

Synthesis, Characterization and Thermal Stability of Maleimide Polymers with Modified-monomers

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ABSTRACT: The novel functionalized N-[4-N₂-(anilino amino carbonyl) phenyl] maleimide (APM) was synthesized starting from p-aminobenzoic acid maleic anhydride and phenyl hydrazine. The homopolymer of APM is synthesized by free radical using AIBN in tetra hydrofuran (THF) solvent at 65°C. The copolymer of APM and methyl methacrylate (MMA) were synthesized using AIBN as a free radical initiator in THF. The nine copolymer samples were synthesized from different feed ratio of comonomers. The copolymer composition and reactivity ratio were determined by nitrogen-elemental analysis and fineman ross method. The reactivity ratio and Alfrey Price Q-e value is as follows: $r_{1(APM)} = 0.14$, $r_{2(MMA)} = 0.72$, $Q = 0.23$ and $e = 2.25$. The homo and copolymers were also synthesized in various solvent initiator system and different time. The synthesized homopolymer and copolymer were characterized by intrinsic viscosity, solubility test, FT-IR, ¹H-NMR spectral analysis and elemental analysis. The molecular weight was determined by gel permeation chromatography (GPC) and thermal behavior was studied by thermo gravimetric analysis. It was observed that such polymers shows better thermal stability than the polymers of vinyl monomers.

Keywords: N-[4-N₂-(anilino amino-carbonyl) phenyl] maleimide, MMA, Reactivity Ratio, Molecular weight, Characterization.

INTRODUCTION

Polymers of N-substituted maleimides and their derivatives represent a class of rigid polymers because of the imide rings in the back bone. This provides the polymers with superior mechanical and thermal stability. [1-3] N-substituted maleimide ranks among the group of useful monomers because, when their units were inserted into some polymer chains as thermoplastic resins, [4] the heat resistant, solvent-resistant, chemical stability and other properties of these materials were greatly improved.

During the early period of polymer science it was quickly recognized that copolymerization possessed some unique features quite different from those of homopolymerization, which means the interpretation for copolymerization is more complicated than that for homopolymerization. [5-7]

The peculiar homo and copolymerization characteristics of the electron deficient maleimide

group make it an attractive monomer for designing special vinyl monomers. Although maleimide undergoes homopolymerization with great difficulty, it copolymerizes quite readily with a variety of vinyl monomers. Apart from enhancing the thermal stability of resultant copolymer, the maleimide group can effectively serve as vehicle for many functional groups for their predefined distribution in a vinyl polymer backbone through free-radical copolymerization. [8-12]

The present paper reports the synthesis and free radical copolymerization of N-[4-N₂-(anilino amino-carbonyl) phenyl] maleimide with methyl methacrylate. The reactivity ratio of modified maleimide monomer in polymerization was studied to determine reactivity ratio. The synthesized polymers have higher molecular weight and better solubility in various solvents. The synthesized polymers degrade at higher temperature. The physical and spectral properties have been studied to characterize the copolymer sample.

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EXPERIMENTAL

Materials

p-Aminobenzoic acid (Spectrochem) and maleic anhydride (S. D. fine chem.) were recrystallized from acetone. MMA (CDH) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl_2 for 6 hrs and distilled. The head and tail fractions were discarded. AIBN (2,22'-azobisisobutyronitrile (spectrochem.)) was recrystallized twice from methanol prior to use. BPO (benzoyl peroxide) (CDH) was used as received. THF (S.D. fine Chem.) was purified by distillation after being refluxed for 2 hr in the presence of sodium [12]. DMF (Spectrochem) and methanol (Spectrochem) used in the present work were of analytical grade and were used as received.

Measurements

$^1\text{H-NMR}$ spectra of monomer and polymer samples were taken in DMSO-d_6 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 $30 \pm 0.2^\circ\text{C}$, 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 $^\circ\text{C}/\text{min}$ from 0 $^\circ\text{C}$ to 600 $^\circ\text{C}$.

