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Synthesis and characterization of polymers of n-benzylmaleimide

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ABSTRACT

This article describes the synthesis of homopolymer of N-benzylmaleimide monomer and copolymer with MMA in THF solvent using AIBN as a free radical initiator. Prepared homopolymer and copolymer samples were characterized by FT-IR, ¹H-NMR, N elemental analysis, solubility test, and intrinsic viscosity. The thermal stability was determined by TGA techniques. Molecular weight of polymers was determined by GPC.

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KEYWORDS

N-Benzyl maleimide;
Characterization;
Thermal stability;
Radical polymerization;
GPC.

INTRODUCTION

Aromatic polymaleimides and their derivatives show higher excellent thermal stability due to maleimide unit present in their backbone. These provide the polymers with superior mechanical and thermal stability. Although maleimide undergoes homopolymerization with great difficulty, it copolymerized quite readily with a variety of vinyl monomers^[1].

Generally aromatic polyimides have found many applications as like high temperature insulators, coating, adhesive and matrices for high- performance composites^[2-4].

Most aromatic polyimides generated by the thermal solid phase imidization show insolubility, which make processing difficult. These undesirable properties limits the wider applications of the polyimides, are due to their chain rigidity as well as poor defined molecular architectures. Addition types of polyimides were developed mainly to overcome processing disadvantages^[5-6].

Many authors have been studied the N-Substituted maleimides and observed that maleimide polymers show

excellent thermally stability^[7-9]. At present there is a considerable interest not only in the synthesis of new type of polymers, but also in the modification of commodity polymers in order to improve their properties to meet requirements for new applications.

In order to investigate the possibility of obtaining better polymers from N- Substituted maleimides. Here we report the homopolymer of N-Benzylmaleimide and its and copolymer with Methyl methacrylate in THF solvent using an AIBN as a free radical initiator. The polymer samples were characterized by IR, ¹H-NMR, solubility test and thermo gravimetric analysis.

EXPERIMENTAL

Materials

Maleic anhydride (SDH, AR) was recrystallized from chloroform. Ailine and benzyl amine was used after distilled. Azobisisobutyronitrile (AIBN, Wilson Laboratory) was recrystallized from methanol prior to use. Tetrahydrofuran (THF), N,N- Dimethylformamide (DMF) were used after distillation^[10].

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Measurements

¹H-NMR spectra of homopolymer and copolymer samples were taken in DMSO-*d*₆ on a Bruker DPX-200/DPX-300 spectrometer at 300/400 MHz. FT-IR Spectra of the polymer samples were recorded on a Perkin Elmer IR Spectrometer using a KBr pellet technique.

The intrinsic viscosity (η) measurements were carried out in DMF at 30°C by Ubbelohde suspended level viscometer. The temperature was controlled by the water thermostat. Weight average molecular weight and Number weight average of the homopolymers and copolymers were determined by gel permeation chromatography technique using THF as a mobile phase and polystyrene as a standard^[11,12]. Thermogravimetric analysis was carried out in air at a heating rate of 10°C/minutes by means of a mettler TA-3000 system.

Methods

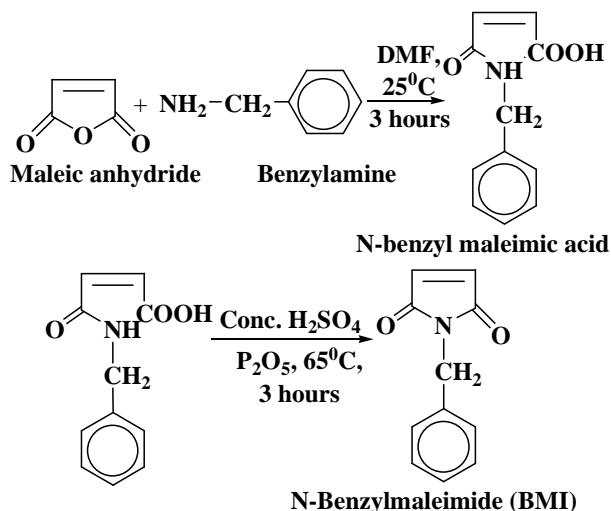
Preparation of *N*-benzylmaleimide (NBMA)

N-Benzylmaleamic acid

Benzylamine (10.88ml, 0.1 mol) and Maleicanhydride (9.8gm, 0.1 mol) were taken in 30ml DMF solvent. The solution stirred for three hours at room temperature. Solution poured in cool water and obtained white solid precipitated. The product was filtered, dried and recrystallized from ethyl alcohol to obtained pure form of NBMA. Yield 90%, m.p. 98°C.

