

Synthesis and characterization of heat resistant poly (2,4di nitro (phenyl amino) maleimide-co-MMA) prepared by free radical

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ABSTRACT

In the present study Copolymer Poly(2,4 dinitro (phenyl amino) maleimide-CO-MMA) [C-DNPAMI] was synthesized with 2,4 dinitro derivative of phenyl amino Maleimides[DNPAMI] and methyl methacrylate[MMA] using Azobisisobutyronitrile [AIBN] as initiator in Tetrahydrofuran [THF] at 650 C. Nine copolymer samples were prepared from different feed ratios of comonomer. The monomer reactivity ratios were determined by Fineman Ross method. The structure of copolymer was confirmed by FT-IR and 1H NMR. The effect of reaction solvent and initiator has been investigated to find suitable conditions for preparation of copolymer with high percentage yield. The molecular weight of polymer sample was determined by GPC. The copolymer was characterized by elemental analysis, Solubility, density, viscosity and thermal analysis. The initial decomposition temperature of copolymer samples were in the range 250 to 550°C.

Keywords: Copolymer, reactivity ratios, GPC, thermal analysis

1. INTRODUCTION

Heat resistance polymers are in biggest demand in two particular application areas, namely electrical and transport application. Many electrical components are required to operate at high temperatures^{1,2}. Further their high specific stiffness and strength with light weight, has led to the use of these polymers in transport application, especially in aerospace industries where weight saving is of vital importance. Besides these two application areas these polymers are also sought for use in more mundane consumer goods especially appliances where exposure to elevated temperature can occur such as hair dryers, toasters and microwave ovens etc.

Aromatic polyimide are one of the most important classes of high performance polymers. They represent a class of useful heat resistance materials among the thermally stable hetero aromatic polymers³. The versatility of the polyamides has the high performance materials is providing incentive for accelerating research and development activity in many directions. However the homo polyamides have certain disadvantages like insolubility, infusibility which make process difficult⁴⁻⁶. The free radical initiated copolymerization of N-substituted maleimide with various vinyl monomers was investigated to overcome these difficulties⁷⁻¹⁴. A number of investigations on the free radical initiated copolymerization of N-substituted maleimides with vinyl monomers have been reported¹⁵⁻¹⁸.

N-Substituted maleimides and their derivatives are well known for their excellent heat-resistance. They can be used as heat-resistant additives in rubber, plastics¹⁹ and as modifying agents for proteins²⁰. The (co)polymers of maleimide usually have a relatively high glass transition

temperature (T_g) and thermal decomposition temperature, since the polymer chains are hindered by the rigid five-membered ring²¹. In the present work we report the synthesis and characterization of nine copoly maleimides of 2,4, [Dinitro (phenyl amino)] maleimide with methyl methacrylate (MMA) by different feed ratios of comonomer. These copolymers show higher stability than the poly methyl methacrylate (PMMA). However, these copolymers were found to have predominantly random distribution of the monomer units in the polymer chain. It has been reported that N-arylmaleimide formed alternate copolymers with methyl methacrylate because maleimides are electron acceptors and methyl methacrylate acts as an electron donor. Hence, this area of research is wide open and lot more work is required to understand the physico-chemical properties of these versatile, thermally stable, high performance polymeric materials. The copolymers of different compositions were prepared to study effect of composition on the polymer properties and determine monomer reactivity ratios.

2. EXPERIMENTAL MATERIALS

2, 4, Dinitro phenyl hydrazine, AIBN and BPO used after recrystallized from ethanol. MMA was purified by shaking two to three times with 5% NaOH solution to eliminate hydroquinone inhibitor. It was dried over anhydrous calcium chloride for 6 hours and distilled. The head and tail fractions were discarded. DMF, THF, 1,4-Dioxane, Acetone, Methyl alcohol, Benzene were used after distillation. All other reagents were of analytical grade and were used as received.

