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Copolymerization of Methyl Acrylate with N-4-Methyl phenyl maleimide and characterization of of the polymers

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ABSTRACT

The N-[4-methyl phenyl) maleimide (MPM) was prepared by maleic anhydride and 4-Toludin. It was homo polymerized and copolymerized with methyl acrylate (MA) in order to study the effect of imide ring in polymer backbone. The homo and copolymerization were carried out in different time and solvent initiator system. The molecular weight was determined by gel permeation chromatography (GPC).The intrinsic viscosity and solubility were determined to characterize the polymers. The structure was elucidated by FT-IR and ^{1}HNMR spectral studies. The thermal behavior was studied by thermo gravimetric analysis. The initial decomposition temperature of polymer was 224° C.

Keywords:- acrylate-malemide copolymers, MA, molecular weight, thermo gravimetry(TGA).

INTRODUCTION

Aromatic polyimides are one of the most important classes of high-performance polymers**.** In the modern technology, the polymer with high thermal stability and excellent mechanical properties are in great demand [1, 2].polymers containing aromatic and/or heterocyclic ring structures are known to have excellent thermal stability because of minimal number of oxidizable hydrogen atoms and high extent of double bond conjugation. Polyimides represent a class of useful heat resistant materials among the thermally stable hetero aromatic polymers [3]. Polymers are widely used in several technological applications. The high demand for new materials requires the preparation of new polymers with enhanced mechanical and thermal properties and the copolymerization technique has been widely used to achieve this target [4]. The incorporated five member planer ring in the backbones of the copolymer ensures higher glass transition temperature, Tg and higher thermal degradation temperature. So N-substituted maleimides are widely used to enhance the heat resistance of polymers such as poly styrene, poly (alkyl methacrylate), poly (vinyl acetate) and poly (vinyl-chloride), [5-11]. N-substituted maleimide polymerize readily in the presence of a radical initiator to give polymers having heat resistance and better mechanical properties [12-16]. Maleimide based copolymers have been found to have versatile applications in many industries ranging from aerospace to micro electronics field [17-18]. We report here the synthesis of monomer, N-(4-chloro-2-nito-phenyl) maleimide and its homopolymerization and copolymerization with MMA. It was found that such copolymers have excellent thermal stability than the polymers of vinyl monomers. Studies of physical, spectral and thermal properties have been carried out in order to characterize the polymers. The effect of different feed ratio of monomers on the properties of copolymers has been examined. The homo and copolymer also synthesized in different solvent-initiator and different time.

EXPERIMENTAL SECTION

Materials

Maleic anhydride was first recrystallized from chloroform and then further purified by sublimation at 50°C. 4-Toludin (CDH, Pure), P_2O_5, and H_2SO_4 were used as received. MA (SDF, AR) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous $CaCl_2$ for 6 hr and distilledAIBN (spectrochem) was recrystallized twice from methanol prior to use DMF, methanol, DMSO etc. used in the present work were of analytical grade and purity better than and were used as received. THF was purified by distillation after being refluxed for 2hr. in the presence of sodium

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 200/300MHz. The internal reference used was TMS. FT-IR spectra were taken in a shimadzu 8201 PC (4000-400 cm^{-1}) FT-IR spectrometer, using KBr pellet technique. The viscosity measurements Ubbelohde viscometer. The thermo grams in air were obtained on a mettle TA-3000 system, at heating rate of 10°C /min.