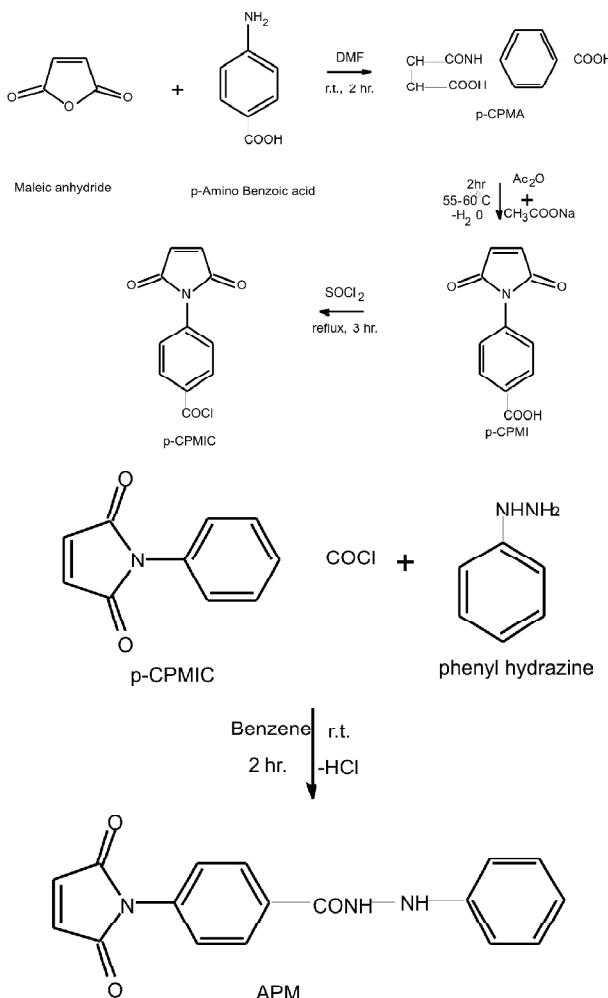
Synthesis of N-[4-N₂- (anilino amino-carbonyl) phenyl] maleimide (APM)

APM monomer was synthesized in four steps from maleic anhydride, p-aminobenzoic acid and phenyl hydrazine (described below and shown in Scheme 1). N-[4-(Chlorocarbonyl) phenyl] maleimide (p-CPMIC) was prepared according to a previously published procedure. [13]

Synthesis of APM

A benzene solution of phenyl hydrazine (0.5mol in 100 ml benzene) was added drop wise to a CPMIC (11.75gm 0.5mol) solution in benzene (100ml) at 0-5 $^\circ\text{C}$ and the mixture was stirred at room temperature for 2 hours. The precipitated product was filtered, washed with water, dried and

then recrystallized twice from ethanol to obtain pure APM in a 72% yield.



Scheme 1

Synthesis of Homopolymers

The homopolymer of APM (0.2mol) was synthesized using AIBN as a free radical initiator in THF, in a round bottom flask (described below and shown in Scheme 2). The reaction mixture was carried out at 65 $^\circ\text{C}$ for 2, 6, 8, 12, 24, 36 hours. No or very less yield of homopolymer was formed if the reaction was carried up to 12 hrs. The yield increased as the time of polymerization is increased. The homopolymer PA was isolated by precipitation in excess quantity of methanol containing 10% water. The precipitated homopolymer was washed with methanol several times and dried in vacuum oven at 70 $^\circ\text{C}$. A summary of polymerization conditions and physical characteristics of homopolymer PA are presented in table 1.

Table 1
Radical Polymerization and Copolymerization of APM with MMA in THF at 65 °C

Polymer Code	Feed mol fraction of APM X_1	Polymn Time (h)	Yield (%)	% N	Appearance	Mol frac of APM in copolymer F_1
CAM ₁	0.1	24	62.10	1.92	L. Orange	0.075
CAM ₂	0.2	24	60.15	3.81	L. Orange	0.175
CAM ₃	0.3	24	58.80	5.13	L. Orange	0.286
CAM ₄	0.4	24	55.20	5.63	Orange	0.349
CAM ₅	0.5	24	54.28	6.35	Orange	0.430
CAM ₆	0.6	24	53.20	6.92	Orange	0.499
CAM ₇	0.7	24	50.80	7.14	Orange	0.528
CAM ₈	0.8	24	48.70	7.49	Orange	0.581
CAM ₉	0.9	24	45.10	8.04	Orange	0.682
PA	1.0	36	44.56	8.68	Orange	1.000

