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Synthesis and Characterization of Hompolymer and Copolymer of Methyl Methacrylate with Maleimide

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ABSTRACT

The N-[2, 4-dinitro-phenyl) maleimide (DNPM) was prepared by maleic anhydride and 2, 4-dinitroaniline. It was homo polymerized and copolymerized with methyl methacrylate (MMA) 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:- Free radical polymerization, maleimide, MMA, molecular weight, thermo gravimetry(TGA).

INTRODUCTION

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 [1]. 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), [2-8]. N-substituted maleimide polymerize readily in the presence of a radical initiator to give polymers having heat resistance and better mechanical properties [9-13]. Maleimide based copolymers have been found to have versatile applications in many industries ranging from aerospace to micro electronics field [14-15]. The authors have initiated studies on the synthesize and characterized the polymers and copolymers of substituted – phenyl maleimide [16-19]. This article investigated the homo and copolymerization of methyl methacrylate with N-[2, 4-dinitro phenyl] maleimide [DNPM] initiated by AIBN in THF solvent. Studies of physical, spectral and thermal properties have been carried out in order to characterize the polymer.

EXPERIMENTAL SECTION

Materials

2, 4- Dinitro-aniline 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 hr and distilled. The head and tail fractions were discarded. 2, 2’-Azobis-isobutyronitrile (AIBN) (spectrochem) was recrystallized twice from methanol prior to use. THF was purified by distillation after being for 2 hr in the presence of sodium [20]. Dioxane and DMSO were used after distillation. DMF and methanol used in the present work were of analytical grade and were used as received.

Measurements

^{1}HNMR spectra of monomer and polymer samples were taken in DMSO-d on a Bruker DPX-200/DPX – 300 spectrometer at 200/300 MHz. The internal reference used way 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 (USLV). The thermograms in air were obtained on a Matler TA-3000 system, at a heating rate of 10° C / min.

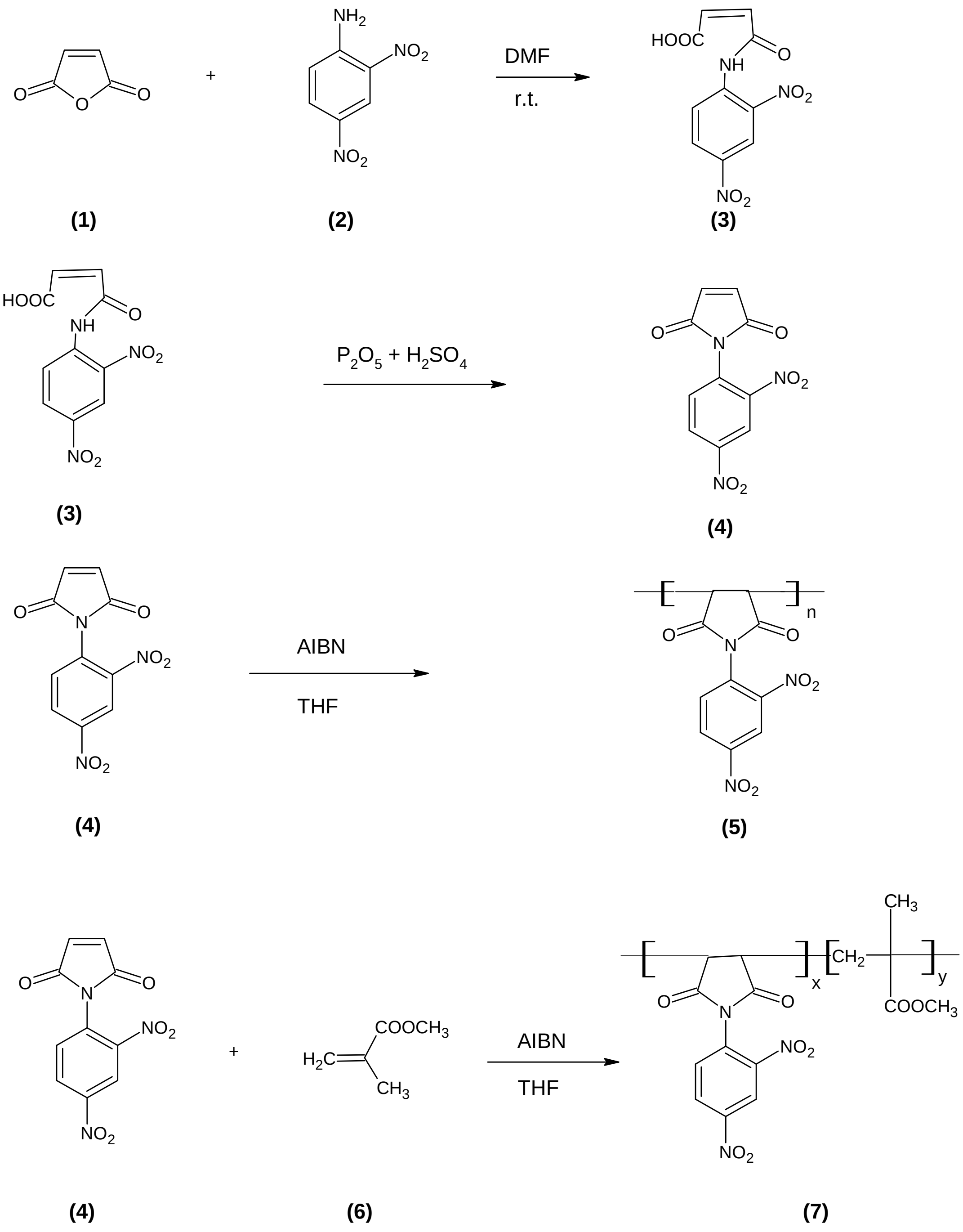
Synthesis of N-(2, 4-dinitrophenyl) maleimic acid

