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Synthesis and free radical homopolymerization of 2-chloro-4-nitro (phenyl) maleimide and thermal study

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ABSTRACT

Free radical homopolymerization of 2, -chloro 4 –nitro (phenyl) maleimide (N-CNPMI) was performed at 70 ^{o}C using Dimethylformamide (DMF) as a solvent and Benzoyl peroxide (BPO) as a free radical initiator to obtain homopolymer (H- DCPNPMI). The effect of different free radical initiators, solvents and time has been investigated. H-CNPMI is characterized by nitrogen percentage, FT-IR and ^{1}H NMR analysis. Thermogravimetric analysis (TGA) characterizes the thermal stability of H-CNPMI. The initial decomposition temperature of H-CNPMI was 180 ^{o}C. The gel permeation chromatography (GPC) determines the molecular weight (1198) and polydispersity index (PDI) 1.181 for H-CNPMI.

Keywords: Free radical homopolymerization, spectral, thermal stability, GPC.

INTRODUCTION

Free radical polymerization is used for the preparation of thermally stable polymers, Aromatic polyimides polymers are considered to have high thermo-oxidative stabilities, chemical resistance and good electrical properties. 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] and 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].

The present study on homopolymerization of 2 -chloro 4 –nitro (phenyl) maleimide (N-CNPMI) may give satisfying results explaining its thermal stability. The study on the physical, spectral and thermal properties were carried out to characterize the polymers. TGA and GPC techniques were carried out to study the thermal stability and molecular weight determination of prepared homopolymer.

EXPERIMENTAL SECTION

Materials

2- chloro 4 –nitro(phenyl) maleimide (N-CNPMI) and maleic anhydride were recrystallized from acetone. Benzoyl peroxide (BPO) (CDH, Mumbai) was used as received. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol prior to use. Tetrahydrofuran (THF) was purified by distillation after being refluxed for 2 hrs in the presence of sodium. Phosphorus pentoxide and concentrated H_2SO_4 (SRL, Mumbai) were used as received. N, N-Dimethylformamide (DMF), Tetrahydrofuran (THF), Dimethyl sulfoxide (DMSO), Acetone, methanol, ethanol and 1, 4-dioxane used were of analytical grade and used as received. ^{1}H 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 from 0°C to 600°C.

Synthesis of 2 -chloro 4 –nitro (phenyl) maleimide (N-CNPMI)

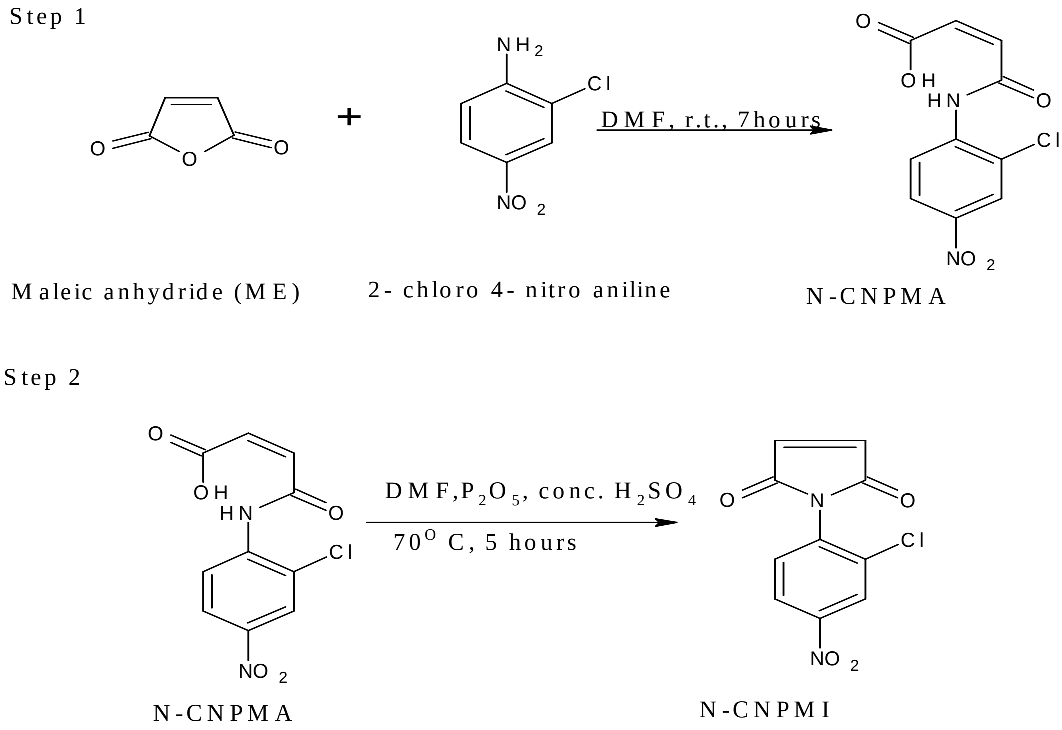
N-CNPMI monomer was synthesized in two steps using maleic anhydride and 2- chloro 4- nitro aniline.

