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Free Radical Initiated Polymerization of N-[4-N′-{(4-chlorophenyl) amino-carbonyl} phenyl] Maleimide and Characterization of Homopolymer and Copolymers with MMA

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N-[4-N′-{(4-chlorophenyl) amino-carbonyl} phenyl] maleimide (N-CPACPMI) was prepared. It was homopolymerized and copolymerized with methyl methacrylate (MMA) in order to study the effect of imide ring in polymer backbone. The copolymer composition was determined by nitrogen element analysis. The monomer reactivity ratio was determined by the Fineman-Ross method. The molecular weight was determined by GPC. The thermal behavior was studied by thermogravimetric analysis. The initial decomposition temperature of polymers were in the 255 to 299°C range.

Keywords: Free radical, maleimide, reactivity ratio, molecular weight, TGA

1 Introduction

At present there is considerable interest in free radical polymerization and copolymerization of N-substituted maleimide (1–5). Polymers of N-substituted maleimide show excellent thermal stability due to a five-membered imide ring rigid backbone. Maleimide based copolymers have been found to have versatile applications in many industries ranging from aerospace to microelectronics field (6, 7). N-substituted maleimides polymerize readily in the presence of a radical initiator to give polymers having heat resistance and better mechanical properties (8–12). Among these polymers, N-(4-carboxy phenyl maleimides are the most attractive classes of polymers due to introduction of phenyl group, molecular motion of the main chain in the polymer is prevented (13,14). In this study, N-[4-N′-{(4-chlorophenyl) amino-carbonyl}phenyl) maleimide (N-CPACPMI) was prepared and its polymerization and copolymerization with MMA is reported. The physical, spectral and thermal properties were undertaken in order to characterize the polymers.

2 Experimental

2.1 Materials

p-Aminobenzoic acid and maleic anhydride 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 h and distilled. The head and tail fractions were discarded. 2,2′-Azobis–isobutironitrile (AIBN) (spectorchem.) was recrystallized twice from methanol prior to use. BPO (benzoyl peroxide, CDH) was used as received. THF was purified by distillation after being refluxed for 2 h in the presence of sodium (15). Dioxane and DMSO were used after distillation. DMF and methanol used in the present work were of analytical grade and were used as received.

2.2 Measurements

^{1}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 samples were recorded on a Shimadzu 8201 PC (4000–400 cm^{-1}) FT-IR spectrometer, using a KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.2°C, using an Ubbelohde suspended level viscometer.

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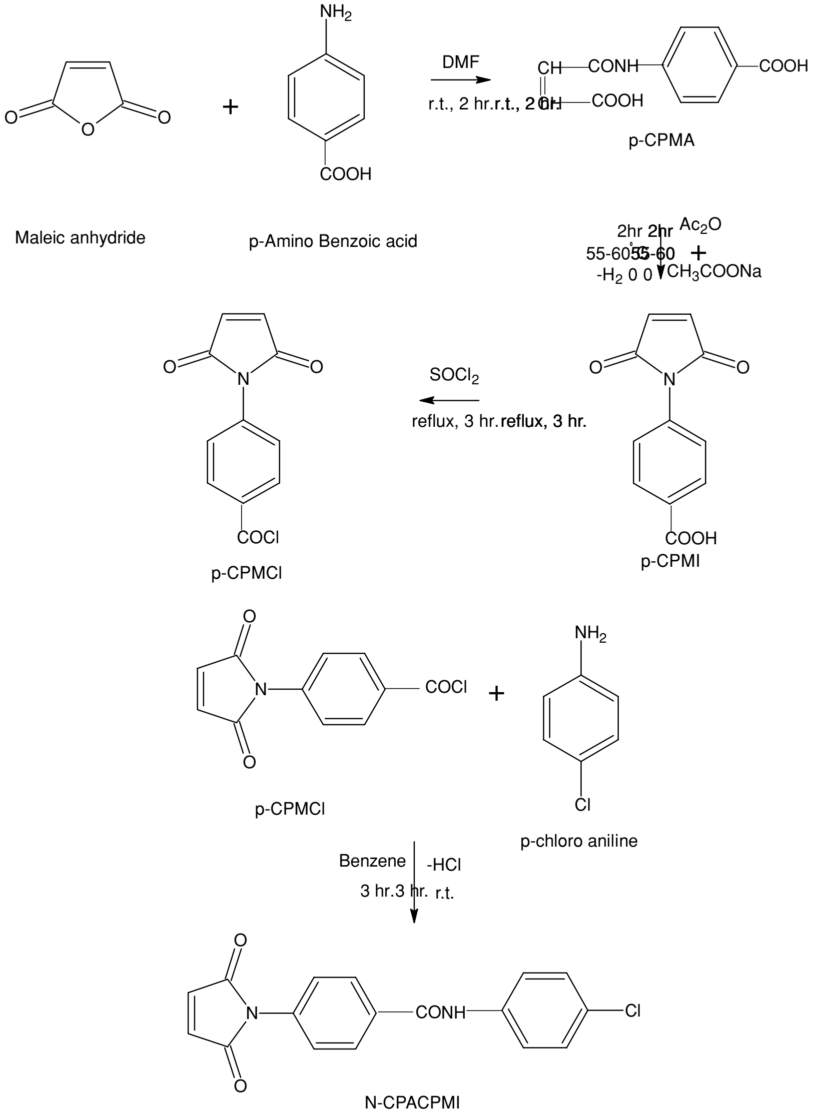


