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Homopolymer Synthesis by Free Radical Polymerization-Characterization and Thermal study of 2,6-dichloro-4-nitro (phenyl)maleimide

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ABSTRACT

Free radical homopolymerization of 2,6 -dichloro 4 –nitro (phenyl)maleimide (N-DCPNPMI) was performed at 70 °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-DCPNPMI is characterized by nitrogen percentage, solubility test, FT-IR, ^{1}H NMR analysis. The intrinsic viscosity of H-DCPNPMI in DMF solution was 0.0578 dL/g. Thermogravimetric analysis (TGA) characterizes the thermal stability of H-DCPNPMI. The initial decomposition temperature of H-DCPNPMI was 150 °C. The gel permeation chromatography (GPC) determines the molecular weight (2768.6) and polydispersity index (PDI) 1.69 for H-DCPNPMI.

Keywords: 2,6-dichloro-4-nitro (phenyl)maleimide, Free radical homopolymerization, spectral, thermal stability, GPC.

INTRODUCTION

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]. 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. 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].

The present study on homopolymerization of 2,6 -dichloro 4 –nitro(phenyl)maleimide (N-DCPNPMI) may gave 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.

MATERIALS AND METHODS

Materials

2,6 -dichloro 4 –nitro(phenyl)maleimide (N-DCPNPMI) 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.

Methods

Synthesis of 2,6 -dichloro 4 –nitro (phenyl)maleimide (N-DCPNPMI)

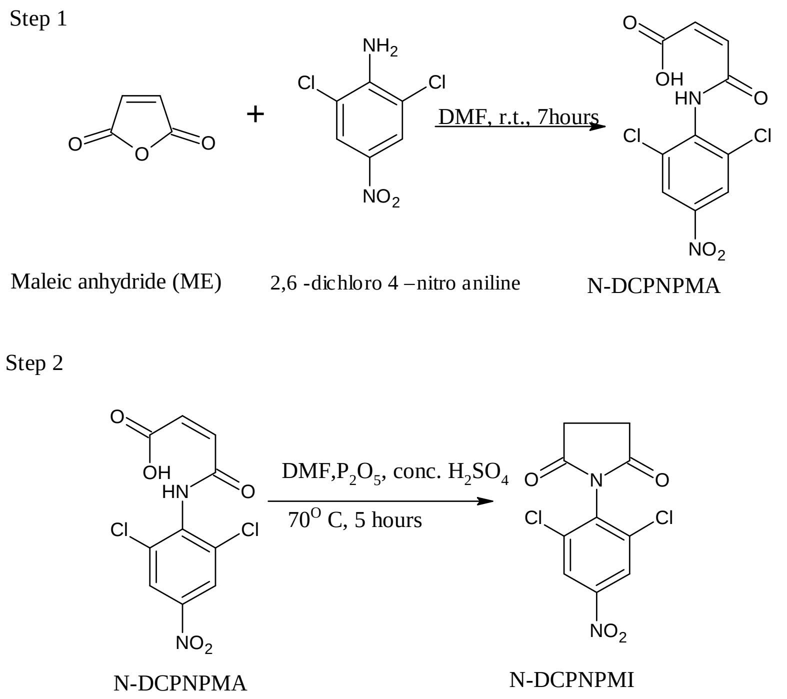
N-DCPNPMI monomer was synthesized in two steps from maleic anhydride and 2,6 -dichloro 4 –nitro aniline (described below and shown in Scheme 1).

2,6 -dichloro 4 –nitro (phenyl)maleiamic Acid (N-DCPNPMA)

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 of2,6 -dichloro 4 –nitro aniline (27.42 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-DCPNPMA. The solid white mass obtained is filtered and dried then recrystallized from ethanol to obtain pure **N-DCPNPMA** (yield 85%, M.P. 155 ^{o}C).

2,6 -dichloro 4 –nitro (phenyl)maleimide (N-DCPNPMI)

The N-DCPNPMI 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 ^{o}C for 5 hours. The mixture was then poured into a crushed ice water to precipitate out the crude N-DCPNPMI. It was filtered and washed with sodium bi-carbonate solution to remove any unreacted N-DCPNPMA residue. The remaining residue left behind was of crude N-DNPCPMI, 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 ^{1}H NMR and elemental analysis.