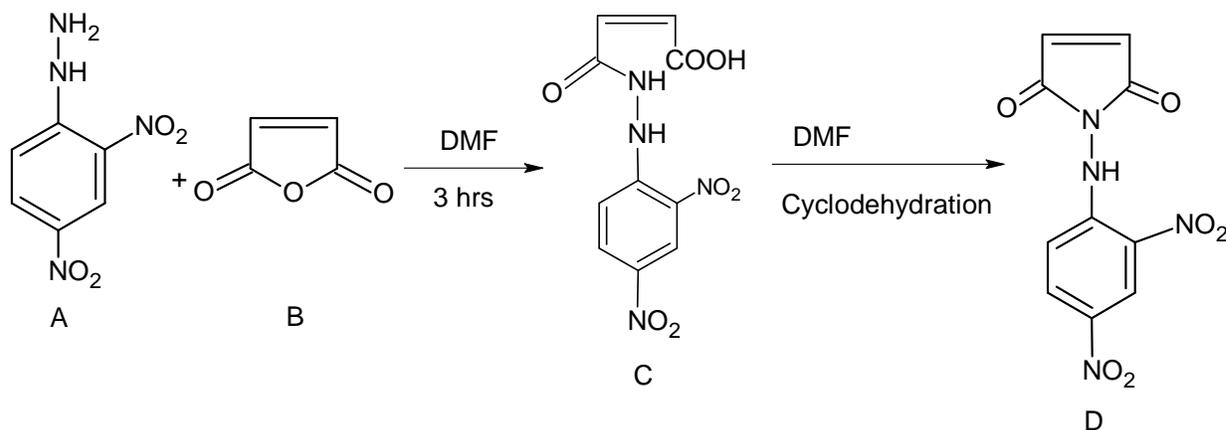
3. MEASUREMENTS

The ¹H-NMR spectra were taken in DMSO-d₆ solvent on Bruker vance Spectrometer S.A.I.F. at 400 MHz with a sweep time of 10 min. at room temperature. The internal reference used was TMS. FT-IR spectra of the monomer and copolymer sample were recorded on a shimadzu 8201 PC (4000-400 cm⁻¹) FT-IR spectrometer, using KBr pellet technique. Elemental analysis was made on elemental analyzers Elementar Vario EL. III Carbo Erba 1108. The densities of solid copolymer sample were determined at 30°C by displacement method with single stem pycnometer using water as solvent. The viscosity measurement was carried out in DMF at 30°C, using ubbelohde suspended level viscometer. The thermogram in air was obtained on Mettler TA-3000 system at a heating rate of 10°C/min from 0°C to 600°C.

4. SYNTHESIS OF MONOMER

Monomer 2,4-[Dinitro (phenyl amino)] maleimide [DNPAMI] was synthesized from maleic anhydride and Nitro derivative of Phenyl hydrazine in two steps (Scheme-1).

Step-I Synthesis of Dinitro (Phenyl amino) maleamic acid [DNPAMA]: A solution of substituted Phenyl hydrazine [A] (0.1 mole in 30 ml DMF) was gradually added to well stirred maleic anhydride [B] (0.1 mole in DMF) in flat bottom flask and stirred for 3 hr at room temperature. The precipitate was filtered and dried at 70°C. It was recrystallized from methanol solvent to obtain pure DNPAMA [C].