Sch. 1. Synthesis of Monomer.

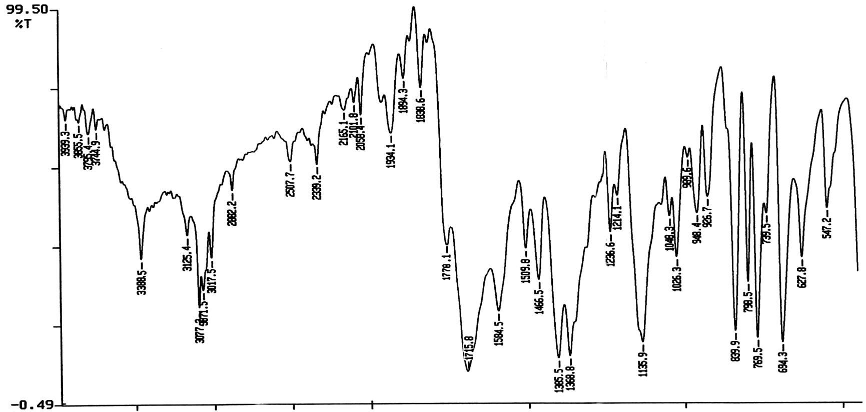


Fig. 1. FT-IR Spectra of N-CPACPMI.

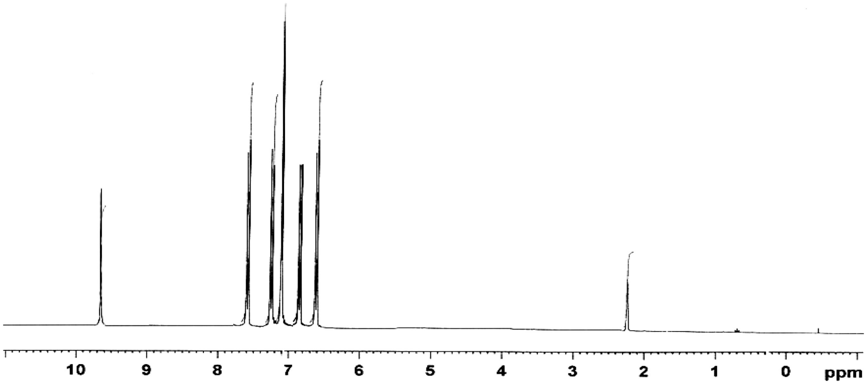


Fig. 2. ^{1}H-NMR Spectra of N-CPACPMI.

