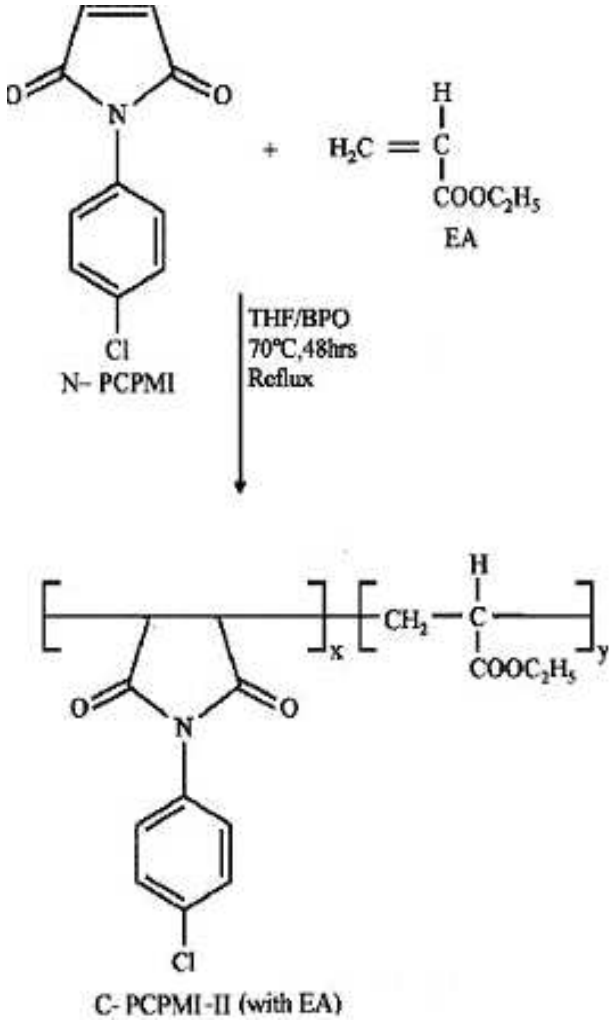
Scheme 1

Copolymerization of 4-Chloro (phenyl) maleimide

Polymerization (described below and shown in Scheme 2)

For 0.5 mol fraction, 2.07 g of N-PCPMI with 1.00 mL of Ethylacrylate (EA) was mixed well in 80 mL THF solvent in a round bottom flask 0.002 g of BPO was added to the reaction mixture as a free radical initiator. It was then refluxed in a long spiral condenser at 70 °C for 48 hours. The copolymer product obtained was in dissolved state in THF. This copolymer product was precipitated in 5% methanol water mixture twice. It was then washed with methanol 2-3 times for purification. It was dried at 60 ^oC under vacuum. The precipitate was brown in color for copolymer obtained with EA, C-PCPMI-II.

Detail summary of copolymerization of N-PCPMI with EA is given in scheme 2 as follows:



Scheme 2

The detail comparative data of copolymerization of N-PCPMI with EA are presented in Table 1.

Table 1: Free radical copolymerization of N-PCPMI with EA in THF at 70°C using BPO

Polymer	Feed mol fraction of N-	Time	Yield	N	η	Color/ State
C-PCPM-II	0.5	48	63.2%	6.93	0.170	Brown(Solid)

RESULTS AND DISCUSSION

Solvent-initiator system

Solvent variation of copolymer C-PCPMI-II using different free radical initiator was done free radically. Such variation helps in obtaining the relatively high yield of copolymer.

The details in Table 2 explained the effects of solvent and initiator on yield of the copolymer of 4-Chloro (phenyl) aleimide. The percentage yield of THF/AIBN system and DMF/BPO system gave comparable results for C-PCPMI-II polymer. DMF/AIBN system gave 65.8% for C-PCPMI-II yield and 61.3% yield for C-PCPMI-II. DMSO/BPO system gave the poorest yield of 59.5% for C-PCPMI-II copolymer. There is 60.1% yield for Acetone/BPO system for C-PCPMI-II. Thus, we can conclude THF/AIBN, THF/BPO and DMF/AIBN gave comparatively better

percentage yield for C-PCPMI-II copolymers. 1, 4 -dioxane/BPO system gave good percentage yield for C-PCPMI-II copolymer.