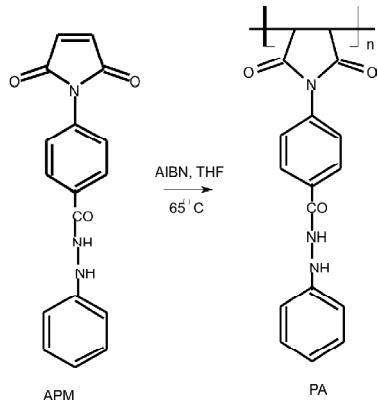
L.Orange = Light Orange, % N= Percentage Nitrogen element analysis

Various homopolymer samples were obtained using different solvent-initiator combination. The percentage yield of homopolymer samples, using different solvent/initiator systems are calculated from following formula and presented in table 2.

Table 2
Percentage Yield of Homopolymer and Copolymer in Various Solvent-initiator Systems

Polymer Code	Solvent	AIBN Yield %	BPO Yield %	Colour
CAM ₅	THF	54.28	50.20	Orange
	DMF	38.20	35.15	Brown
	1,4-Dioxane	42.90	43.80	Orange
	DMSO	42.70	43.10	Red
	Ethyl acetate	50.40	51.15	Orange
	THF	44.56	43.10	Orange
	DMF	24.10	23.90	Brown
	1,4-Dioxane	34.80	38.70	Orange
	DMSO	26.10	25.15	Red

Yield % = 100 x Wt. of polymer /Wt. of monomer



Scheme 2: Homopolymerization

Synthesis of Copolymers

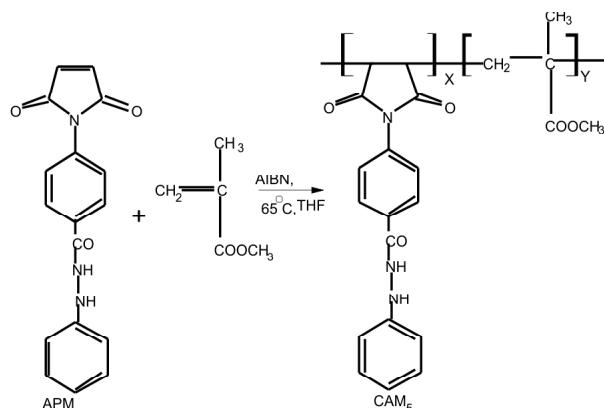
The equimolar amount of APM and MMA in THF were taken in a round bottom flask. The 25mg AIBN was added to the reaction mixture as a free radical initiator(described below and shown in Scheme 3). The reaction mixture was carried out at 65°C for 24 hour. The copolymer was precipitated in methanol-water mixture. The crude product was dissolved in THF and precipitated in methanol. The process of dissolving and precipitation is repeated twice to get rid off unreacted monomer. The nine copolymer samples were synthesized by using different feed ratio of monomer APM and MMA to study of reactivity ratio of monomers. The polymerization conditions and physical properties are presented in table 1.

Table 3
Percentage Yield of Homopolmer and Copolymer in Different Time in THF at 65 °C

Polymer Code	12hr	18hr	24hr	30hr	36hr
	% Yield				
PA	20.18	22.10	25.15	28.70	44.56
CAM ₅	40.88	44.15	54.28	56.20	57.70

Various copolymer samples were obtained using different solvent-initiator combination. The percentage yield of copolymer samples, using different solvent/initiator systems are calculated from following formula and presented in table 2.

Yield % = 100 x Wt. of polymer /Wt. of monomer

**Scheme 3:** Copolymerization with MMA

RESULTS AND DISCUSSION

Solvent-initiator System

The free radical homopolymerization of APM and copolymerization with MMA were carried out using different solvent and initiator at 65 °C. The yield of obtained polymers was calculated and find to suitable condition in which to prepare homo & copolymaleimide with relatively high yield. The effect of initiator and solvent were investigated in details. The effect of reaction solvents and initiator on yield of PA and CAM_5 was found in different pairs of solvent initiator is summarized in table 2.