2 -chloro 4 –nitro (phenyl) maleiamic Acid (N-CNPMA)

A solution of maleic anhydride (9.8g, 0.1mol) in 40 mL DMF was gradually added over a period of 10 minutes to a well-stirred solution of2 -chloro 4 –nitro aniline (17.3 g, 0.1 mol) in 40 mL DMF. The mixture was stirred for 7 hours at room temperature. The resulting solution was poured into a large amount of crushed ice to precipitate crude N-CNPMA. The solid white mass obtained is filtered and dried then recrystallized from ethanol to obtain pure N-CNPMA (80% yield M.P. 100°C).

2 -chloro 4 –nitro (phenyl) maleimide (N-CNPMI)

The N-CNPMI 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-CNPMI. It was filtered and washed with sodium bi-carbonate solution to remove any unreacted N-CNPMA residue. The remaining residue left behind was of crude N-CNPMI, 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-CNPMI were obtained. It has a yield of 75% and melting point 120℃. The purity of the obtained monomer was checked by FT-IR and ^{1}H NMR and elemental analysis.



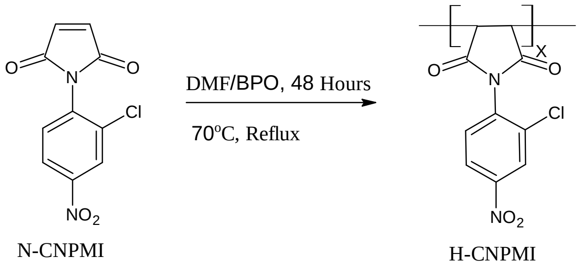
Scheme 1

The **IR spectrum** showed absorption frequencies at 3165.5 cm^{-1} (Aromatic -CH stretching), 3020.9 cm^{-1} (Hetero (imide ring) C-H stretching), 1784.6, 1718.4 cm^{-1} (Symmetric and asymmetric C=O stretching in Hetero ring), 1127.8 cm^{-1} (C-N-C stretching), 1365.6 cm^{-1} (Aromatic –CN stretching), 1620.6 cm^{-1} and 1502.5 cm^{-1} (Aromatic HC=CH stretching of benzene), 1640.1 cm^{-1} (Hetero C=C stretching), 1585.9 and 1340.1 cm^{-1} (N=O asymmetric and symmetric stretching of NO_2), 1041.4 cm-1 (Cl group ortho to phenyl ring), 929.1 cm^{-1} (Hetero CH=CH bending deformation), 896.2, 763.5 and 669.1 cm^{-1} (Aromatic C-Cl stretching).

^{1}H NMR (300 MHz, TMS, $CDCl_3$, δ ppm) : 7.03 ppm (Doublet, 1H ortho to phenyl ring), 7.30 ppm (Doublet, 1H near NO_2 group and meta to phenyl ring), 7.93 ppm (Singlet, 1H meta to phenyl ring lying between NO_2 and Cl groups, 6.77 ppm (Singlet 2H, CH=CH in imide ring).

Homopolymerization of N-DCPNPMI

Free radical homopolymerization of N-CNPMI (0.1 mol, 2.87 gm), were carried out with BPO as a free radical initiator in DMF (80 mL), in a round bottom flask. Reaction mixture was refluxed at 70°C for 48 hours. The homopolymer (H-CNPMI) was isolated by precipitation in methanol containing water. The precipitated homopolymer was washed with methanol several times and dried in a vacuum oven.