Table 2: Variation in percentage yield of C-PCPMI-II in different solvent initiator system after 48 hrs

Solvent/Time(hrs)	AIBN (% yield)	BPO (% yield)
	C-PCPMI-II	C-PCPMI-II
THF/48 hrs	64.2%	63.2%
DMF/48 hrs	65.18%	64.3%
Acetone/48 hrs	64.17%	60.1%
DMSO/48 hrs	63.12%	59.5%
1, 4 dioxane/48 hrs	62.3%	61.3%

Effect of time on polymer yield

The effects of time on percentage yield of C-PCPMI-II are summarized in Table 3. It reveals that N-PCPMI gave better yield of copolymerization after 48 hrs in DMF solvent. It is also observed that after 72 hrs the yield of copolymerization decreases.

Table 3: Free radical copolymerization of N-PCPMI with EA at different time

Time (hrs)	(DMF)/ AIBN (% yield)	(DMF)/BPO (% yield)
	C-PCPMI-II	C-PCPMI-II
12	43.5%	45.6%
24	62.3%	61.2%
36	62.5%	63.1%
48	65.18%	64.3%
72	47.3%	44.3%

Solubility

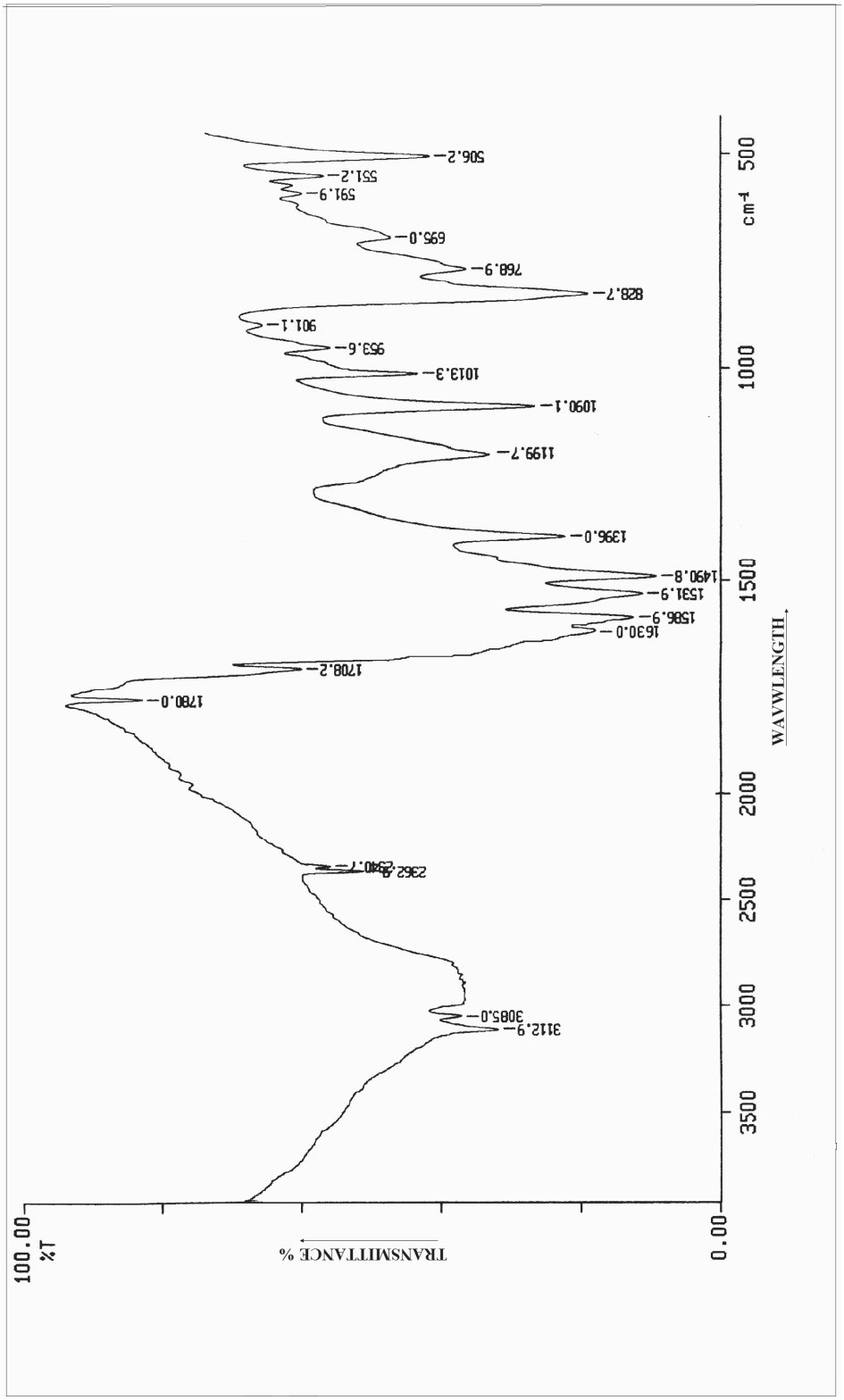
The solubility of monomer, synthesized copolymers samples were determined in polar and non polar solvents and have been summarized in Table 4.