The table 2 presented that very low yield is obtained in DMF and DMSO solvent. Examining all the aspect, AIBN-THF system is most suitable system for obtaining the better yield of PA. The effect of reaction solvents and initiator on yield of CAM_5 is summarized in Table 2. The percentage yield of CAM_5 from Dioxane-AIBN system is equivalent with the DMSO-BPO system. Examining all the aspect, AIBN-THF system is most suitable system for obtaining the better yield of CAM_5 .

Effect of Time on Polymer Yield

The effect of reaction solvents and time on yield of PA and CAM_5 was formed in different time is summarized in table 3. Table 3 reveals that APM gave better yield at 36 hour in homopolymerization and in 24 hour in copolymerization.

Solubility

Table 4 summarizes the relative solubilities of homo and copolymer samples in number of polar and non-polar solvents at 30 °C. The investigated

homo and copolymer both samples are soluble in tetrahydrofuran (THF), N-N'-dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO), acetone, 1, 4-dioxane and cyclohexanone. Individual copolymer is soluble in dichloromethane, n-hexane and ethyl acetate and partially soluble in toluene. Solubility behaviour in the later solvents depends on the composition of polymer. The solubility of copolymer is more than homopolymer in the solvent taken. The solubility of polymer is depending on composition of polymer. In homopolymer, only maldimide unit is present in polymer back bone. Due to rigid imide ring, homopolymer causes difficult to soluble in organic solvents. In copolymer vinyl monomer unit present in backbone which causes polymer is easily soluble in different solvents.

Intrinsic Viscosity $[\eta]$ and Molecular Weight

Intrinsic viscosity $[\eta]$ is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the polymer coil in a given solution. The values of intrinsic viscosity $[\eta]$ in DMF solution at 30 °C are listed in table 5. The value of $[\eta]$ decreases from 0.217 to 0.150 dl/gm for copolymer to homopolymer. The value of $[\eta]$ depends on the composition of APM. Intrinsic viscosity of homopolymer is less then copolymer and indicating the content of APM is increased then value of η is decreased.

Table 4
Solubility Behaviour of Monomer, Homopolymer and Copolymer in Polar and Non-polar Solvents at 30 °C

Solvent	APM	PA	CAM_5
Acetone	S	S	S
Cyclohexanone	S	S	S
1, 4-dioxane	S	S	S
THF	S	S	S
DMF	S	S	S
DMSO	S	S	S
Dichloromethane	IS	PS	S
Chloroform	IS	IS	PS
CCl_4	IS	IS	IS
Xylene	IS	IS	IS
Toluene	IS	IS	PS
Benzene	IS	S	S
n-Hexane	IS	PS	S
Ethyl acetate	S	PS	S

S= Soluble, IS= Insoluble PS= Partially Soluble

Table 5
The Intrinsic Viscosity, Density and Molecular Weight of Polymers

Polymer Code	Number	Weight Average (Mn) (g/mol)	PDI Start	Mw Average (Mw) (g/mol)	Intrinsic Viscosity (g/mol)
PA	453.6	558.6	1.2317	2386.5	0.150
CAM ₅	1118.5	2358.4	2.1085	28568.7	0.217

The molecular weight of synthesized homo and copolymer were determined by GPC. The molecular weight of synthesized polymers is summarized in table 5. Table 5 revels that intrinsic viscosity increases with molecular weight. Intrinsic viscosity of copolymer is more than that of homopolymer since molecular weight of copolymer is more than homopolymer.

Intrinsic viscosity of polymer is dependent on molecular weight. The dependence of intrinsic viscosity on molecular weight of polymer is given by Kuhn–Mark Howink equation as [14-16]

$$[\eta] = KM^\alpha$$

$$\log \eta = \log K + \alpha \log M$$

The molecular weight of copolymer is higher than homopolymer so intrinsic viscosity is also greater than homopolymer. In copolymerization of APM and MMA, higher reactivity of MMA long chain polymer is formed so molecular weight of CAM₅ is higher than PA.