Method:-

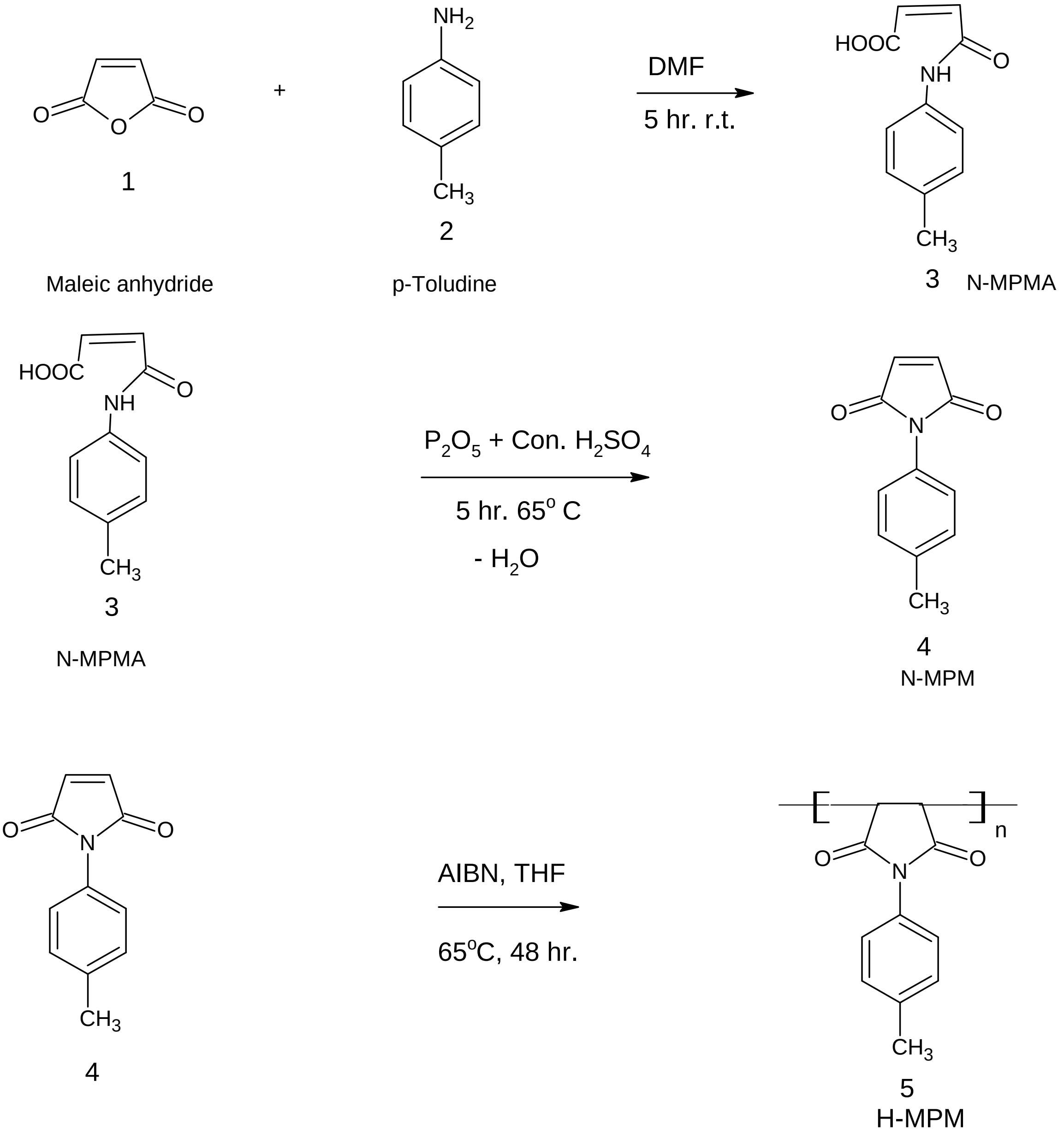
Synthesis of N-(Methyl-phenyl) maleimide (MPM) monomer has been prepared in two steps from maleic anhydride and 4-Toludin.