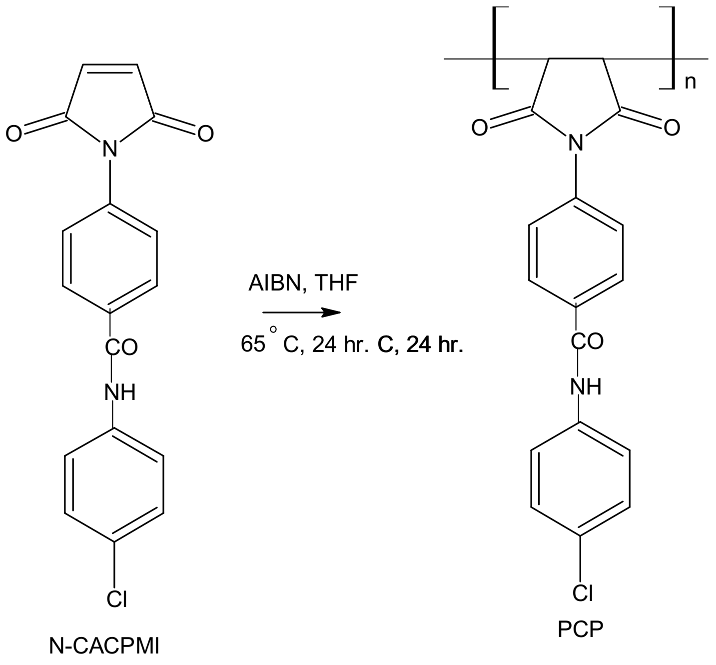
Elemental analysis was made on a Carlo Erba Model NA 500 series analyzer. The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10°C/min from 0°C to 600°C

2.3 Methods

N-CPACPMI monomer was synthesized in four steps from maleic anhydride, p-aminobenzoic acid and 4-chloro aniline (described below and shown in Scheme 1). N-[4-(Chlorocarbonyl) phenyl) maleimide (p-CPMCl) was prepared using p-aminobenzoic acid, maleic anhydride and thionyl chloride according to a previously published procedure (16).

2.4 Synthesis of N-[4-N′-{(4-chlorophenyl) amino-carbonyl} phenyl) Maleimide

A benzene solution of p-chloro aniline (0.5 mol in 75 ml benzene) was added dropwise to a CPMCl (11.75 gm 0.5 mol) solution in benzene (100 ml) at 0–5°C. The mixture was stirred at room temperature for 3 h. The precipitated product was filtered, washed with water, dried and then recrystallized twice from ethanol to obtain pure N-CPACPMI (mp 148°C) in 68% yield. The purity and structure of the monomer was ascertained by IR and ^{1}H-NMR spectra (Figs. 1 and 2). FT-IR Spectrum (KBr, wave number cm^{-1}): 3400–3300 (-NH), 1509 (CONH), 1778, 1715 (CONCO) 1385(C-N), 948, 694 (CH=CH) cm^{-1}. ^{1}H NMR (300 MHz, TMS, DMSO-d_6, δ ppm) 7.14 (s, 2H, CH=CH); 6.62–6.71 (d, 2H in phenyl ring meta- to maleimido);



Sch. 2. Homopolymerization.

Table 1. Free radical polymerization and copolymerization of N-CPACPMI with MMA in THF at 65°C.

	Feed Mol Fraction				
Polymer Code	*N-CPACPMI*	*MMA*	*Polym. Time*	*Yield (%)*	*Appearance*
$CCPM_1$	0.1	0.9	12	71.50	L. Yellow-Solid
$CCPM_2$	0.2	0.8	12	69.10	L. Yellow-Solid
$CCPM_3$	0.3	0.7	12	65.80	L. Yellow-Solid
$CCPM_4$	0.4	0.6	12	64.70	L. Yellow-Solid
$CCPM_5$	0.5	0.5	12	62.30	Yellow-Solid
$CCPM_6$	0.6	0.4	12	58.40	Yellow-Solid
$CCPM_7$	0.7	0.3	12	56.15	Yellow-Solid
$CCPM_8$	0.8	0.2	12	55.40	Yellow-Solid
$CCPM_9$	0.9	0.1	12	53.15	Yellow-Solid
PCP	1.0	0.0	24	52.62	Yellow-Solid

Table 2. Percentage yield of and physical properties of homo and copolymaleimides in various solvent-initiator systems