Spectral Characterization

The purity and structure of the monomer was ascertained by FT-IR and ¹H NMR spectra. FT-IR: 3400-3300 (-NH), 1784, 1723 (CONCO) 1399(C-N), 950, 694 (CH=CH) cm⁻¹. ¹H NMR (300 MHz, TMS, DMSO-d₆, δ ppm) 7.25 (s, 2H, CH=CH); 6.72-6.79 (d, 2H in phenyl ring meta- to maleimido); 6.83-6.89 (d, 2H in phenyl ring ortho- to maleimido); 9.63 (s, 1H, CONH); 8.10-8.26 (d, 2H in phenyl ring ortho- to amide); 7.82-7.89 (t, 2H in phenyl ring meta- to amide); 4.0 (s, 1H in amine proto) and 7.56-7.77 (t, 1H in phenyl ring para- to amide). Above data of FT-IR and 1H NMR spectral analysis are confirmed the structure of APM monomer.

The structure of polymers was confirmed by FT-IR spectrum and ¹H-NMR spectrum (300MHz in DMSO- d₆) of PA is shown following peak and chemical shift. The sharp absorption band at 950

cm⁻¹ and chemical shift δ at 7.25 ppm due to CH=CH in a monomer is disappeared in FT-IR spectra (fig. 1) and ¹H NMR spectra (fig. 2). Its indicated that formation of polymer chain by opening of the double bond of vinyl group of imide ring.

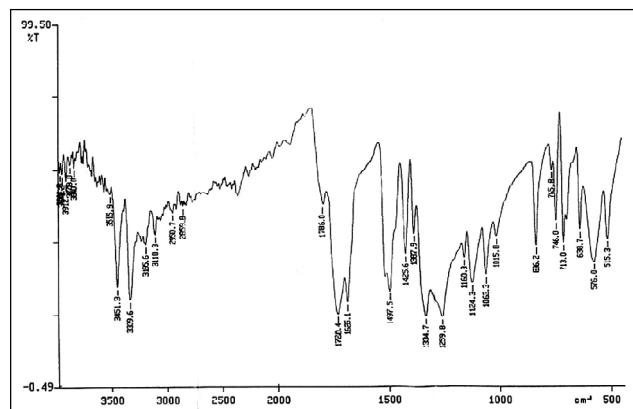


Figure 1: FT-IR spectra of PA

In FT-IR spectra (fig.1), the presence of absorption bands at 1786 and 1720 cm⁻¹ due to asymmetric and symmetric 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 1497(Ar- N stretch), 1387 (C-N stretch), 1160 (C-N-C) cm⁻¹. The strong intense band at 1625 cm⁻¹ in IR spectra was observed due to correspond to the amide group.

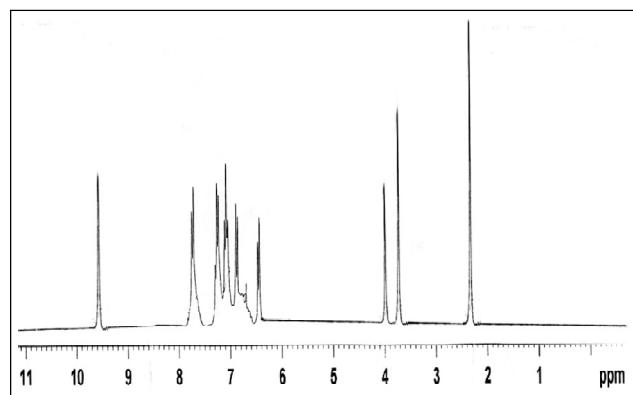


Figure 2: ¹H NMR Spectra of PA

In ¹H NMR spectra (fig. 2), the δ observed at 7.25 ppm due to CH = CH in the monomer has shifted to 3.6-3.8 ppm in the polymer, as a result of the formation of a semi flexible poly (substituted methine)-[CH-CH]_n - group[17] The broad peak at 7.0-8.1 ppm corresponds to 9 Ar-H and 4.01 ppm for the amine (-NH) proton of aniline group.