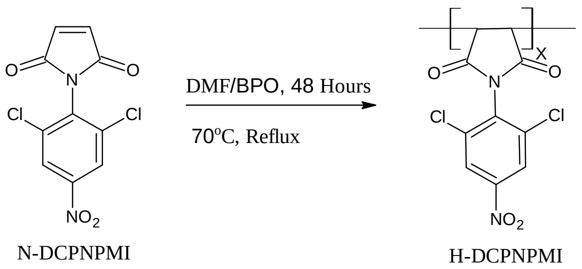
Scheme 1

The **FT-IR spectrum** showed absorption frequencies at 3162.5 cm^{-1} (Aromatic -CH stretching), 3021.5 cm^{-1} (Hetero (imide ring) C-H stretching), 1780.4, 1712.1 cm^{-1} (Symmetric and asymmetric C=O stretching in Hetero ring), 1127.6 cm^{-1} (C-N-C stretching), 1364.4 cm^{-1} (Aromatic –CN stretching), 1623.5 cm^{-1} and 1505.1 cm^{-1} (Aromatic HC=CH stretching of benzene), 1641.0 cm^{-1} (Hetero C=C stretching), 1584.1 and 1342.1 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} (Hetero CH=CH bending deformation), 895.4, 762.3 and 670.2 cm^{-1} (Aromatic C-Cl stretching).

^{1}H NMR (300 MHz, TMS, $CDCl_3$, δ ppm) : 8.10 ppm (Singlet, 2H in phenyl ring), 6.64 ppm (Singlet 2H, CH=CH in imide ring).

Homopolymerization of N-DCPNPMI
(Described below and shown in Scheme 2)

Radical homopolymerization of N-DCPNPMI (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-DCPNPMI) 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 **FT-IR spectrum** showed absorption frequencies at 3160.5 cm^{-1} (Aromatic -CH stretching), 3020.6 cm^{-1} (Hetero (imide ring) C-H stretching), 636.2 cm^{-1} (Hetero C-H deformation), 1781.3 and 1714.6 cm^{-1}(Symmetric and asymmetric C=O stretching in Hetero ring), 1127.3 cm^{-1} (C-N-C stretching), 1364.4 cm^{-1} (Aromatic –CN stretching), 1627.1, 1502.2 and 1484.3 cm^{-1} (Aromatic HC=CH stretching of benzene), 1583.6 and 1313.5 cm^{-1} (N=O asymmetric and symmetric stretching of NO_2), 1044.3 cm^{-1} (Cl group ortho to phenyl ring), 773.4 cm^{-1}, 670.7 cm^{-1}, 892.1 cm^{-1} Aromatic C-Cl stretching).

^{1}H NMR (300 MHz, TMS, $CDCl_3$, δ ppm) : 3.69 ppm (Singlet, 2H in –CH-CH- imide ring), 8.12 ppm (Singlet, 2H in phenyl ring).

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

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

Polymer	Feed mol ratio	Time (hrs)	Yield (%) (%)	N (%)	η (dL/g)	Color/ State
H-DCPNPMI	0.1	48	33.2	9.78	0.0578	Brown (Soild)

RESULTS AND DISCUSSION

Solvent-initiator system

Solvent variation of homopolymer (H-DCPNPMI) using different free radical initiator was done free radically. Such variation helps in obtaining the relatively high yield of copolymers. The details in Table 2 explained the effects of solvent and initiator on yield of the homopolymer of 2,6-Chloro 4- Nitro (phenyl)maleimide).

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

Solvent/Time in 48 hours	AIBN(%yield)	BPO(%yield)
	H-DCPNPMI	**H-DCPNPMI**
THF	30.1	30.0
DMF	28.2	33.2
Acetone	23.3	26.3
DMSO	20.2	25.4
1,4-dioxane	24.5	26.4

Table 3: Free radical copolymerization of N-DCPNPMI at different time

Time (hours)	(DMF\AIBN) % yield	(DMF\BPO)
	H-DCPNPMI	**H-DCPNPMI**
12	52.28%	50.1%
24	62.3%	60.7%
36	64.4%	63.1%
48	66.2%	64.3%
72	52.3%	53.4%

Effect of time on polymer yield

The effect of time on percentage yield of H-DCPNPMI is summarized in **Table 3**. It reveals that N-DCPNPMI gave better yield of copolymerization after 48 hrs in DMF solvent. It is also observed that after 72 hrs the yield of copolymerization decreases.