PolymerCode	*Solvent*	*Yield %*	*Yield %*	*Appearance*
PCP	THF	52.62	50.28	Yellow
	DMF	36.18	38.60	Brown
	1,4-Dioxane	48.80	48.00	Yellow
	DMSO	36.70	36.10	Red
	Ethyl acetate	51.70	52.30	Yellow
$CCPM_5$	THF	62.30	55.80	Yellow
	DMF	40.30	42.70	Brown
	1,4-Dioxane	60.18	62.00	Yellow
	DMSO	42.80	40.10	Red
	Ethyl acetate	61.25	56.70	Yellow

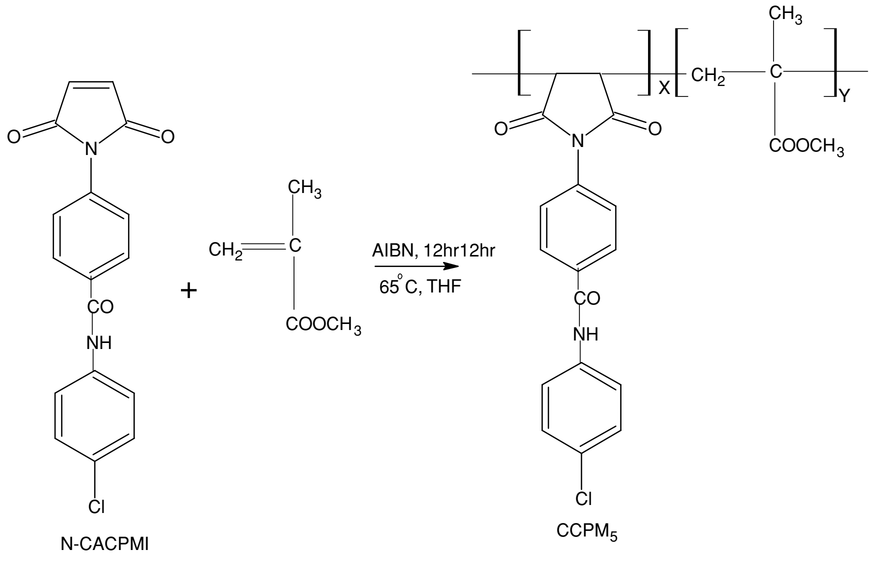
6.81–6.92 (d, 2H in phenyl ring ortho- to maleimido); 9.73 (s, 1H, CONH); 7.62–7.73 (d, 2H in phenyl ring ortho- to amide); 7.25–7.35 (t, 2H in phenyl ring meta- to amide).

Table 3. Percentage yield of homo and copolymaleimide in different time in THF at 65°C.

	% Yield				
Polymer Code	*12 h*	*18 h*	*24 h*	*30 h*	*36 h*
PCP	20.18	22.10	25.15	28.70	44.56
$CCPM_5$	40.88	44.15	54.28	56.20	57.70

2.5 Homopolymerization

The homopolymerization of N-CPACPMI monomer was carried using AIBN as a free radical initiator in THF at 65°C (described below and shown in Scheme 2). After a prescribed time the mixture was poured into a large amount of methanol to precipitate the homopolymer. The precipitated homopolymer was washed with methanol several times and dried in vacuum oven at 70°C. A summary of polymerization conditions and physical characteristics of



Sch. 3. Copolymerization

Table 4. Parameters for Fineman-Ross method to determine the reactivity ratios of monomers

Polymer Code	*Mole ratio Feed*	*Mole Fraction of N-CPACPMI*			
	$x_1{:}x_2$	*Feed* X_1	*Copolymer* F_1	$X_1^2(F_1\text{-}1)\ F_1\ (1\text{-}X_1)^2$	$X_1(1\text{-}2F_1)\ (1\text{-}X_1)\ F_1$
$CCPM_1$	1:9	0.1	0.082	−0.1381	1.1327
$CCPM_2$	2:8	0.2	0.195	−0.2580	0.7820
$CCPM_3$	3:7	0.3	0.290	−0.4496	0.6206
$CCPM_4$	4:6	0.4	0.351	−0.8218	0.5676
$CCPM_5$	5:5	0.5	0.440	−1.2727	0.2727
$CCPM_6$	6:4	0.6	0.495	−2.6233	0.0303
$CCPM_7$	7:3	0.7	0.570	−4.1072	−0.6405
$CCPM_8$	8:2	0.8	0.632	−9.3164	−1.6708
$CCPM_9$	9:1	0.9	0.718	−31.8134	−5.4662