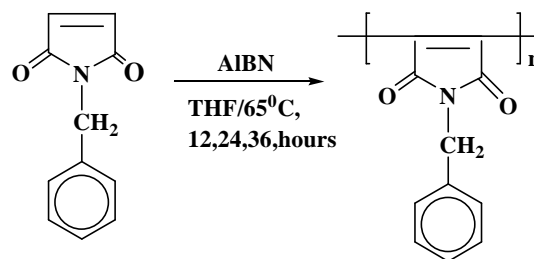
N-benzylmaleimide (NBMA)

N-Benzylmaleamic acid was taken in DMF solvent and treating with conc. H₂SO₄ and P₂O₅. The solution kept for stirring three hours at 65°C. Solution poured in cool water or ice water to obtain the white colour precipitated of NBMI. The precipitate was filtered and dried. NBMI was recrystallized from ethyl alcohol solvent. The yield was 70%, M.P. 99-100°C. The purity and structure of the monomer was determined by Elemental analysis, IR, ¹H-NMR study. IR(KBr) ν cm⁻¹ 3075(Aromatic-H stretch), 1775, 1709(Symmetric and asymmetric stretch of C=O in a five member imide ring), 1586, 1509, 1466 (C=C, Aromatic), 1329, 1309(C-N stretch) and 952, 908 (CH=CH), ¹H-NMR (400MHz, TMS) DMSO-*d*₆, δ , ppm: 7.15 (s, 2H CH=CH), 5.6 (s 1H, CH₂), 7.52, 7.78 (m, 5H phenyl).



Synthesis of homopolymer

Synthesis of homopolymer of *N*-Benzylmaleimide was carried out in THF solvent using AIBN as a free radical initiator at 65°C. The reaction mixture was refluxed for 48 hours. The prepared polymer was isolated in excess quantity of methanol water mixture. The crude polymer was purified by dissolving in THF and reprecipitating from a methanol water mixture. The precipitated polymer PBM were washed with methanol several times and dried at 60°C under vacuum. The homopolymer was synthesized on different time and percentage yield are given in TABLE 1.



Synthesis of copolymer

In equimolar amount of NBMI and MMA, solvent THF was taken and free radical initiator AIBN was taken in round bottom flask fitted with reflux condenser at 65°C on 48 hours. The copolymer CBMM was isolated by methanol water mixture. The crude form of polymer was purified by dissolving in THF and reprecipitate from a methanol water mixture. The precipitated copolymer were washed with methanol several times and dried at 60°C under vacuum. The nine

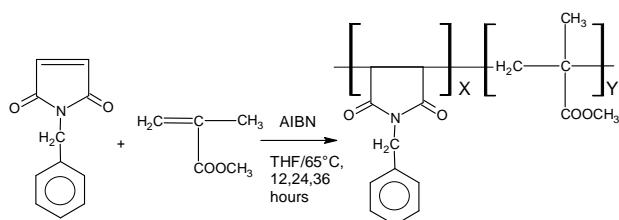


TABLE 1: Polymer code, yield, physical state and colour of homopolymers

Polymer code	Time (hrs)	Yield %	State	Colour
PBM	12	19.17	Solid	White
	24	25.64	Solid	White
	36	27.48	Solid	White
	48	39.45	Solid	White

TABLE 2: Polymer code, Yield, physical state and colour of copolymers

Polymer code	Time (hrs)	Yield %	State	Colour
CBMM	12	24.25	Solid	White
	24	39.91	Solid	White
	36	47.25	Solid	White
	48	53.45	Solid	White

TABLE 3 : Copolymers of BMI with MMA (Time 12 hrs. initiator AIBN)

Polymer code	Feed mol ratios NBMI:MMA	Yield %	State	Colour
CBMM 1	1:9	35.9	Viscous liquid	White
CBMM 2	2:8	34.4	Viscous liquid	White
CBMM 3	3:7	37.1	Solid powder	White
CBMM 4	4:6	38.6	Solid powder	White
CBMM 5	5:5	39.0	Solid powder	White
CBMM 6	6:4	40.0	Solid powder	White
CBMM 7	7:3	41.1	Solid powder	White
CBMM 8	8:2	42.0	Solid powder	White
CBMM 9	9:1	45.0	Solid Powder	White

copolymer samples using different feed ratio of comonomers were synthesized and physical properties are described in TABLE 3. The copolymers were synthesized in different time and yield are given in TABLE 1. Reaction schemes is given above:

RESULTS AND DISCUSSION

1. Effect of time on yield

The homopolymerization and copolymerization were carried out in THF solvent at varies time. The effect of yield with time is given in TABLES 1 and 2. TABLES reveals that the yield of polymers was increased with increasing of time.