The FT-IR spectrum of CAM_5 is shown in figure 3. The major characteristic absorption bands are observed at 3400- 3300 (broad, -NH stretch), 1782, 1714 (C=O symmetric and asymmetric stretch in a five member imide ring and C=O stretch of ester), 1602, 1518 (aromatic and C=C). These characteristic bands confirm that units of both the monomers APM and MMA both are present in the copolymer samples.

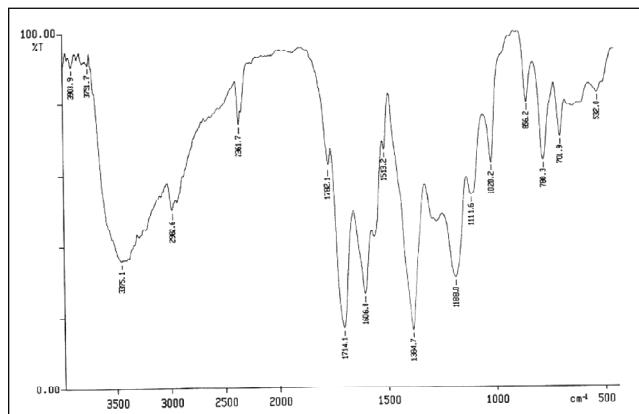


Figure 3: FT-IR Spectra of CAM_5

The ^1H NMR spectra (fig. 4) of CAM_5 showed the following chemical shifts. The δ at 6.82-8.21 ppm observed due to 9 Ar- H protons. A δ at 9.72 (broad) ppm appeared for 1H in -CONH- group of APM segment and δ observed at 4.01 ppm is 1H in -NH of aniline group. The δ observed at 3.25-3.71 ppm corresponds to overlapping of 2H -(CH₂-CH)- in the polymer main chain and 3H (-OCH₃) of MMA segment. The δ in the range 1.05-2.05 ppm is of 2H of methylene group and 3H of -CH₃ group.

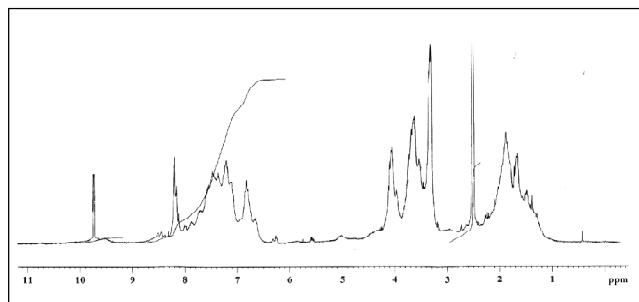


Figure 4: ^1H -NMR Spectra of CAM_5

Copolymer Composition and Reactivity Ratio

The results of free radical copolymerization of APM with MMA in THF at 65 °C in the presence of AIBN are summarized in Table 1. Copolymer composition was determined from the nitrogen-element analysis of obtained copolymer samples.

In such case percentage nitrogen of copolymer is used to estimate copolymer composition [18]. Figure 5 presented the comonomer copolymer composition curve. As shown in that figure copolymer composition was strongly influenced by the comonomer composition. The monomer reactivity ratios were calculated using Finemann-Ross [19] method (Fig. 6). The equation was given by Fineman and Ross (FR):

$$\frac{X_1(F_1 - F_1)}{X_2 F_1} = -r_2 + \frac{F_2 X_1^2}{F_1 X_2^2} r_1$$

or

$$\frac{X_1(1 - 2F_1)}{(1 - X_1)F_1} = -r_2 + \frac{(F_1 - 1)X_1^2}{F_1(1 - X_1)^2} r_1$$

or

$$a_2 = r_2 + a_1 r_1$$

Where $a_2 = X_1(1-2F_1) / (1-X_1)F_1$ and $a_1 = X_1^2(F_1-1) / (1-X_1)^2F_1$. A plot of the left hand side $X_1(1-2F_1)/(1-X_1)F_1$ versus $X_1^2(F_1-1)/(1-X_1)^2F_1$ gives the r_1 and r_2 as the slope and the intercept, respectively. The values of r_1 (APM) and r_2 (MMA) are given in Table 6.