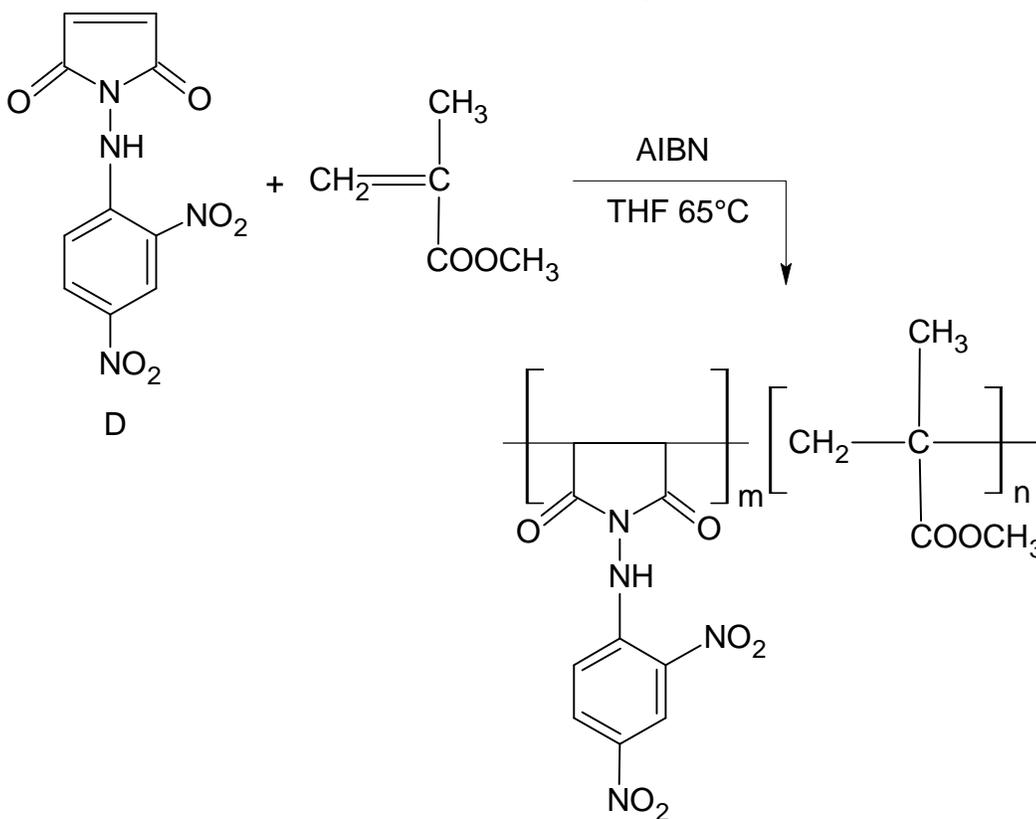


Scheme - 1

Step-II Synthesis of 2,4 dinitro (Phenyl amino) maleimide [DNPAMI]: Cyclodehydration was carried by treating DNPAMA (0.1 mol in 30 ml DMF) with concentrate. H₂SO₄ (1 ml) and P₂O₅ (7.4 gm) for 3 hrs at 70°C. The reaction mixture was cooled and poured into crushed ice water to obtain the yellow colour precipitate of DNPAMI [D]. The precipitate was filtered and washed several times with water and finally dried. DNPAMI was recrystallized from methanol solvent.

4.1 Synthesis of Copolymer 2, 4, [Dinitro (phenyl amino)] maleimide with methyl methacrylate [C-DNPAMIMMA]

Calculated amounts of monomer DNPAMI [D] with MMA in 70 ml THF were taken in a round bottom flask. Then 20 mg AIBN was added to the reaction mixture as a free radical initiator. The copolymerization reaction was carried out at 65°C for 24hrs. Polymer samples were isolated in water containing 20% methanol. The copolymers were purified by first dissolving then in THF and then, reprecipitating in excess quantity of methanol-water mixture. The precipitated copolymer was washed with methanol several times and dried at 60°C under vacuum (Scheme-2).



5. RESULTS AND DISCUSSION

5.1 Monomer Reactivity Ratio and Copolymer Composition

Reactivity ratios of a given pair of monomers can be experimentally determined by polymerising mixtures of two monomers in varying ratios to low conversion (usually less than 10% so as to minimise the effect of the change in

the monomer ratio as polymerisation progress) and then analysing the resultant copolymer for its monomeric composition. The copolymer composition for each feed ratio was calculated by substituting the respective values of r_1 and r_2 obtained employing the Finemann-Ross method. In the copolymerization of maleimide with MMA, the product values of r_1 and r_2 are significantly greater than zero, indicating formation of random copolymers by phenyl amino maleimide or substituted phenyl amino maleimide with MMA.