2. Solubility behaviour

TABLE 4: Relative solubility of monomer, homopolymer and copolymer at 30°C

Solvents	NBMI	CBMM	PBM
THF	S	S	S
DMF	S	S	S
DMSO	S	S	S
Dioxane	S	S	S
Acetone	S	S	S
Chloroform	S	S	S
Ethyl acetate	S	S	S
Benzene	S	S	IS
Toluene	S	PS	IS
CCl ₄	PS	IS	IS
CH ₂ Cl ₂	PS	S	S
Ethanol	S	S	S
Methanol	S	S	IS
N-Hexane	IS	PS	IS
Cyclohexanone	PS	PS	IS
Xylene	S	PS	IS
1-Butanol	IS	IS	PS
2-Butanol	IS	IS	PS

TABLE 5: The physical properties of Homopolymer and copolymers

Polymer code	Solvent	Temp.	[η]	Mw
HBMI	DMF	30°C	0.031	5675
CBMI	DMF	30°C	0.062	25581

The solubility of investigated homo and copolymer samples is given in TABLE 4. The investigated homo and copolymaleimides show excellent solubility in THF, DMF, DMSO, CHCl₃, dichloromethane, acetone and Cyclohexanone.

3. Physical properties

Some of the physical properties of polymers were investigated. Intrinsic viscosity [η] of polymers is measure of hydrodynamic volume and depends on the molecular weight as well as on the size of the polymer coil in a given solution. The values of intrinsic viscosity [η] were carried out in DMF solution at 30°C, using an Ubbelohde viscometer. The value of intrinsic viscosity of homopolymer and copolymer are summarized in table 5. Table reveals that the viscosities of homopolymer are less than as comparative copolymer. The molecular weight of homo and copolymers were determined by GPC and average molecular weight is given in TABLE 5. The chromatogram of polymers is given below and indicates that molecular weight of homopolymer is less than that of copolymer.