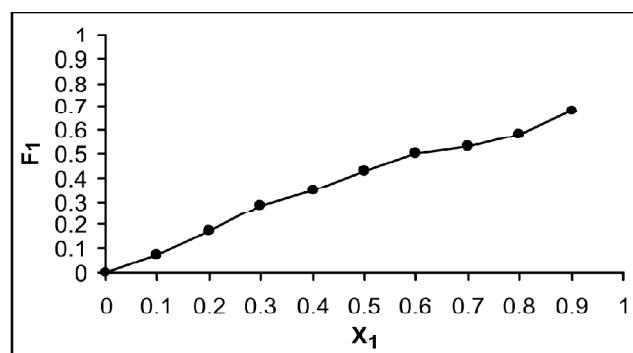


Figure 5: Dependence of the Copolymer Composition F_1 on the Comonomer Feed Composition X_1 for Radical Copolymerization of APM (M_1) and MMA (M_2)

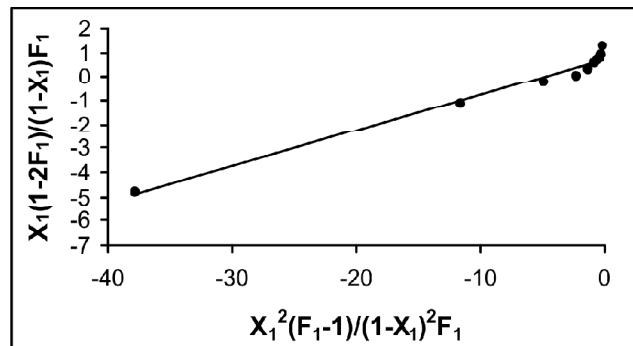


Figure 6: Fineman-Ross plot for CAM

The Q_1 and e_1 values for the APM monomer, calculated using the Alfrey and Price equation [20] are presented in Table 6. The Alfrey-Price Q-e schemes form the reactivity ratios:

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

$$r_1 r_2 = \exp[-(e_1 - e_2)^2]$$

For this purpose values of $Q_2 = 0.74$ and $e_2 = 0.40$ for MMA were used according to literature data [21] and the relative values of Q_1 and e_1 for APM were calculated.

Table 6
Monomer Reactivity Ratio in Copolymer

System	r_1	r_2	Q	e
APM -MMA	0.14	0.72	0.23	2.25

The value of r_1 is lower than r_2 and less than unity. This value indicates weakly ordered with predominantly random distribution of the monomer units in copolymer chain. The value of Q_1 and e_1 obtained are large. The large e_1 value correlates with strong electron acceptor nature on the maleimide monomer.

Thermal Properties

It is well known that polymaleimide is potential heat-and chemical-resistant material, so maleimide is widely used as a comonomer for modified polymeric systems. Only single step degradation at temperature over 300 °C was observed for polymaleimide in TGA. The thermograms were obtained by heating homopolymer and copolymer sample in air at 10 °C/min and shown in figure 7 and 8. The synthesized maleimide polymers degrade in two steps. The first decomposition step occurred around 380°C, which may corresponds to the decomposition of aromatic amide segment and aliphatic alkyl ester segment of MMA in copolymer. The second step is degrading around 500°C, which may correspond to the rigid imide segment of maleimide unit in polymer.

The initial decomposition temperature T_i , temperature for maximum weight loss T_{max} , and

final decomposition temperature T_f of first and second degradation steps are given in table 7. The results in table 7 indicate that the relative thermal stability on the basis of T_i follows on the order PA>CAM₅.

Table 7
Thermal Behaviour of Homopolymer and Copolymer

Polymer Code	Degradation Step	T_i °C	T_{max} °C	T_f °C	Residue at 500 °C
PA	I	294	330	380	40 %
	II	405	460	580	
CAM ₅	I	250	325	370	22%
	II	380	470	510	

Table 7 reveals that the content of APM in the feed is 100% in the homopolymer began to decompose at higher T_i and weight loss for the first step became smaller. The first step weight loss ranged from 32-37%. The weight loss for the second step became larger increasing from 45-48%. The total weight loss of PA upto 500 °C is 60%.