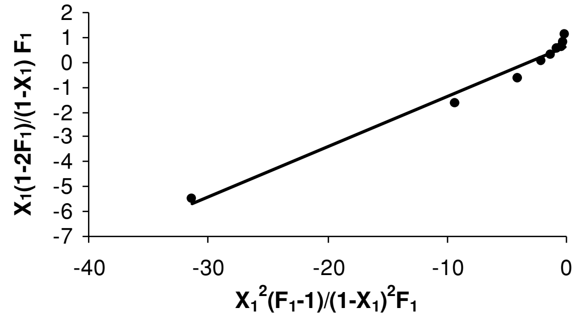


Fig. 3. Fineman-Ross plot for CCPM.

Table 5. Monomer reactivity ratios r_1 and r_2 and Q and e values of maleimides in copolymerization systems

System	r_1	r_2	*Q*	*e*
N-CPACPMI-MMA	0.20	0.63	0.30	2.10

homopolymer PCP are presented in Table 1. Homopolymerization was also carried out using different solvent-initiators and time. The physical properties and percentage yields of homopolymer samples, using different solvent/initiator systems and time are presented in Tables 2 and 3.

2.6 Copolymerization

The copolymerization of N-CPACPMI monomer was carried using AIBN as a free radical initiator in THF at 65°C (described below and shown in Scheme 3). After a prescribed time, the mixture was poured into a large amount of methanol to precipitate the copolymer. 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. Finally obtained crude was filtered and dried in vacuum at 70°C.

The copolymerization was also carried using different feed ratio of comonomer and nine copolymer samples were synthesized. The polymerization conditions and physical properties are presented in Table 1.

Copolymerization of equimolar amount of comonomers was also carried using different solvent-initiators and time. The physical properties and percentage yields of homopolymer samples, using different solvent/initiator systems and time are presented in Tables 2 and 3.

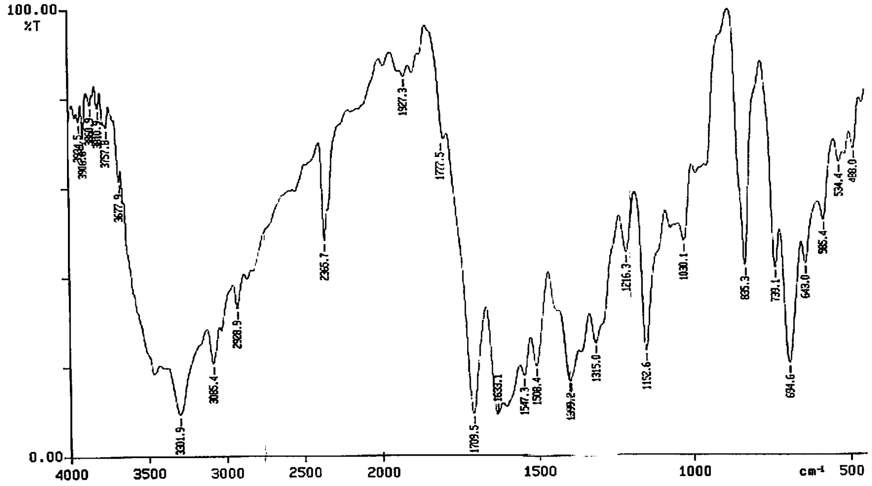


Fig. 4. FT-IR spectra of PCP.