Table 1: Parameters for Finemann-Ross methods to determine Reactivity ratios in copolymer of C-DNPAMIMMA

Code	Mol Ratio Feed	Mole fractional of DNPAMI		Finemann-Ross Method	
	$x_1:x_2$	Feed X_1	Copolymer F_1	$\frac{X_1(1-2F_1)}{(1-X_1) \times F_1}$	$\frac{X_1^2(F_1-1)}{(1-X_1)^2 \times F_1}$
C-DNPAMIMMA1	1: 9	0.1	0.0775	1.212	- 0.1469
CDNPAMIMMA2	2:8	0.2	0.1263	0.879	- 0.4319
CDNPAMIMMA3	3:7	0.3	0.1633	0.767	- 0.9412
CDNPAMIMMA4	4:6	0.4	0.1889	0.495	- 1.9083

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CDNPAMIMMA5	5:5	0.5	0.2089	0.379	- 3.787
CDNPAMIMMA6	6:4	0.6	0.2247	- 1.675	- 7.79
CDNPAMIMMA7	7:3	0.7	0.2377	- 2.15	- 17.462
CDNPAMIMMA8	8:2	0.8	0.2479	- 5.135	- 48.541
CDNPAMIMMA9	9:1	0.9	0.2591	- 9.736	- 120.32

Table 2: Monomer reactivity ratio r_1 and r_2 of Monomers

Polymer code	Reactivity Ratio (Finemann-Ross Method)	
	r_1	r_2
C-DNPAMI-MMA	0.089	0.33

5.2 Spectral Analysis

FT-IR spectra (Fig. 1) with characteristic absorption frequencies 2975 (aromatic and alkene (C-H stretch), 3437.1 (N-H stretch), 1782.7 and 1718.7 (symmetric and asymmetric stretch of C=O in a five member imide ring, 1594.5 (C-NO₂) groups stretching 1450, 1430 (C=C, aromatic), 1351.2 (C-N stretch)26 and 910.7 (CH=CH)26 are consistent with the structure of Dinitro phenyl amino maleimide (DNPAMI).

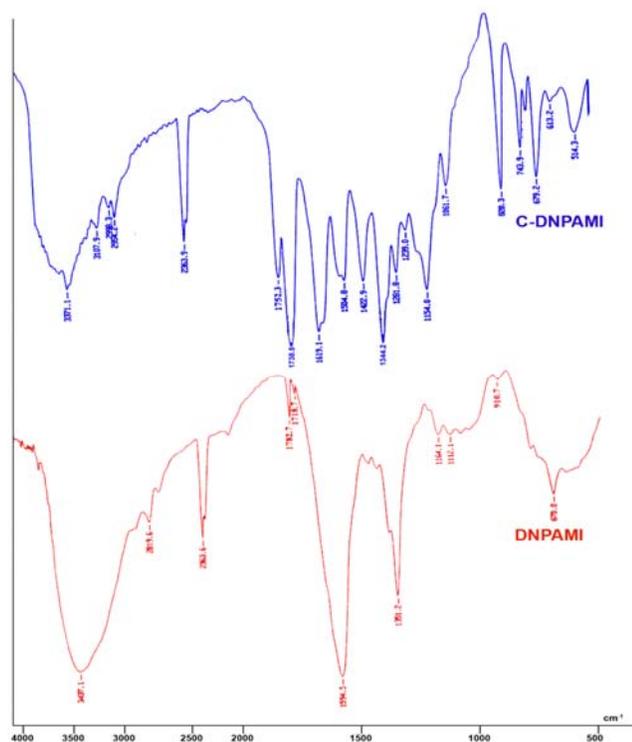


Fig 1: FT-IR Spectra of Monomer (DNPAMI) and Copolymer(C-DNPAMI)

¹H-NMR (Fig. 2) 400 MHz, ref. TMS, solvent DMSO-d₆, δ , (ppm) of DNPAMI shows (a) two methine (CH=CH) protons at 7.4 and 6.9 (S) ppm, (b) three aromatic protons δ 7.5 - 8.5 ppm (1n) (c) 3.86 (S, 1H, N-H).