Scheme 2

The **IR spectrum** showed absorption frequencies at 3160.1 cm^{-1} (Aromatic -CH stretching), 3020.9 cm^{-1} (Hetero (imide ring) C-H stretching), 638.1 cm^{-1} (Hetero C-H deformation), 1782.5 and 1718.1 cm^{-1}(Symmetric and asymmetric C=O stretching in Hetero ring), 1126.5 cm^{-1} (C-N-C stretching), 1365.6 cm^{-1} (Aromatic –CN stretching), 1627.1, 1502.2 and 1487.3 cm^{-1} (Aromatic HC=CH stretching of benzene), 1587.7 and 1314.7 cm^{-1} (N=O asymmetric and symmetric stretching of NO_2), 1042.1 cm^{-1} (Cl group ortho to phenyl ring), 929.1 cm^{-1}, 772.5 cm^{-1}, 671.8 cm^{-1}, 894.2 cm^{-1} Aromatic C-Cl stretching).

^{1}H NMR (300 MHz, TMS, $CDCl_3$, δ ppm) : 3.30 ppm (Singlet, 2H in –CH-CH- imide ring), 7.00 ppm (Doublet, 1H ortho to phenyl ring), 7.50 ppm (Doublet,1H near NO_2 group and meta to phenyl ring), 8.20 ppm (Singlet, 1H meta to phenyl ring lying between NO_2 and Cl groups.

A summary of polymerization conditions and physical characteristics of H-DCPNPMI are presented in **Table 1**.

Table 1: Free Radical Homopolymerization of N-CNPMI in DMF at 70°C for 48 hours using BPO

Polymer	Feed mol ratio	Time (hrs)	Yield (%)	N (%)	η (Dl/g)	Color/ State
H-CNPMI	0.1	48	27.31	11.2 %	0.0512	Yellow/ Solid

RESULTS AND DISCUSSION

Solvent-initiator system

Solvent variation of homopolymer using different free radical initiator was done free radically. Free radical polymerization method applied for their preparation to find suitable condition in which the highest yield of the homopolymer is obtained. The effect of reaction solvents and initiator on yield of H-CNPMI is summarized in **Table 2**. The percentage yield of the H-CNPMI is the highest in 1, 4 dioxane/AIBN system. THF/BPO system has comparable yield of H-CNPMI with that of THF/AIBN system, 1, 4 dioxane/BPO systems. Acetone/BPO and DMSO/BPO system gave approximately same percentage yield but better solvent for good percentage yield of H-CNPMI and BPO is prove to be good initiator for the synthesis of H-CNPMI.

Table 2: Variation in percentage yield of H-CNPMI in different solvent initiator system after 48 hours

Solvent/Time in 48 hours	AIBN(%yield)	BPO(%yield)
	H-CNPMI	**H-CNPMI**
THF	29.02%	28.40%
DMF	26.02%	27.31%
Acetone	25.00%	26.20%
DMSO	25.10%	26.00%
1,4-dioxane	30.10%	29.60%

Effect of time on polymer yield

The effect of time on percentage yield of H-CNPMI is summarized in **Table 3**. It reveals that N-CNPMI 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-CNPMI at different time

Time (hours)	**(DMF\AIBN) % yield**	**(DMF\BPO) % yield**
	H-CNPMI	**H-CNPMI**
12	20.1%	40.12%
24	23.40%	47.50%
36	26.80%	50.1%
48	27.31%	68.30%
72	19.20%	40.10%

Solubility

Table 4 summarizes the relative solubility of Homopolymer sample H-CNPMI in number of polar and non-polar solvents at 30°C. The investigated homopolymer sample is readily soluble in THF, DMF, DMSO, acetone, 1,4 dioxane, carbon tetrachloride, chloroform, dichloromethane and insoluble in water cyclohexanone. Solubility behaviour in the later solvents depends on the composition of polymer.

Table 4: Solubility Behaviour of N-CNPMI (monomer) and H-CNPMI (homopolymer) in Polar and Non-polar Solvents at 30°C

Solvents	N-CNPMI	H-CNPMI
Ethanol	S	S
Methanol	S	S
Acetone	S	S
DMF	S	S
THF	S	S
DMSO	S	S
Water	IS	IS
Ethylacetate	S	S
Benzene	IS	IS
Xylene	IS	S
Cyclohexane	IS	PS
CCl_4	IS	IS
1, 4 dioxane	S	S
Toluene	IS	IS

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

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 H-CNPMI in DMF solution at 30 ± 0.1 ^{o}C (Table 1) is 0.0512 dL/g for H-CNPMI.