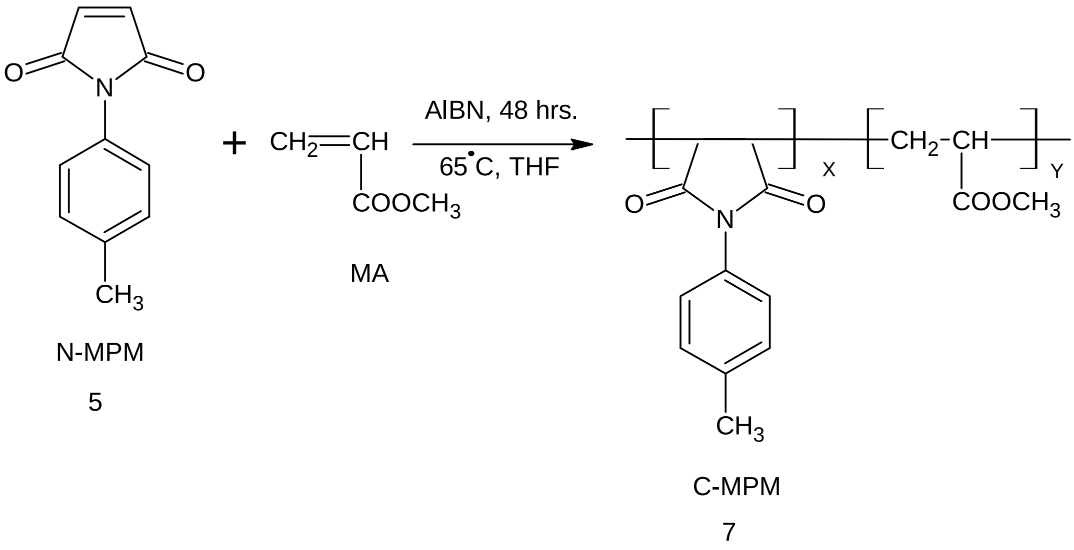
Synthesis of N-(Methyl-phenyl) maleimic acid (N-MPMA)

The solution of maleic anhydride (9.81 g, 0.1 mol) in DMF was gradually added over a period of 15 min to a well stirred solution of 4-toludin (10.8 g, 0.1 mol) in DMF. The solution was stirred for 5 hr. at room temperature. The solution was poured into crushed ice. Yellow precipitate of MPMA was obtained. The precipitate was filtered and dried at 55°C and then recrystallized from ethyl alcohol to obtain pure MPMA in a 80% Yield (m.p. 100^{0}C). The IR spectrum showed absorption bands at 3150-2680 (carboxylic acid O-H), 3310-NH, 822 (CH=CH), 670 (C-H bending) in cm^{-1}.

Synthesis of N-(4-Methyl-phenyl) Maleimide (N-MPM):

N-(Methyl-phenyl) maleimic acid (0.1 mol) in 70 ml DMF was taken in a flat round-bottomed flask. The solution was treated with conc. H_2SO_4 and P_2O_5. The whole solution was stirred for five hours. The resulting solution was poured in cooled water and yellow precipitate was obtained. It was recrystallized from ethyl alcohol. Yield was 70%, m.p. 98^0C). The IR spectrum showed absorptions bands at 3175 cm^{-1} (CH=CH), 2960 cm^{-1} (CH_3) str. 1709 -1770 cm^{-1}(C=O str. five member imide ring), 1460 cm^{-1}(aromatic C=C str.), 762 cm^{-1} (C=C) str. ^{1}HNMR 5.24 ppm (–CH), 7.34-6.90 (m, Ar′) 2.5 (–CH_3 ,S)





N-MPM 5

MA

C-MPM 7

Reaction scheme

Polymerization:-

Homopolymerization: - N-(Methyl-phenyl) MI (2.25 gm for 0.01 mol) and 40 ml THF were taken in a flat round-bottomed flask and the initiator AIBN was added. The solution was reflux for 48 hr at 65°C. The homopolymer was isolated by using an excess quantity of methanol water-mixture. The crude H-MPM was purified by dissolving it in THF and precipitating from a methanol water mixture. It was dried under vacuum at 60°C. The homopolymerization was carried out for different time and the yields are given in Table 5. Percentage yield of homopolymer in various solvent –initiator systems are given in Table.6

IR (KBr) cm^{-1} 3082 (Ar-H), 1772, 1713 (C=O), 1512 (-CH), 1390 (C-N), 833(p-sub.). ^{1}HNMR δ 2.4 ppm (–CH_3), 7.0-8.2 (m, Ar′).