Table 4: Solubility behaviour of monomer N-PCPMI, copolymer C-PCPMI-II in polar and non-polar solvents at 30 ± 0.1 ^{o}C

Solvent	N-PCPMI	C-PCPMI-II
Ethyl alcohol	PS	S
Methanol	S	S
Acetone	S	S
DMF	S	S
THF	S	S
DMSO	S	S
Water	IS	IS
Ethylacetate	IS	S
Benzene	S	PS
Xylene	IS	S
Cyclohexane	IS	PS
CCl_4	IS	S
1, 4 -dioxane	S	S
Toluene	IS	IS
Propan-ol	IS	S

S = Soluble, PS = Partially soluble, IS = Insoluble

Figure 1: IR Spectra of N-PCPMI



Intrinsic Viscosity

Intrinsic viscosity (η) is a measure of hydrodynamic volume and depends on molecular weight of the copolymer as well as on the size of the polymer coil in the solution. The average value of C-PCPMI-II in DMF solution at 30 ± 0.1 ^{o}C (Table 1) is 0.170 dL/g for C-PCPMI-II respectively.

Spectral characteristics

In this study, FT-IR and ^{1}H NMR spectroscopy is used to characterize the copolymer.

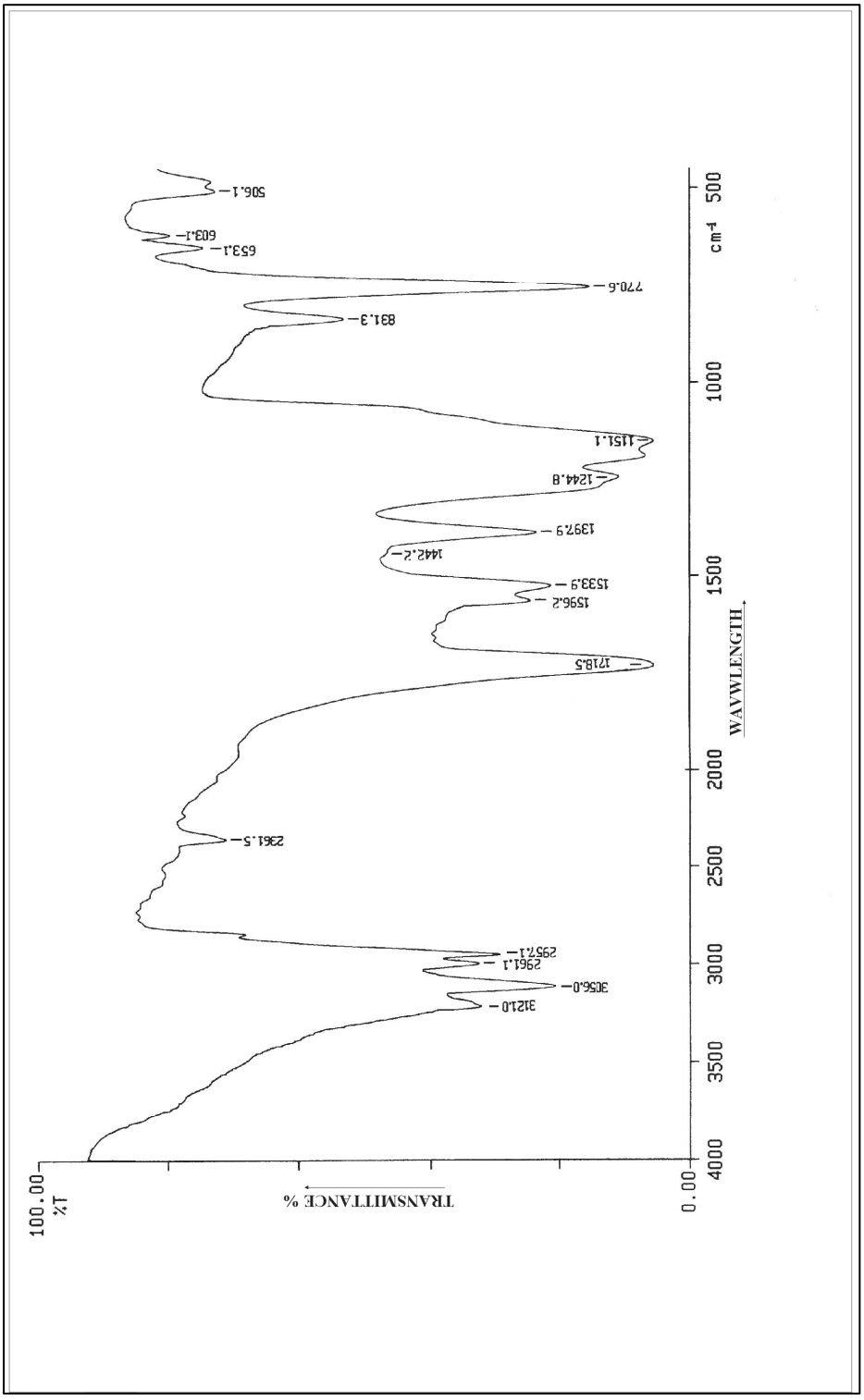


Figure 2: IR Spectra of C-PCPMI-II

In FT-IR spectrum of C-PCPMI-II in Figure 2, the major characteristics absorption bands are observed are at 3056 cm^{-1} (aromatic C-H stretching), 3121.0 cm^{-1} for alkene C-H stretch, 1718.5 cm^{-1} (C=O stretch in a five membered imide ring), 1596.2 and 1533.9 cm^{-1} for aromatic C=C stretch. The imide group is also confirmed by 1397.9 cm^{-1} (Ar C-N stretching), 1165.3 cm^{-1} (C-

N-C). The bands at 2961.1and 2957.1 cm^{-1} are of C-H stretch in CH_2CH_3 in EA showing that both the monomer units are present in copolymer sample. Compared with IR spectra of monomer N-PCPMI [Figure 1], The absence of 953 cm^{-1} band and also, the presence of 603.1 cm^{-1} band confirm copolymer, C-PCPMI-II formation.