Spectral Characterization

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

(a) In FT-IR spectrum of N-CNPMI (shown in **Figure** 1), 1784.6 and 1718.4 cm^{-1} is attributed to the symmetric and asymmetric stretching of the carbonyl group in the imide ring only confirms monomer formation. Imide ring formation in N-CNPMI is also confirmed by 1365.6 cm^{-1} aromatic –CN stretching. The characteristics band of hetero C=C stretching at 1640.1 cm^{-1} and hetero CH=CH bending at 929.1 cm^{-1} also confirms monomer formation.

(b) In FT-IR spectrum of H-CNPMI (shown in **Figure 2**), 1711.4 cm^{-1} and 1780.2 cm^{-1} is attributed to the symmetric and asymmetric stretching of the carbonyl group in the imide ring only, which shows that imide ring is intact during polymerization. The imide group is also confirmed by 1365.6 cm^{-1} (Ar C-N stretching), 1126.5 cm^{-1} (C-N-C stretching). Compared with IR spectra of monomer N-CNPMI, it is found that the characteristics band of the double bond at 1640.1 cm^{-1} of hetero (HC=CH stretching) and 929.1 cm^{-1} of CH=CH bending are absent and appearance of 637.9 cm^{-1} of hetero aromatic C-H deformation in homopolymer formation.

Figure 1: The FT-IR spectrum of N-CNPMI (Monomer)

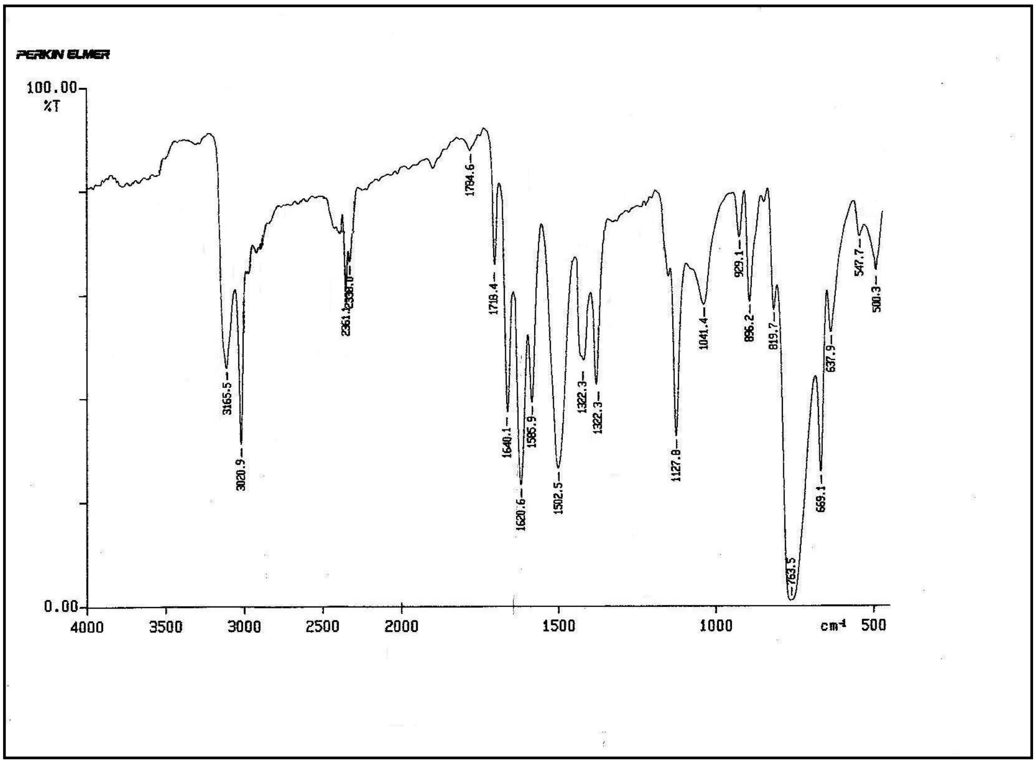
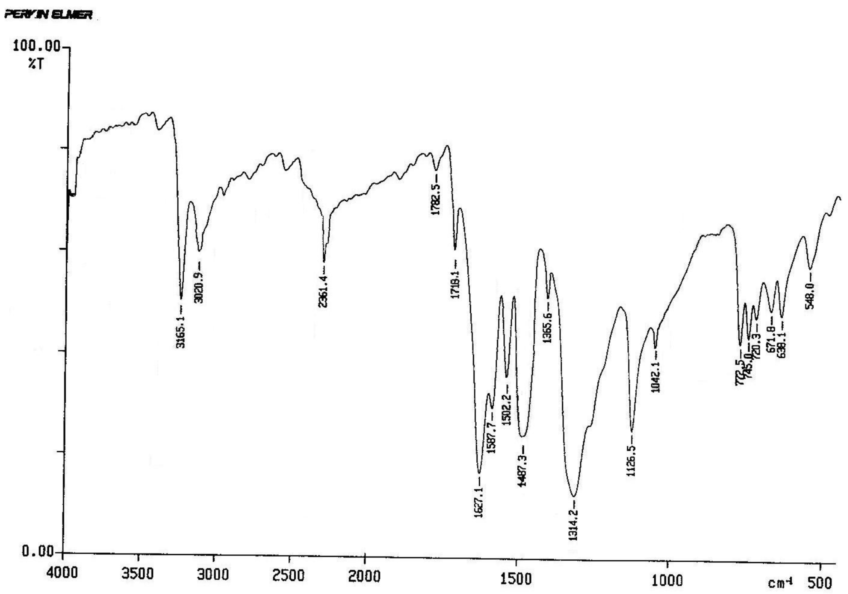