Solubility

Table 4 summarizes the relative solubility of Homopolymer sample H-DCPNPMI 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-DCPNPMI (monomer) and H-DCPNPM I (homopolymer) in Polar and Non-polar Solvents at 30°C

Solvents	N-DCPNPMI	H-DCPNPMI
Ethanol	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	IS
Xylene	IS	IS
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-DCPNPMI in DMF solution at 30 ± 0.1 ^{o}C (Table 1) is 0.0578 dL/g for H-DCPNPMI.

Spectral Characterization

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

For **H-DCPNPMI** the major characteristics absorption bands are observed at3160.5 cm^{-1} (aromatic C-H stretching), 3020.6 cm^{-1} for hetero C-H stretching, 1781.3 and 1714.6 cm^{-1} (C=O stretching in a five membered imide ring), 1627.1, 1502.2 and 1484.3 cm^{-1} for aromatic C=C stretching. The imide group is also confirmed by aromatic C-N stretching band at1364.4 cm^{-1}. Compared with IR spectrum of monomer N-DCPNPMI, it is found that the characteristic band of the double bond at 929.1 cm^{-1} disappeared in the homopolymer and the presence of band at 636.2 cm^{-1} also confirms the homopolymer formation.

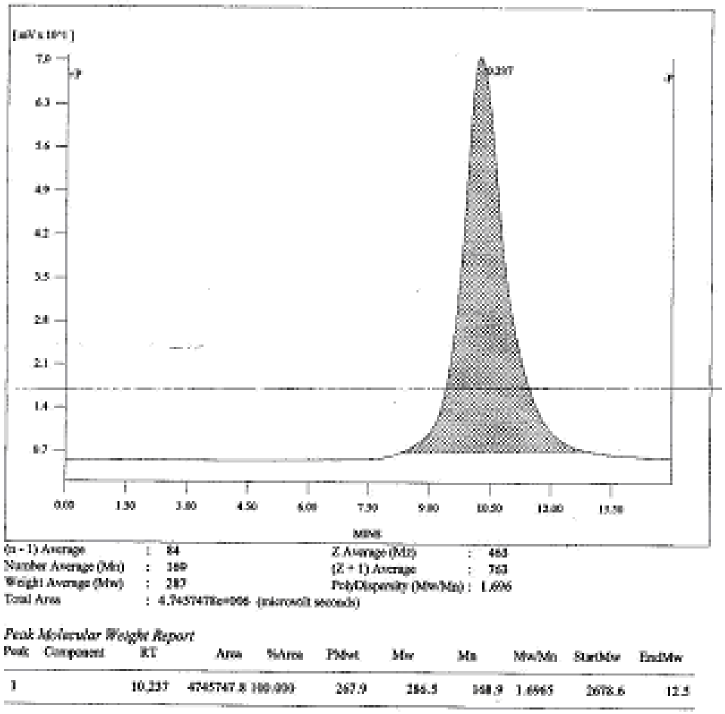
For **H-DCPNPMI**, it is concluded that the peak at δ 3.69 ppm appeared for 2H Singlet in –CH-CH- imide ring in the polymer main chain. The absence of peak at δ 6.64 ppm for vinyl protons of N-DCPNPMI (monomer) indicate that free radical polymerization had occurred via the opening of the double bond had taken place.

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, shown in **Figure 1.** 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	Weight average	PDI (Mw/Mn)	Start
H-DCPNPMI	168.9	286.5	1.69	2678.6



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(n - 1) Average          :  84           Z Average (Mz)            :  463
Number Average (Mn)      :  169          (Z + 1) Average           :  763
Weight Average (Mw)      :  287          PolyDispersity (Mw/Mn) :  1.696
Total Area               :  4.7457478e+006  (microvolt seconds)

Peak Molecular Weight Report
Peak  Component    RT       Area      %Area     PkMwt    Mw      Mn     Mw/Mn   StartMw   EndMw
1                  10.237   4745747.8 100.000   267.9    286.5   168.9  1.6965  2678.6    12.5
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Figure 1: GPC of H-DCPNPMI