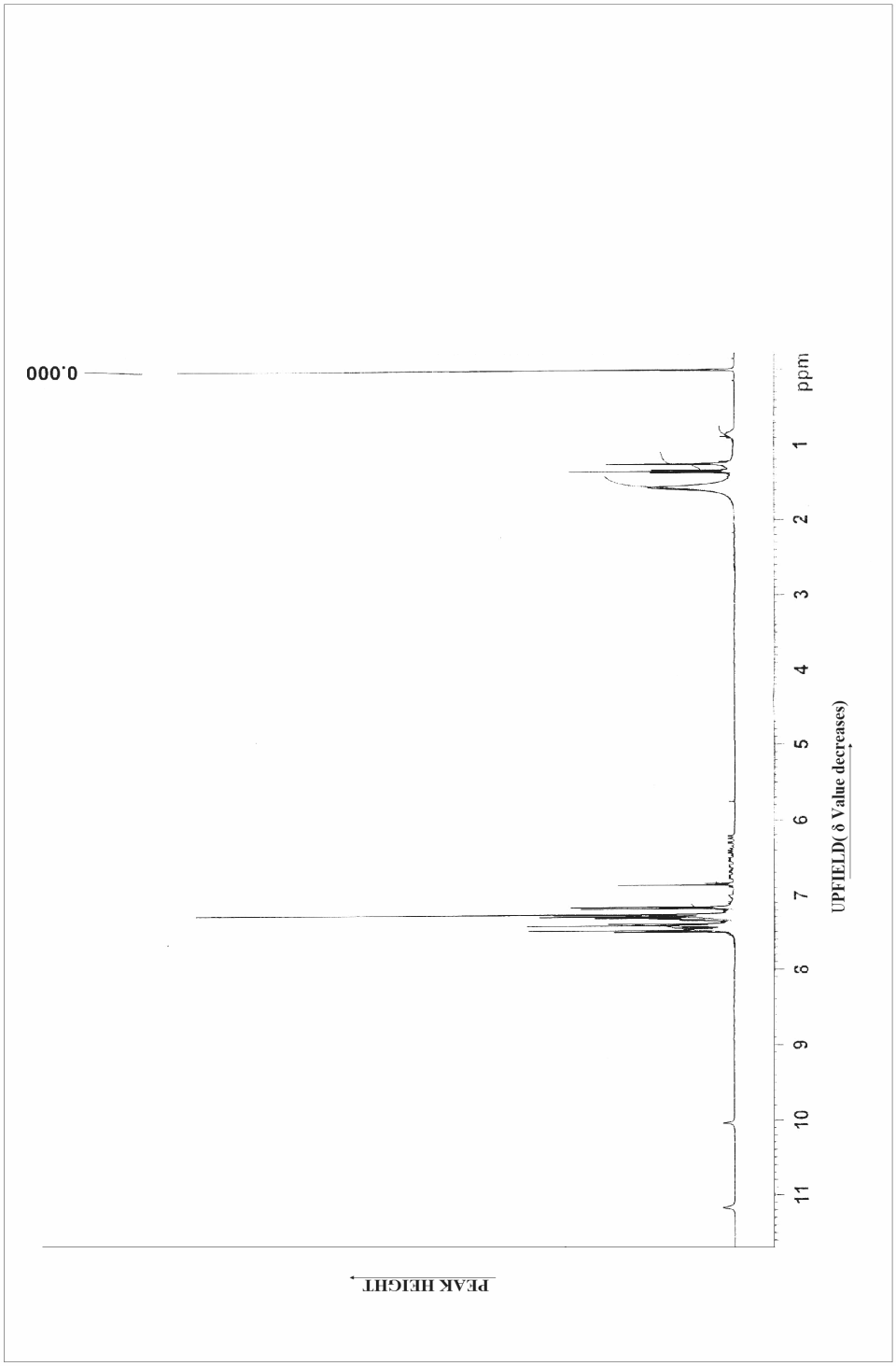


Figure 3: ^{1}H – NMR Spectra of N-PCPMI

The ^{1}H-NMR spectra of C-PCPMI-II in Figure 4 showed the following chemical shifts. The peak at δ 7.08-8.08 ppm is of 4H aromatic proton in phenyl ring. The peak at δ 3.66 ppm appeared for 2H –(CH-CH)- in the polymer main chain. The presence of peak at δ 1.6-1.85 ppm for 3 H (-

CH_2CH_3) of EA segment and 2H of CH_2 segment at δ 2.5-3.0 ppm, and also the absence of peak at δ 6.88 ppm for vinyl proton of N-PCPMI (monomer) Figure 3 and δ 5.0-6.0 ppm for EA indicate that free radical polymerization has occurred via the opening of the double bond.