Figure 2: The FT-IR spectrum of H-CNPMI (Homopolymer)



Gel permeation chromatography (GPC)

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 homopolymer contain no impurities. Since, polydispersity index (PDI) is greater than 1.5 the process is free radical polymerization. Starting molecular weight of H-DCPNPMI is 9510. Summary of number average molecular weight, weight average, polydispersity index, start molecular weight, end molecular weight are as follows in **Table 5**.

Table 5: GPC characterization of H-PCPMI

Polymer	**Number average (Mn)**	**Weight average (Mw)**	**Polydispersity index Mw/Mn**	**Start Mw**	**End Mw**
H-CNPMI	307.8	320.8	1.181	1198	130.7

Thermal Properties

Homopolymerization shows one-step degradation for H-CNPMI. TGA was carried out in air at heating rate of 10°C/min. The results of percentage weight loss suffered from 100°C to 500°C at 100 °C intervals are furnished in **Table 6**. The temperature for initial decomposition T_i, final decomposition T_f and maximum rate of weight loss T_{max} determined from TGA are given in **Table 7**. H-CNPMI shows single step degradation. H-CNPMI initial degradation from 150°C involving about 2..27% weight loss leading to 89.12 % weight loss at 400°C and 93.81% weight loss at 500 °C.

Table 6: TGA characterization of H-PCPMI

Polymer code	**T_i**	**T_{max}**	**T_f**	**Residue at 500°C**
H-CNPMI	180	200	250	6.19%

Table 7: Percentage Weight loss of homopolymer H-PCPMI at various temperatures from the TGA

Polymer	**150°C**	**200°C**	**250°C**	**300°C**	**350°C**	**400°C**	**500°C**
H-CNPMI	2.27	30.62	85.15	86.32	88.32	89.12	93.81

CONCLUSION

Homopolymerization proceed through the free radical mechanism. The most suitable initiator-solvent pair for the homopolymerization was 1, 4 dioxane/AIBN system .The homopolymer (H-CNPMI) found to be soluble in THF, DMF, acetone, ethanol, DMSO, 1, 4 dioxane and insoluble in water and CCl_4. TGA analysis concluded that T_i for H-CNPMI of is 180 ^oC. Homopolymer is thermally more stable than copolymer. But, other properties are improved in copolymer. Molecular weight observed for H-CNPMI was 1198 and the polydispersity index (PDI) was 1.181. Polydispersity index less than two (PDI < 2) shows the H-CNPMI synthesized by free radical polymerization.

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