Copolymerization: - The copolymerization was carried out at 65°C for 18, 24, 30, 36, 48, 54 h. employing equimolar amount of co monomers MA and N-MPM in 40 ml THF with 0.25 mg AIBN. The copolymer was isolated from an excess quantity of methanol containing water. After dissolving the crude copolymer in THF, it was precipitated from an excess quantity of methanol water mixture. The process was repeated three times to purify the copolymer sample. The precipitated copolymer was washed with methanol several times and dried at 60° under vacuum. The copolymer sample was prepared using different feed ratio of co monomers are given in Table 7. Copolymerization was carried out for different time and yield are given in Table 5 percentage Yield of copolymer in various solvent –initiator systems are given in Table 6.

IR (KBr) cm^{-1} 3078(Ar-H), 1745, 1735 (C=O), 1447-1508 (NO_2), 1342 (C-N), 1208 (C-O-C), 1150 (C-C) ,822 (C-Cl). ^{1} HNMR δ 2.5-2.9 (–CH), 6.27-7.15 (m, Ar′), 3.1 (CH_3), 2.9 (CH_2), 3.6 (OCH_3).

RESULTS AND DISCUSSION

The monomer N-(4-Methyl-phenyl) maleimic acid **3** have been synthesized by the treatment of 4-Toludin with maleic anhydride. Which is confirmed by 3150-2680cm^{-1} owing to carboxylic-OH str. as well as -NH str. at 3310 cm^{-1} in IR spectrum. Compound **3** react with P_2O_5+H_2SO_4 after the cyclodehydration of acid into imide give compound **4** N-(4-Methyl-phenyl) maleimide. Synthesis of this compound is conformed of disappear of both carboxylic acid and NH band in IR region and we get two new band 1770, 1709due to synthesis of C=O functional group. Compound N-(4-Methyl-phenyl) maleimide was reflux at 48 hr. in the present of AIBN in THF solvent gave homopolymer **5**. It shows C-C at 1170 cm^{-1} IR and δ 2.4 CH_3 of $(–CH–CH–)_n$ in ^{1}HNMR spectra. Compound N-(4-Methyl-phenyl) maleimide further reflux at 48 hr. with methyl acrylate in the presence of AIBN in THF at 65^0 C gave co-polymer **7** of compound **4** which give C-O-C str. 1208 cm^{-1} in IR , ^{1}HNMR δ 3.1 ppm due to CH_3 and δ 3.6 ppm due to OCH_3 of acrylate unit.

Solubility behavior: - The solubility of synthesized homo and copolymer samples was determined in polar and non polar solvents and has been summarized in Table-1. The homopolymer (H-MPM) and copolymer (C-MPM) are completely soluble in THF, DMF, acetone, toluene, xylene, 1-4 dioxane and DMSO. The homopolymer and copolymer insoluble in carbon tetrachloride. The solubility behavior of the homo and copolymer depends on the composition of the polymer.

Intrinsic viscosity ŋ

Intrinsic viscosity ŋ is a measure of hydronamic volume and depends on molecular weight, as well as on the size of the polymer coil in a given solution. The value of ŋ in DMF solution at 30^0 C are listed in Table 2. Intrinsic viscosity of homopolymer is lower then copolymer.

Thermal Properties: It is well known that polymaleimide is potential heat and chemical resistant; therefore maleimide is very useful for improving the polymeric properties. The thermograms were obtained by heating the homopolymer and copolymer samples in air (10°C/min.)

The results of percentage weight loss suffered from 200°C to 600°C at 100°C intervals are furnished in Table 3. The initial decomposition temperature Ti, temperature for maximum weight loss T_{max} and final decomposition temp. T_f are given in Table.4

The results in table 3 indicate that the relative thermal stability on the basis of Ti follows the order H-MPM > C-MPM. The thermogram of H-MPM shows the single step degradation. Initial degradation from 220°C involving about 1.2 %, weight loss 300°, 400°C, 500° C and 550°C weight loss at 34.8%, 86.8%, 91.5. % and 94.7%.