Thermal Properties

Homopolymerization shows single step degradation of H-DCPNPMI, shown in **Figure 2**. TGA was carried out in air at heating rate of 10°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 6** for homopolymer of 2,6 -dichloro 4 –nitro (phenyl)maleimide. The one step weight loss was range to 1 to 90 %. The total weight loss of H-DCNPMI up to 250°C is 90%. H-DCPNPMI shows one-step degradation. T_i of H-DCPNPMI is 150°C for first step. Percentage weight loss of the homopolymer H-DCPNPMI from 100°C to 250°C is given in **Table 7**.

Table 6: TGA characterization of H-PCPMI

Polymer	**T_i**	**T_{max}**	**T_f**	**Residue at**
H-DCPNPMI	150	190	220	10%

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

Polymer	**100°C**	**150°C**	**200°C**	**250°C**
	1.1%	6.4%	46.6%	90%

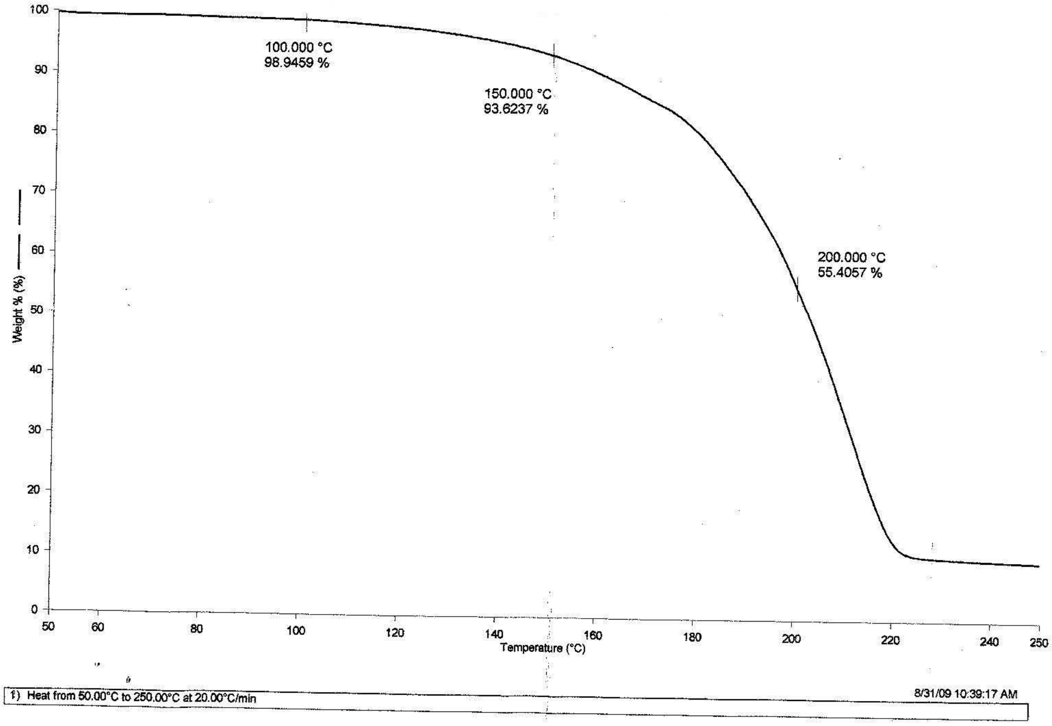

Figure 2: TGA of H-DCPNPMI

CONCLUSION

Free radical polymerization process was used for the synthesis of homopolymer of N-DCPNPMI. The homopolymer structure is confirmed by FT-IR and ^{1}H NMR spectral studies. The polymers are found to be soluble in THF, DMF, Acetone, DMSO, 1, 4 dioxane, ethanol, methanol etc and insoluble in water, benzene and toluene. The DMF/BPO system gives comparatively better yield for the homopolymer (H-DCPNPMI). TGA reports shows thermal degradation occurs in one step and T_i value for H-DCPNPMI is 150°C for first step. GPC report gives molecular weight of H-DCPNPMI. Molecular weight of H-DCPNPMI is 2678.6.

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