Take a well stirred solution of 2,4-dinitro aniline (18.1 g, 0.1 mol) in DMF, the solution of maleic anhydride (9.89, 0.1 mol) in DMF was gradually added over a period or 10 min. Then the mixture was stirred for 5 hr at room temperature. The resulting solution was poured into a large amount of crushed ice to precipitate crude DNPMA. The crude DNPMA was filtered, dried and then recrystallized from ethanol to obtained pure DNPMA.

Synthesis of N-(2, 4-dinitrophenyl) maleimide

Cyclodehydration of the maleimic acid, an intermediate to maleimide was carried out by treating former with conc. H_2SO_4 and P_2O_5. Then this solution poured in crushed ice obtained to solid DNPM was precipitate. The crude DNPM was filter and washed with 10 % $NaHCO_3$ solution and dried at 60-70°C and then recrystallized from ethanol to obtained pure DNPM.

1. N-(2, 4-dinitro phenyl) maleimic acid: yield 80 %
2. N-(2, 4-dinitro phenyl) maleimide: yield 70 %



Reaction scheme

Polymerization

Radical homopolymerization of DNPM, were carried out with AIBN as free radical initiator in THF in a round bottom flask. Reaction mixture was refluxed at 65°C for 48 hrs. The homopolymer of DNPM was isolated by precipitation in methanol containing water. The precipitated homopolymer was washed with methanol several times and dried in a vaccum oven.

Copolymerization

The reaction was carried out in the round bottom flask in equimolar amount of DNPM and MMA in THF and was refluxed after adding 25 mg AIBN at 65° C for 48 hr. The copolymer precipitated in methanol containing water mixture. The precipitated copolymer was filter and washed with methanol several times and dried.

RESULT AND DISCUSSION

The N- (2, 4-dinitro-phenyl) malemic acid 3 have been synthesized by the treatment of 2, 4-dinitro aniline with maleic anhydride. This is confirmed by 3150 – 2674 cm-1 owing to carboxylic –CH str. as well as –NH str. at 3330 cm-1 in IR spectrum. Compound 3 treated with P_2O_5 + H_2SO_4 after the cyclodehydration of acid into imide give compound 4 {N-(2, 4-dinitro-phenyl)} maleimide. Synthesis of this compound is confirmed by disappear of both carboxylic acid and NH band in IR region and we get two new band 1721, 1785 due to C=O functional group. Compound N-(2,4-dinitro-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}in IR spectra and δ 3.1 ppm of$(–CH–CH–)_n$ in ^1H NMR spectra. Compound N-(2, 4-dinitro phenyl) maleimide further reflux at 48 hr. with MMA in the presence of AIBN in THF at 65°C gave copolymer 7 of compound 4 which give C-O-C str. 1240 cm^{-1} in IR spectrum, ^{1}HNMR δ 0.86 ppm due to CH_3 and 3.25 ppm due to OCH_3 of acrylate unit. The spectral data are given in Table 1.

Table 1: Spectral data of synthesized compounds

Compound No.	Spectral Data
3	IR (cm^{-1}); 3150 – 2474 (-OH str.), 3300 (N-H str.), ^{1}HNMR (δ) : 6-51 (CH), 11.0 (COOH), 8.0 (NH), 8.18 – 9.10 (m, Ar)
4	IR (cm^{-1}): 3160 cm^{-1} (CH=CH), 1721-1785 (C=O str.) 1566-1440 (-C-NO_2 str.), ^{1}HNMR (δ) : 7.01 (–CH), 7.1 – 7.83 (m, Ah)
5	IR (cm^{-1}): 3150 (Ar-H str.). 1751, 1725 (C=O str.), 1170 (C-str.) ^{1}H NMR(δ): 3.1 (-CH) 7.1 – 8.0 (m, Ar)
7	IR (cm^{-1}): 3130 (Ar-H str.) 1741, 1717 (C=O str.) 1240 (C-C-C str.) ^{1}H NMR (δ): 0.6 (CH_3), 3.25 (OCH_3), 1.5 – 1.6 CH_2

Thermal properties

Thermal stability of the homopolymer H-DNPM and copolymer, C-DNPM was investigated by TGA. TGA was carried out in air atmosphere at heating rate of 100°C/min. The thermal stability data are given in Table 2 and Table 3.