The thermogram of copolymer shows the step-by-step degradation. In copolymer initial weight degradation from C-MPM 196 °C, involving about 0.81%, 300°C, 400°C, 500°C and 550°C, weight loss at 20.0%, 57.69%, 77.98% and 86.20%

Table 1: **Solubility behavior of monomer, homopolymer and copolymer in polar and non polar solvents at 30^{0}C**

Solvent	N-MPM	H-MPM	C-MPM
Ethyl alcohol	PS	S	S
Methyl alcohol	PS	S	S
Acetone	S	S	S
THF	S	S	S
DMF	S	S	S
DMSO	S	S	S
Ethyl acetate	S	PS	PS
Benzene	IS	IS	IS
1,4-Dioxane	S	S	S
Toluene	S	S	S
Cyclohexanone	S	S	S
Xylene	S	S	S
Chloroform	S	S	S
Carbon tetrachloride	IS	IS	IS

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

Table 2: **Radical polymerization and copolymerization of N-MPM with MA in THF at 65^{0}C**

Polymer Code	Feed mol fraction	Polymerization time(h)	Yield (%)	(ŋ) dl/g	Appearance
H-MPM	1.0	48	24.35	0.0415	Yellow
C-MPM	0.5	48	34.55	0.0862	Yellow

Table 3: **Percentage Weight loss of homo and Copolymer at various temperatures from the TGA**

Polymer Code	200^{0}C	300^{0}C	400^{0}C	500^{0}C	550^{0}C
H-MPM	1.2	34.8	86.8	91.5	94.7
C-MPM	0.81	20.0	57.69	77.98	86.20

Table 4: **Thermal behavior of homo and copolymers**

Polymer Code	T_i (^{0}C)	T_{max} (^{0}C)	T_f (^{0}C)	Residue at 500 ^{0}C (%)
H-MPM	220	400	550	8.55
C-MPM	196	300	550	22.02

Table 5: **Effect of time on yield of homo and copolymer**

Polymer Code	18 hr.	24 hr.	30 hr.	36 hr.	48 hr.	54 hr.	60 hr.
H-MPM	15.20%	20.12%	22.58%	27.19%	29.38%	31.80%	32.20%
C-MPM	43.60	48.10	52.50	57.90	59.30	60.10	60.80

Table 6: Percentage yield of homopolymer and copolymer in various solvent initiator systems

Solvent	AIBN		BPO	
	H-MPM % yield	**C-MPM % yield**	**H-MPM % yield**	**C-MPM % yield**
THF	29.38	59.30	29.01	58.25
DMF	19.12	38.10	17.22	32.10
Acetone	16.52	35.20	16.05	31.27
Ethyl acetate	15.20	30.12	14.51	27.10
1,4-dioxane	25.61	28.20	24.82	25.63

Table 7: Radical polymerization and copolymerization of N-MPM and MMA in THF at 65°C

Polymer Code	Feed Ratios N-MPM : MA	Polymer time (h)	Yield (%)	State	Appearance
CMPM-1	1 : 9	48	49.79	Viscous solid	Light yellow
CMPM-2	2 : 8	48	45.19	Viscous solid	Light yellow
CMPM-3	3 : 7	48	40.20	Viscous solid	Light yellow
CMPM-4	4 : 6	48	36.18	Solid	Yellow
CMPM-5	5 : 5	48	34.55	Solid	Yellow
CMPM-6	6 : 4	48	32.20	Solid	Yellow
CMPM-7	7 : 3	48	30.12	Solid	Yellow
CMPM-8	8 : 2	48	27.06	Solid	Yellow
CMPM-9	9 : 1	48	25.16	Solid	Yellow
H-MPM-10	10 : 0	48	24.35	Solid	Light yellow

CONCLUSION

Homopolymerization and copolymerization proceed through the free radical mechanism. The most suitable initiator – solvent pair for the homo and copolymerization was found to be AIBN-THF. The investigated homo and copolymaleimides show excellent solubility in THF, DMF, acetone, toluene, xylene, 1, 4-dioxane and DMSO. The homo and copolymer were characterized by IR and ^{1}HNMR spectral analysis. Synthesized homopolymer show good thermal stability than copolymer but other properties are improved in copolymerization.

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