4. Spectral characterizations

The FT-IR spectrum and ¹H-NMR spectrum

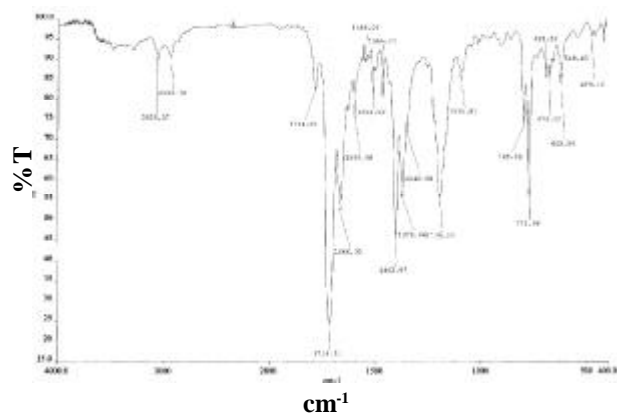


Figure 1 : FT-IR spectra of PBM

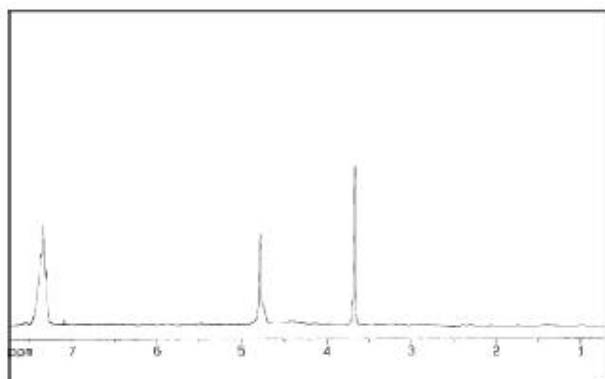


Figure 2 : ¹H-NMR spectra of PBM

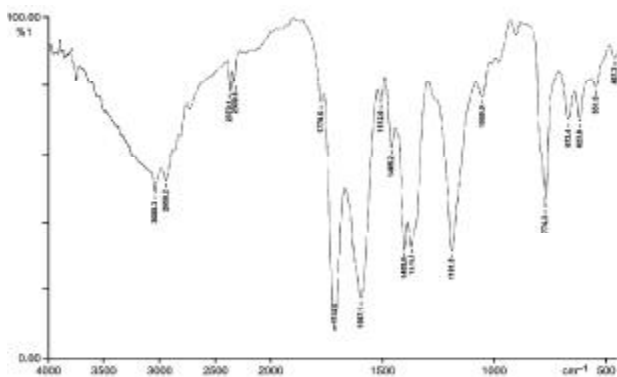


Figure 3 : FT-IR spectra of CBMM

(300MHz in DMSO- d_6) of PBM are shown in figures 1 and 2. The absence of a sharp band at 952cm^{-1} and chemical shift δ at 7.15 ppm due to $\text{CH}=\text{CH}$ in a monomer having a vinyl group, such as monomer NBMI, indicates the formation of polymer via vinyl group polymerization^[13,14].

The presence of absorption bands at 1784 and 1714cm^{-1} due to symmetric and asymmetric stretching of $\text{C}=\text{O}$ in the five member imide ring indicates that the imide ring remained intact in the polymerization. The

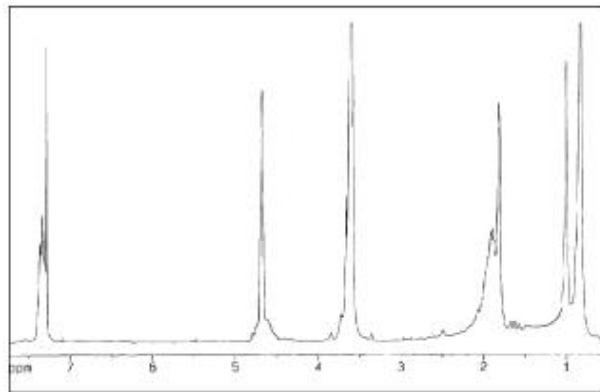


Figure 4 : ¹H-NMR spectra of CBMM

imide group is also confirmed from the bands observed at $1466(\text{Ar}-\text{N}$ stretch), $1372(\text{C}-\text{N}$ stretch), $1195(\text{C}-\text{N}-\text{C})$ and 772cm^{-1} .

The FT-IR spectrum and ^1H -NMR spectrum (300MHz in DMSO- d_6) of CBMM are shown in figures 3 and 4. The δ observed at 7.15 ppm due to $\text{CH}=\text{CH}$ in the monomer has shifted to 3.4-4.1 ppm in the polymer, as a result of the formation of a semi flexible poly (substituted methine) $-\text{[CH}-\text{CH}]_n-$ group^[15]. The broad peak at 7.0-8.1 ppm corresponds to 5 Ar-H.

The major characteristic absorption bands are observed at 1779, 1714 ($\text{C}=\text{O}$ symmetric and asymmetric stretch in a five member imide ring and $\text{C}=\text{O}$ stretch of ester), 1597, 1512 (aromatic) and 1191 ($\text{C}-\text{O}-\text{C}$ of ester). These characteristic bands confirm that units of both the monomers NBMI and MMA are present in the copolymer samples. The ^1H NMR spectra of the copolymer showed the following chemical shifts. The δ at 7.1-7.84 ppm of Aromatic hydrogen.. A δ observed at 4.87 ppm is 2H in $-\text{CH}_2$ of benzyl segment. The δ observed at 3.4-3.9 ppm corresponds to overlapping of 2H $-(\text{CH}-\text{CH})-$ in the polymer main chain and 3H $(-\text{OCH}_3)$ of MMA segment. The δ in the range 0.84-2.4 ppm is of 2H of methylene group and 3H of $-\text{CH}_3$.

6. Thermal properties

The thermal behaviour of the synthesized homopolymers and copolymers were investigated by TGA. The TGA Curve of PBM and CBMM is shown in figure 5 and 6. The initial decomposition temperature, temperature for maximum weight loss and final decomposition temperature of homopolymer and copolymers are summarized in TABLE 6. The results of percentage weight

TABLE 6: Thermal behaviour of homopolymaleimides and copolymaleimides

Polymer code	T _i	T _{max}	T _f	Residue at, 550 ^o C
PBM	200	400	550	26.21
CBMM	190	300	550	3.70

TABLE 7: Percentage weight loss of homo and copolymer at various temperatures from the TGA

Polymer code	200 ^o C	300 ^o C	400 ^o C	500 ^o C	550 ^o C
PBM	4.29 %	39.96 %	95.89 %	96.05 %	96.30 %
CBMM	4.96 %	50.35 %	67.59 %	71.60 %	73.79 %