Table 2 shows the thermal behaviour of homopolymer H-DNPM. The homopolymer of DNPM begins to degrade at around 224° C and performs decomposition in two steps. Table 2 also shows the thermal behaviour of copolymer C-DNPM. The degradation of copolymers starts at around at 220° C and performs a two step degradation.

The result in Table 3 indicate that the relative thermal stability on the basis of T_i follows the order H-DNPM > C-DNPM. The result of percentage weight loss suffered from 200° C to 500° C. The weight loss of H-DNPM below 0.8 to 9.0 % up to 300° C and copolymer samples in initial decomposition below 1.2 to 34 % up to 300° C.

Table 2: Thermal behaviour of homo and copolymer

Polymer code	Degradation Step	T_i ° C	T_{max} ° C	T_f ° C	Residue at 500° C
H-DNPM	I II	224 400	342 458	400 575	18.5 %
C-DNPM	I II	220 315	290 328	315 550	8.55 %

Table 3: Percentage weight loss of homopolymer and copolymer at various temperatures

Polymer code	Weight Loss (%)				
	200° C	300° C	400° C	500° C	550° C
H–DNPM	0.8	9.5	52.1	81.5	89.7
C–DNPM	1.2	34.8	86.8	91.5	94.6

Solubility of Polymers

Table 4 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, acetone, cyclohexanone, ethyl acetate. The homo and copolymer partially soluble in ethanol, methanol, DMSO, 1, 4-dioxane. Solubility behaviour in later solvents depends on the composition of polymer.

Table 4: Solubility behaviour of monomer, homopolymer and copolymer in polar and non polar solvent at 30°C

Solvent	DNPM	H-DNPM	C-DNPM
Ethanol	PS	PS	PS
Methanol	PS	PS	PS
Acetone	S	S	S
DMF	S	S	S
THF	S	S	S
DMSO	PS	PS	PS
Water	IS	IS	IS
Ethyl acetate	S	S	S
Benzene	IS	IS	IS
1,4-Dioxane	PS	PS	PS
Toluene	IS	IS	IS
Cyclohexanone	S	S	S
Xylene	IS	IS	IS
Chloroform	IS	IS	IS
Carbon tetra chloride	IS	IS	IS

Effect of Solvent – Initiator and Time on Polymerization

The yield of homo and copolymer in different solvent initiator are given in Table 5 and it 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 6. This indicates that the yield of polymer increases with increasing time.

Table 5: Percentage yield of homo and copolymaleimides in various solvent initiator systems

Polymer code	**Solvent**	**AIBN % yield**	**BPO % yield**
H-DNPM	THF	21.83	18.15
	DMF	12.14	11.20
	1,4-Dioxane	19.25	17.52
	DMSO	15.20	13.12
	Acetone	14.58	12.02
C-DNPM	THF	44.90	42.05
	DMF	35.12	37.02
	1,4-Dioxane	29.25	29.42
	DMSO	31.20	32.60
	Acetone	32.16	30.26

Table 6: Percentage yield of homo and copolymaleimide in different time in THF solvent

Solvent	**% yield**					
	18 hr	**24 hr**	**30 hr**	**36 hr**	**48 hr**	**54 hr**
H-DNPM	11.15	14.65	15.26	19.05	21.83	22.02
C-DNPM	32.15	35.65	36.26	40.05	44.90	45.02

Physical Properties

The intrinsic viscosity (η) and molecular weight of present polymer samples are listed in Table 7. The value of (η) depends on molecular weight as well as on the size of polymer coil in given solution.

Table 7: The intrinsic viscosity and molecular weight of C-DNPM

Polymer	**H (dl/g)**	**M_W (g/mol)**	**State**	**Appearance**
C-DNPM	0.186	18765.6	Solid	Brown

CONCLUSION

The free radical homo polymerization of DNPM and copolymerization with MMA has been carried out in THF at 65°C. The most suitable initiation-solvent pair for the homo and copolymerization was found to be AIBN-THF. The investigated homo and copolymaleimide show excellent solubility in THF, DMF, acetone, ethyl acetate, cyclohexanone. The characterization of homo and copolymer was carried out by IR and ^{1}H NMR spectral analysis. The synthesized polymers have good thermal stability and degrade in two steps. The homopolymer possessed better thermal stability then the copolymer and it degraded in two-steps.

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