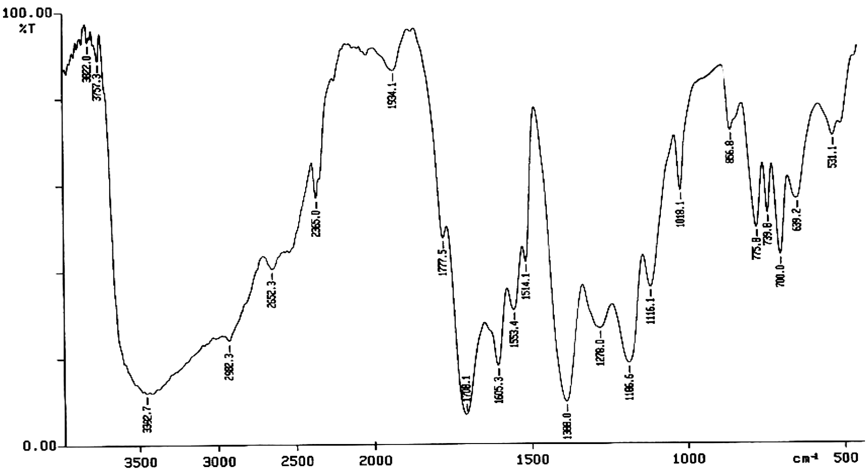


Fig. 5. FT-IR spectra of $CCPM_5$.

3 Results and Discussion

3.1 Monomer Reactivity Ratio and Copolymer Composition

The copolymerization data for the N-CPACPMI and MMA are listed in Table 4. The data were calculated by Fineman Ross method (17). The straight line was determined by the least square rule shown in Figure 3. The slope of this line indicates the reactivity ratio of N-CPACPMI and intercept of the line indicates the reactivity ratio of MMA. The Q_1 and e_1 values for the N-CPACPMI monomer were calculated using Alfrey-Price equation (18) and presented in Table 5. The value of r_1 is lower than r_2 and less than unity. This value indicates that the reactivity of MMA is higher than the maleimide unit. The Q_1 and e_1 obtained are large. The large e_1 value correlates with a strong electron acceptor nature on the maleimide monomer.

Table 6. Solubility behaviour of monomer, homopolymer and copolymer in polar and non-polar Solvents at 30°C.

Solvent	*N-CPACPMI*	*PCP*	*$CCPM_5$*
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	S	S
Chloroform	S	PS	S
CCl_4	IS	IS	S
Xylene	IS	IS	PS
Toluene	IS	IS	PS
Benzene	IS	PS	S
n-Hexane	IS	IS	PS
Ethyl acetate	S	IS	S

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

3.2 Solubility of Polymers

Table 6 summarizes the relative solubilities of homo and copolymer samples in a number of polar and non-polar solvents at 30°C. The investigated homo and copolymer both samples are soluble in THF, DMF, DMSO, acetone, 1,4-dioxane, cyclohexanone and dichloromethane. the Individual copolymer is soluble in benzene and ethyl acetate and partially soluble in n-hexane, xylene and toluene. Solubility behavior in later solvents depends on the composition

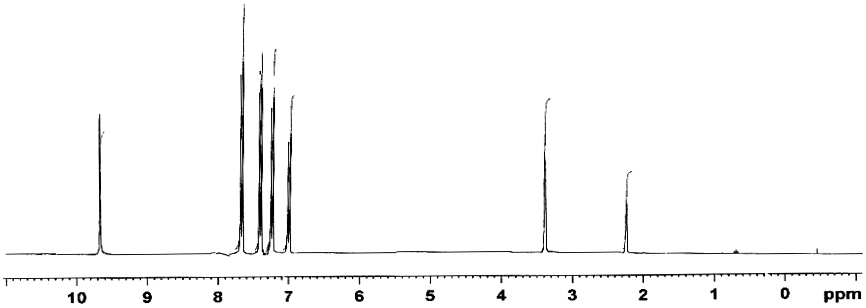


Fig. 6. ^{1}H-NMR spectra of PCP.