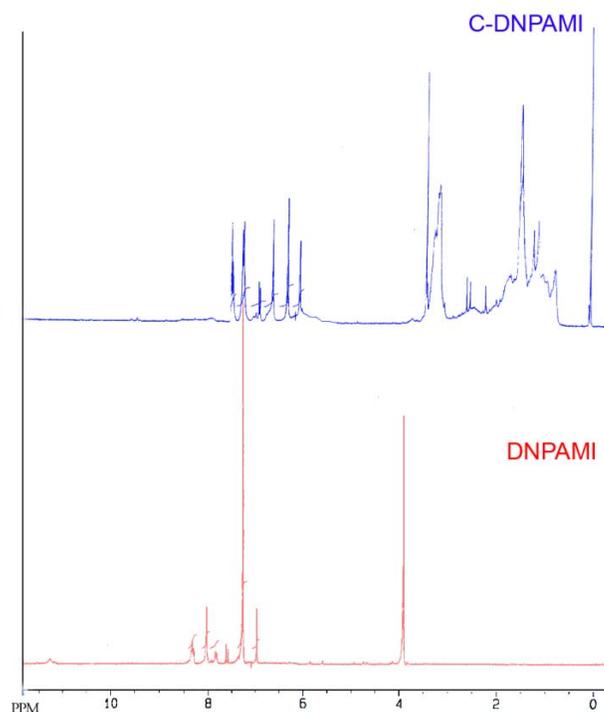


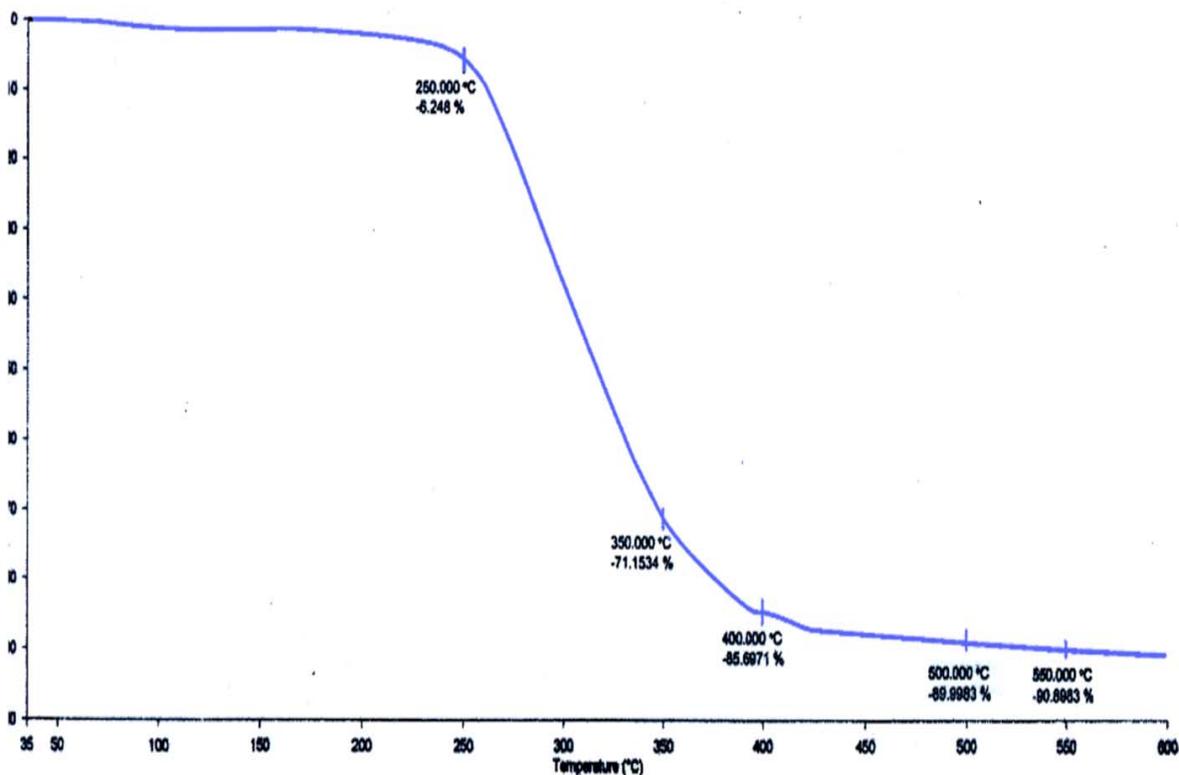
Fig 2: ¹H-NMR Spectra of Monomer (DNPAMI) and Copolymer (CDNPAMI)