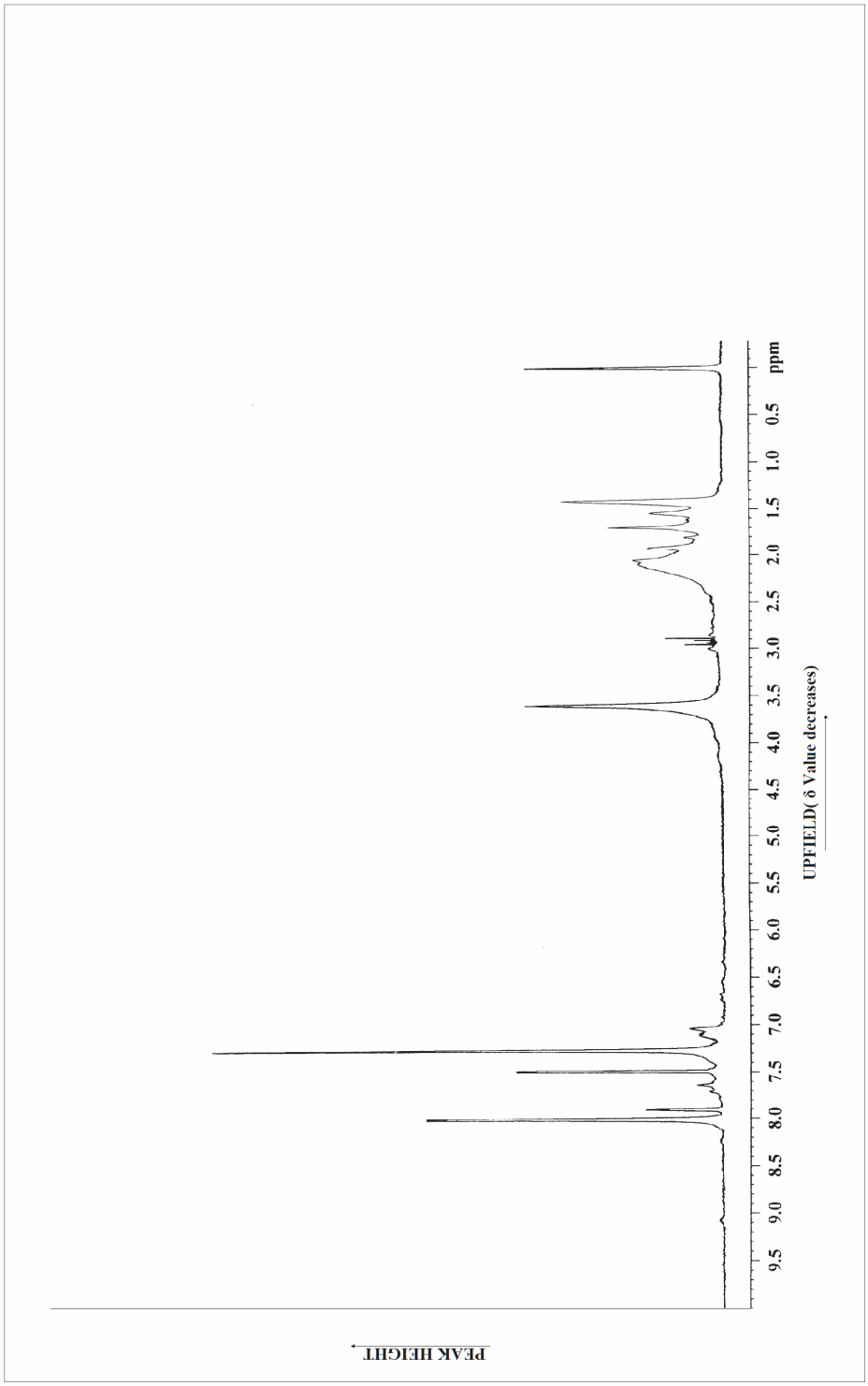


Figure 4: ^{1}H NMR Spectra of C-PCPMI-II

Thermalgravimetric Analysis

The copolymer C-PCPMI-II [Figure 5] show two-step degradation shows step-by-step degradation. TGA was carried out in air at heating rate of 20°C/min. The temperature for initial

decomposition T_i, final decomposition T_f and maximum rate of weight loss T_{max} determined from TGA are summarized in table 5 for both copolymers of 4-Chloro (phenyl) maleimide with EA.