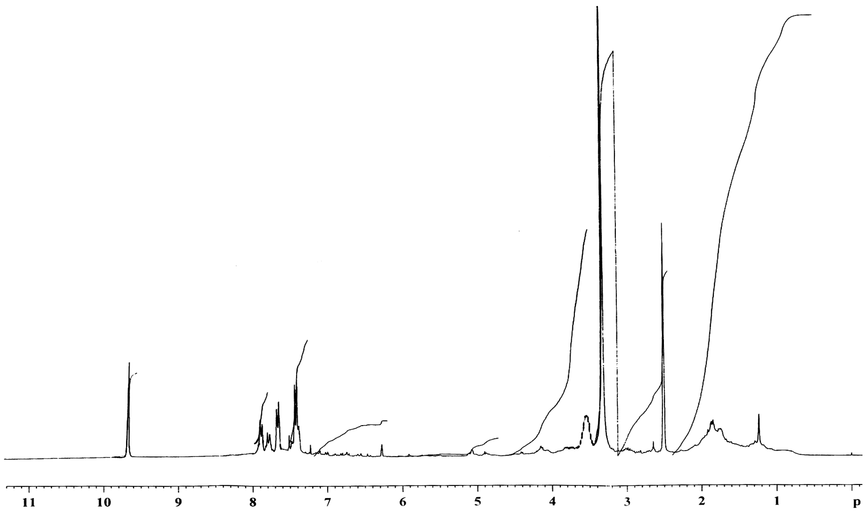


Fig. 7. H-NMR spectra of $CCPM_5$.

of polymer. The solubility of copolymer is more than the homopolymer in the solvent taken.

3.3 Effect of Solvent-Initiator and Time on Polymerization

The yield and physical properties of homo and copolymer in various solvents are given in Table 2. Table 2 indicates that a better yield is obtained at THF-AIBN solvent initiator system. This result indicates that the stability and life of radical of AIBN is more than BPO. The yields of homo and copolymer obtained at different times are presented in Table 3, which indicates that the yield of polymer increases with increasing time.

3.4 Spectral Characterization

The FT-IR spectra of homopolymer PCP is shown in Figure 4. In the IR spectra, a shoulder peak at 1777, 1709 cm^{-1} is attributed to the symmetric and asymmetric stretching of the carbonyl group in the imide ring only. Its peaks indicate that the imide ring remained intact during polymerization. The peak at 1584 cm^{-1} assigned to the CH stretching of imide ring of monomer is absent in polymer and indicates that polymerization occurs by opening of the double bond.

In ^{1}H-NMR spectra (Fig. 5) the signal at 7.14 ppm assigned to the vinyl proton of the N-CPACPMI monomer is absent and a new broad signal appears around 3.52 ppm which is assignable to the semi-flexible polymethine $-[CH\text{-}CH)_n$- protons. The FT-IR spectra of copolymer $CCPM_5$ are shown in Figure 6. For $CCPM_5$ copolymer, absorption band of the C=C with imide ring (948 cm^{-1}) and vinyl group at 990 cm^{-1} of MMA disappeared completely. The absorption of the –NH stretch of amide (3400–3300 cm^{-1}), CO symmetric and asymmetric stretch of imide ring at 1777, 1708 cm^{-1} and 1186 cm^{-1} for COC stretching of acrylate unit. These results indicate the presence of both monomeric units.

The result was further identified by ^{1}H-NMR spectra (Fig. 7). The aromatic protons from broad absorption at 7.31–8.21 ppm and amide proton are observed at 9.51 ppm. The peak at 3.42 ppm are assigned to the absorption of the $-[CH\text{-}CH)_n$- protons within maleimide ring and peaks at

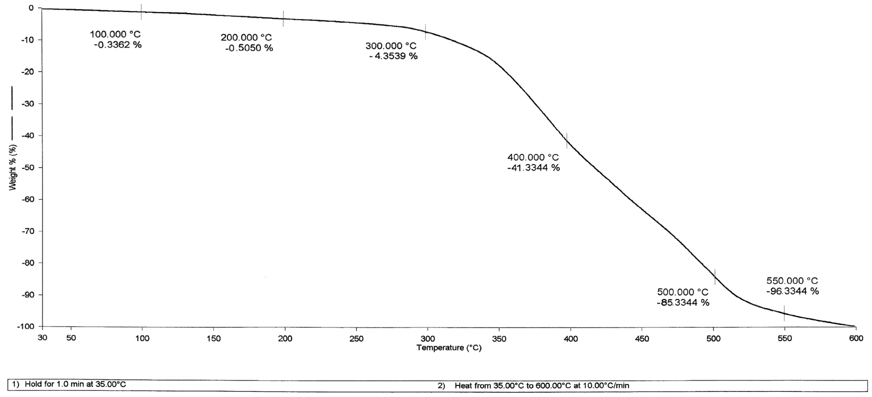


Fig. 8. TGA Curve of PCP.