Table 7 reveals that the copolymer CAM₅ decomposes through a two-step procedure. As the copolymer sample content of APM is 50%, the copolymer began to decomposition at lower T_i and weight loss for the first step became larger as compared to homopolymer. The first step weight loss was in range 50 to 52 %. The weight loss for second step is 25 to 30%. The total weight loss of CAM₅ upto 500 °C is 88%. The results of percentage weight loss suffered from 100 °C to 600 °C at 100 intervals are furnished in table 8.

Table 8
Percentage Weight Loss of Homo and Copolymer at Various Temperatures from the TGA

Polymer Code	200 °C	300 °C	400 °C	500 °C	600 °C
	Weight loss (%)				
PA	1.2	10.2	40.9	59.6	68
CAM ₅	1.6	20.3	563	78.8	81

Figure 7 and 8 shows that at initial decomposition temperature (T_i), the decomposition of polymer is start and weight loss of polymer is very low. In polymer PA 8-9% weight is loss at T_i and copolymer CAM₅ 4-5% weight is loss at T_i .

Table 8 revels that weight loss was below 20 to 22% up to 300 °C in copolymer sample & 100% content of APM feed in homopolymer weight loss

was below 10 % up to 300 °C. The results in table 7 indicate that the thermal stability tends to increases from the copolymer to homopolymer.

It is evident that the PA degrades at high temperature than the copolymer. In copolymer – CH₂-C- linkage of vinyl monomers is present in polymer backbone with maleimide unit. The decomposition of the alkyl ester group in the side chain is start and lower temperature due to olefin elimination by thermolysis [22]. Due to this, degradation of copolymer is start at lower temperature with respect to homopolymer.

CONCLUSION

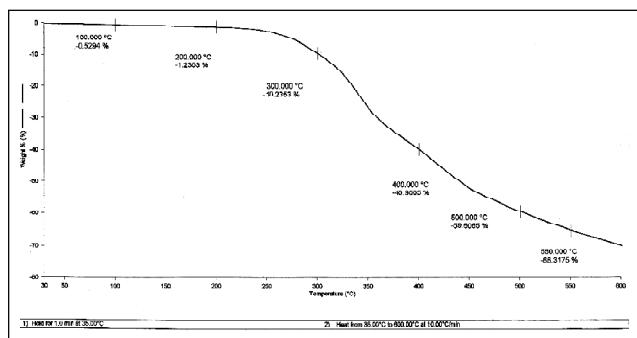


Figure 7: TGA Curve of PA

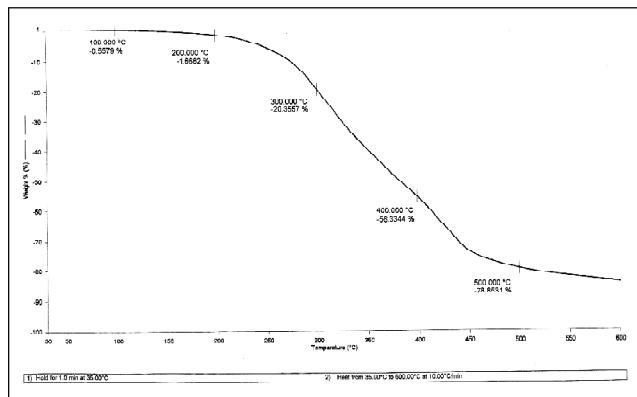


Figure 8: TGA Curve of CAM₅

The N-[4-N'-(anilino amino carbonyl) phenyl] maleimide was synthesized and homo and copolymers have been synthesized using free radical initiator. The most suitable solvent initiator pair for the synthesis of homo and copolymer was found to be AIBN-THF. The synthesized polymers show better solubility in many more solvents. The value of reactivity ratio of both monomers shows that vinyl monomer is more reactive than maleimide monomer during

polymerization. The polymers was characterized by intrinsic viscosity, molecular weight and solubility. The structure of polymers was confirmed by FT-IR spectra and ¹H NMR spectral analysis. The thermal behaviour was studied by TGA. It was observed that such polymers have better thermal stability than the polymers of vinyl monomers.

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