Percentage weight loss of the copolymer C-PCPMI-II from 100^oC to 500 ^oC is shown in table 5. The initial T_i value for C-PCPMI-II is 270 ^oC for first step shows 8% percentage weight loss and second step initial T_i value is 600 ^oC shows upto 60% weight loss. Hence, from the data in table 6 it is concluded that C-PCPMI-II is thermally stable.

Table 5: TGA characterization of C-PCPMI-II

Polymer	T_i	T_{max}	T_f	Residue at 500°C
C-PCPMI-II	270	320	470	30.4%

Table 6: Percentage Weight loss of copolymer C-PCPMI-II at various temperatures from the TGA

Polymer	100°C	200°C	300°C	400°C	500°C
CPCPMI-II	0.66	5.72	26.31	64.66	69.58

Gel permeation chromatography

Molecular weight usually decreases while the polydispersity index increases with increasing the maleimide content indicating higher rate of transfer to the maleimide monomer. GPC traces show that the copolymer contains no impurities. Summary of number average molecular weight, weight average, polydispersity index, start molecular weight, end molecular weight are as follows in Table 7. Since, polydispersity index is greater than 1.5, the process is free radical polymerization. Starting molecular weight of C-PCPMI-II [Figure 6] is 8050.

Table 7: Gel permeation chromatography characterization of N-PCPMI-I and C-PCPMI-II

Polymer	Number average	Weight average	Polydispersity	Start	End
C- PCPMI-II	783.4	1190.1	1.5191	8050	340.3

Antimicrobial Activity

Antimicrobial activity of monomer N-PCPMI and copolymer of N-PCPMI with EA against bacteria and fungi was carried out. It has been observed that the presence of chlorine in N-PCPMI and C-PCPMI II shows antimicrobial activity. The antimicrobial activity of monomer and copolymer against bacteria and fungi are shown in following table 8, 9, 10, 11. N-PCPMI and C-PCPMI II screens their antimicrobial activity against bacteria (***Escherichia coli, Bacillus subtilis,*** and ***staphylococcus aureus***), fungi **(*Aspergillus niger, Alternaria solani*)**.

Table8: Antibacterial activity of N-PCPMI, C-PCPMI 1, C-PCPMI II against bacteria *Escherichia coli*

Code	Concentration (µg/ml) of compound taken					Result
	50	100	250	500	1000	
	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	
N-PCPMI	18 mm	20.3 mm	24 mm	30 mm	36 mm	+
C-PCPMI II	7.3 mm	8.1 mm	9.3 mm	11.3 mm	12 mm	+

Key : Value exclude cup borer diameter (6.00 mm) and are mean of three replicates
Ni : No Inhibition
+ : Showing activity

Table 9: Antibacterial activity of N-PCPMI, C-PCPMI II against bacteria *B. subtilis*

Code	Concentration (µg/ml) of compound taken					Result
	50	100	250	500	1000	
	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	
N-PCPMI	20.1 mm	22.3 mm	24.1 mm	28.3 mm	30 mm	+
C-PCPMI II	8.4 mm	9.7 mm	10.9 mm	12.1 mm	14 mm	+

Table 10: Antibacterial activity of N-PCPMI and C-PCPMI II against bacteria *S. aureus*

Code	Concentration (µg/ml) of compound taken					Result
	50	100	250	500	1000	
	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	Zone of inhibition	
N-PCPMI	17.6 mm	19.5 mm	20.3 mm	22.1 mm	24 mm	+
C-PCPMI II	9.1 mm	10.1 mm	11.2 mm	14.6 mm	16 mm	+

The antifungal activity of N-PCPMI and C-PCPMI II was also carried out. It is concluded that the monomer N-PCPMI has shown 76% inhibition against. *Alternaria solani* and 100% inhibition against *Aspergillus niger*. While the copolymer C-PCPMI II has shown 100% inhibition against against both the fungi (*Alternaria solani, Aspergillus niger*) at 1000 µg/mL concentration of the compound taken. Shown in table 11.Thus we conclude that the monomer N-PCPMI and copolymer C-PCPMI II shows good antimicrobial activity than its monomer.