The FT-IR spectra of C-DNPAMI are shown in (Fig. 1) The major characteristic absorption bands are observed at 3107.9, 2998.3, 2954.2 (C-H stretch, CH₃, and CH₂ in MMA), 3371.1 cm⁻¹ at N-H stretch, 1752.3, 1738.5 cm⁻¹ (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1504.8 and 1344.0 (asymmetric and symmetric stretching Ar-NO₂ group), 1619.1 (C=C stretch, aromatic), 1422.9 (C-H bend - CH₂), 1281.8, 1239.0, 1154.0 (asymmetric and symmetric C-O-C stretch), 743.9 cm⁻¹ (out of plane C-H band of mono substituted benzene ring) and 613.2 (out of plane aromatic ring C=C bend). These characteristic bands confirm that units of both the monomers DNPAMI and MMA are present in the copolymer samples. The absence of characteristic band of vinyl group 910.7 cm⁻¹ indicates the polymer formation via vinyl group.

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The results further confirmed by ¹H-NMR Spectra of C-DNPAMI (Fig-2). The ¹H-NMR of copolymer, C-DNPAMI shows the chemical shift δ for three aromatic protons at 6.9-8.6 ppm. The δ observed at 3.5-3.71 ppm

corresponds to overlapping of 2H - (CH-CH) in the polymer main chain and 3H (-OCH₃) of MMA segment. N-H singlet at 3.94. For 3H (-CH₃) around 0.85-1.51 ppm and 2H of methylene group is appeared at 1.6-2.36 ppm.



Thermogram of C-DNPAMI

Fig 3: TGA Curve of Copolymer (CDNPAMI)

5.3 Effect of Solvent-initiator

The percentage yield of copolymer was determined in different solvents and observed in maximum cases that THF-AIBN system gives high percentage yield as compared to DMF, ethyl acetate, acetone and dioxane solvents. Because of THF solvent has higher viscosity compared to other solvents. Thus higher percentage yield is obtained in copolymer. Further DMF solvent has less viscosity compared to other solvents. Thus less percentage yield is obtained in homo and copolymers. The reason may be higher the viscosity more life of free radicals and hence more polymerization.

Table 3: Effect of solvent in C-DNPAMI percentage yield

Solvent	Solvent viscosity	Polymerization Time	AIBN initiator Yield%	BPO initiator Yield%
DMF	1.2991	12h	39.18	38.10
Acetone	1.3588	12h	39.89	40.10
EA	1.3701	12h	42.39	41.93
Dioxane	1.4165	12h	50.37	49.48
THF	1.4975	12h	52.93	45.11

5.4 Solubility

Monomer DNPAMI is completely soluble in THF, DMF, DMSO, acetone, cyclohexanone. It is partially soluble in dioxane, methyl acetate, ethyl acetate, 1-butanol, 2-butanol. It is insoluble in CHCl₃, benzene, toluene, CCl₄, CH₂Cl₂, ethanol, methanol, n-hexane, xylene and

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water. Copolymer C-DNPAMI is completely soluble in THF, DMF, dioxane, acetone, chloroform, methyl acetate, ethyl acetate, CH₂Cl₂, cyclohexanone. It is insoluble in ethanol, methanol, xylene and water. It is partially soluble in DMSO, benzene, toluene, CCl₄, 1-butanol and 2-butanol.