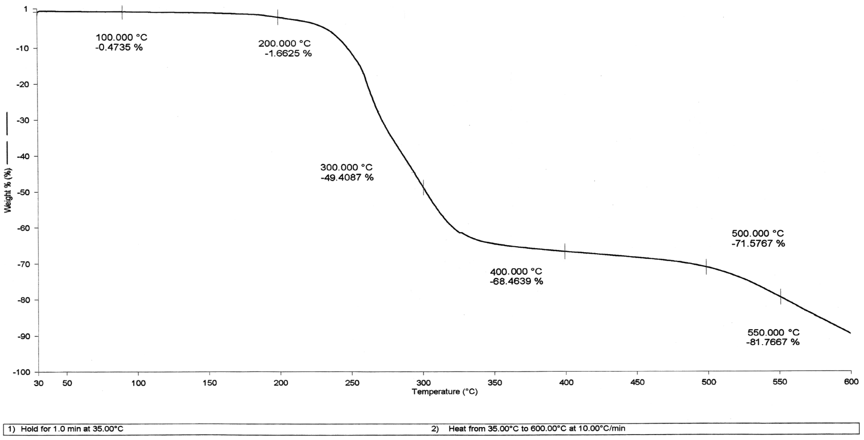


Fig. 9. TGA Curve of $CCPM_5$.

1.76–1.21 ppm to the absorption of methylene group of MMA. These spectral data confirmed that the polymerization reaction happened via the opening of double bond of both monomers.

3.5 Thermal Properties

Thermal stability of the homopolymer, PCP and copolymer, $CCPM_5$ was investigated by TGA. TGA was carried out in air atmosphere at heating rate of 10°C/min. The TGA curve shown in Figures 8 and 9 and thermal stability data are given in Table 7. These polymers and copolymers showed excellent stability similar to poly(N-PMI) and poly(N-alkyl PMI).

Figure 8 shows the thermal behavior of the homopolymer PCP. The homopolymer of N-CPACPMI begins to degrade at around 300°C and performs decomposition in two steps. The homopolymer, losing about 50% of its weight at 450°C and the other 50% decomposes completely at about 600°C. Figure 9 shows the thermal behavior of the copolymer $CCPM_5$. The degradation of copolymer starts at around at 255°C and performs a two-step degradation. The weight loss of the first step is higher than the second step. The comparisons of thermal degradation of PA and copolymer $CCPM_5$ which contain an equimolar amount of comonomers are shown in the figures. It is evident that the homopolymer degrades at a higher temperature than the copolymer. The lower T*i* for copolymer $CCPM_5$ may be due to the decomposition of the alkyl ester groups in the side chain presumably due to olefin elimination by thermolysis, (19) which could start at a lower temperature than the decomposition temperature of the polymaleimide accompanying the main chain scission.

Table 8. Percentage weight loss of homopolymer and copolymer at various temperatures

	Weight loss (%)				
Polymer Code	200°C	300°C	400°C	500°C	600°C
PCP	0.5	4.3	41.3	85.3	99
$CCPM_5$	1.6	49.4	68.4	71.5	91

4 Conclusions

The free radical homopolymerization of N-CPACPMI and copolymerization with MMA has been carried out in THF at 65°. The most suitable initiator–solvent pair for the homo and copolymerization was found to be AIBN-THF. The investigated homo and copolymaleimide show excellent solubility in THF, DMF, DMSO, acetone, 1, 4-dioxane and cyclohexanone. The characterization of homo and copolymer was carried out by elemental, IR and ^{1}H-NMR spectral analysis. The value of reactivity ratio of MMA is higher than N-CPACPMI, indicates that MMA is more reactive than N-CPACPMI monomer. The synthesized polymers have good thermal stability and degrade in two steps. The

Table 7. Thermal behavior of homopolymer and copolymer

Polymer Code	*Degradation Step*	$T_i^\circ C$	$T_{max}^\circ C$	$T_f^\circ C$	*Residue at 500° C*
PCP	I	299	380	430	15%
	II	445	510	590	
$CCPM_5$	I	255	340	450	29%
	II	495	560	600	

homopolymer possessed better thermal stability than the copolymer and it degraded in two-steps.

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