Table 11: Percentage growth of fungi at 1000 µg/ml concentration of N-PCPMI and C-PCPMI II

Codes	**Percentage growth of fungi at 1000 µg/mg concentration of compound**			
	Alternaria solani	**Result**	***Aspergillus niger***	**Result**
Control	100%	-	100%	-
N-PCPMI	Nil	+	Nil	+
C-PCPMI II	Nil	+	Nil	+

Nil : No growth of fungi
+ : Showing activity

CONCLUSION

Free radical polymerization process was used for the synthesis of copolymers of N-PCPMI with EA. The polymer found to be soluble in THF, DMF, Acetone, DMSO, 1, 4 dioxane etc. The DMF/AIBN and THF/BPO system give comparatively better yield for the copolymerization of N-PCPMI monomer.

T_i of C-PCPMI-II is 270 ^oC thus, it is concluded that the copolymer C-PCPMI-II is thermally stable. Thermal degradation occurred in two steps. GPC report gives molecular weight of C-PCPMI-II copolymer. Molecular weight of C-PCPMI-II is 9510. Chlorine content is important to impart antimicrobial activity in the copolymers. It is concluded that copolymer of 4-Cl (phenyl) maleimide is very effective antimicrobial agent. C-PCPMI II shows the best antibacterial acitiviy against *S. aureus* and the best anti fungal activiy against *Alternaria solani* and *Aspergillus niger* and N-PCPMI shows the best antibacterial acitiviy against in both *Escherichia coli* and *Aspergillus niger*.

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REFERENCES

[1] C.B. Patel, N.I. Malek, S.L. Oswal, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry***, 2006**, 43, 289.
[2] R. Vukovic, D. Fles, A. Erceg, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry: Pure and Applied Chemistry*, **1997**, 34(9), 1619 -1628.
[3] M.Z. Elsabee, M.W. Sabaa, H.F. Naguib, K. Furuhata, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **1987**, 24(10), 1207 - 1221.
[4] S.L. Oswal, N.S. Sarkar, V.K. Bhandari, H.B. Oza, C.B. Patel, *Iranian Polymer Journal*, **2004**, 13(4), 297-305.
[5] C.E. Scroog, Polyimides, *Journal of Polymer Sci*ence (Macromol Rev.), **1976**, 2 (1), 161-208.
[6] B.L. Hiran, S.N. Paliwal, *Malaysian Polymer Journal (MPJ*), **2008**, 3(2), 1-12.
[7] B.L. Hiran, J. Chaudhary, S.N. Paliwal, S. Meena, P.R. Chaudhary, *E-Journal of Chemistry* , **2007**, 4(2), 222.
[8] Z. Lin, L. Shi, J. Hung, *J. Macromol. Sci., Pure and Applied Chem.*, **2000**, A 37, 219-238.
[9] I .E. Schalti, D.A. Baskan Y. Ygci, *Polymer Bulletin*, **2000**, 44, 261-268.
[10] C. Samyna, W. Ballet, T. Verbiest, B.M. Van, A. Persons, *Polymer*, **2001**, 42, 8511-8516.
[11] Aneja K R, Experimental Microbiological Plant, Pathology and Tissue Culture, Wishwa Prakashan, **1993**.
[12] Prakashan M and Arora C K, Pathological Techniques, Anmol Publications Pvt. Ltd., **1998**, 1st Ed.
[13] Patel, Patel M.G. Patel K.H. and Patel R.M. *Express polymer letters* vol., 2 No., 10, **2008**, 727-734.