5.5 Molecular Weight of Copolymer

Molecular weight and polydispersity index of copolymer was determined by Gel permeation Chromatography (GPC) method by using THF solvent. The number average molecular weight (M_n) Weight Average molecular weight (M_w) and Polydispersity (M_w/M_n) are given in Table -4. Many properties of a polymeric material eg. Solubility, melt and solution viscosity, mold ability etc. depend on its molecular weight. The knowledge of molecular weight is thus every important. Poly dispersity is also a very important parameter. It gives an idea of the

lowest and the highest molecular weight species as well as the distribution pattern of the intermediate molecular weight species. The weight average and number average ratio gives to poly dispersity index (PDI). The poly disperse nature of the polymer is the basis of the concept of average molecular weight. In copolymer of C- DNPAMI the PDI value more than two indicating that they are present in multiform.

5.6 Physical Properties

Density (ρ) depends on packing of molecules in polymer chains. The density of copolymer sample was determined at 30°C by displacement method with single stem pycnometer using water as solvent. The Intrinsic Viscosity (η) of copolymer was determined by Ubbelohde Suspended Level Viscometer in DMF at 30° C.

Table 4: Density, Intrinsic Viscosity and Molecular weight of Copolymers

Polymer	ρ (g/cm ³)	η (dl/g)	M _n	M _w	M _w /M _n	Start Mw	End Mw
CDNPAMI	0.9030	0.280	369	890	2.4119	28970	50

5.7 Thermal Analysis

Polymaleimide is potential heat and chemical resistant material. Generally vinyl polymer shows less stability as compared to Maleimides polymers. Therefore, MMA copolymerized with DNPAMI to obtained better thermal stability.

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The thermogram was obtained by heating the copolymer sample in air 10°C/min. The typical curve for copolymer is given in Fig.3. The decomposition temperature with % weight loss for C-DNPAMI is summarized in Table

The copolymer C-DNPAMI is decomposing through one step procedure. As the copolymer sample content of DNPAMI is 50% the copolymer began to decomposition at lower T_i. The first step weight loss was range to 71% to 85%. The weight loss of C-DNPAMI up to 550°C is 91%.

C-DNPAMI show the two step degradation Table 5. The first rapid stage of decomposition may be due to bond rupture and volatilization of low molecular weight fragments produced during decomposition. The second slow stage of decomposition at higher temperature than that of first stage, suggests increased extent of cross linking resulting into somewhat more stable residue which at still higher temperature instantaneously undergoes the degradation into volatile products.

Table 5: Thermal behaviour of copolymer

Polymer	T _i	T _{max}	T _f	Residue at 500°C
C-DNPAMI	250°C	350°C	400°C	11.01%
	400°C	500°C	550°C	

Table 6: Percentage weight loss of copolymer at various temperature from the TGA

Polymer	200°C	300°C	400°C	500°C	550°C
	Weight loss (%)				
C-DNPAMI	2%	44%	85%	90%	91%

6. CONCLUSIONS

The free radical copolymerization of 2, 4 di nitro (phenyl amino) maleimide has been carried out with MMA. The monomer reactivity ratios were determined by Fineman Ross method. In the copolymerization the product values of r₁ and r₂ are significantly greater than zero, indicating formation of random copolymers. THF-AIBN system was found most suitable solvent-initiator pair. The copolymer was characterized by FT-IR and ¹H NMR. Molecular weight and polydispersity index of copolymer was determined by Gel permeation Chromatography (GPC) method by using THF solvent and the PDI value indicating that they are present in multiform. MMA copolymerized with DNPAMI to obtained better thermal stability and copolymer degrades in two steps.

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