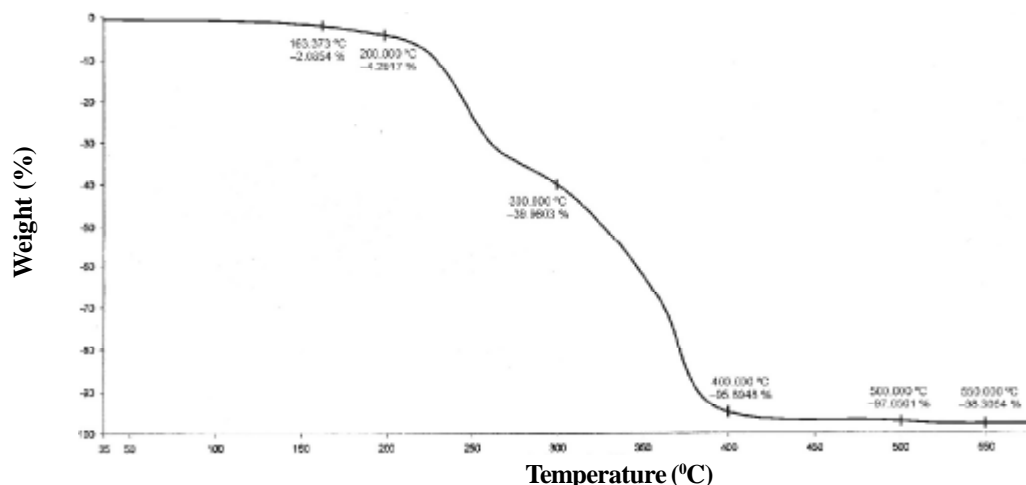


Figure 5: TGA curve of PBM

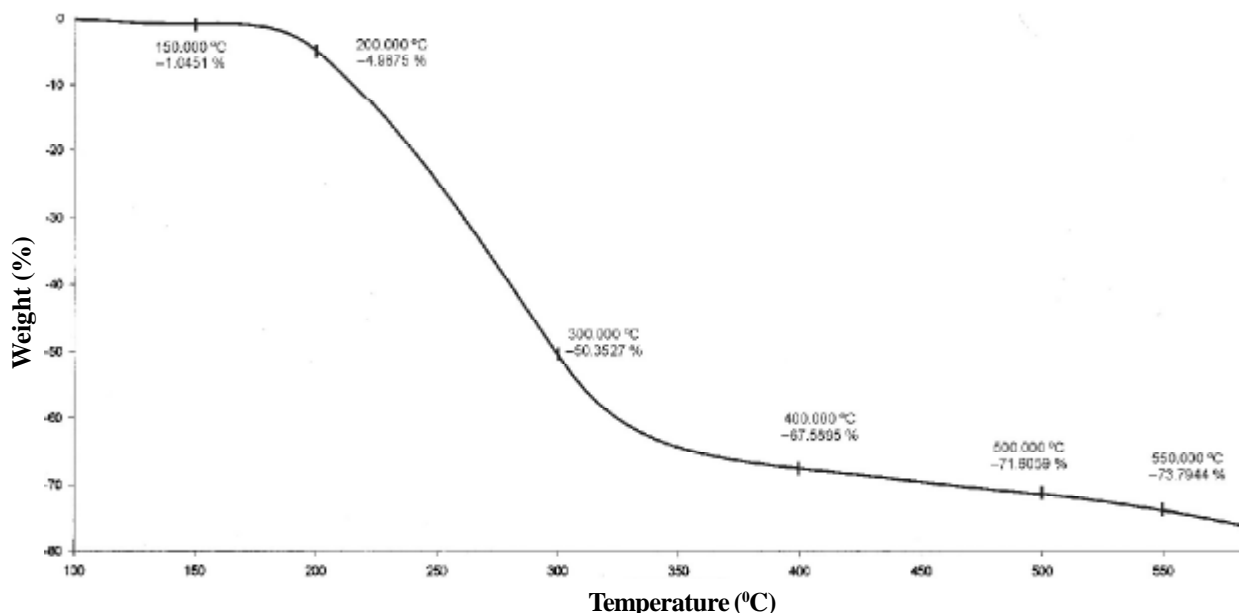


Figure 6 : TGA curve of CBMM

loss suffered from 100^oC-600^oC at 100 intervals are furnished in TABLE 7.

The TGA results indicate that the homopoly maleimides are more stable as compare to copolymaleimides. This is due to in homopolymers only single maleimides unit involved while in copolymers both units are involved in backbone. The TGA results showed that the decomposition temperature increased with the increasing the content of substituted N-benzylmaleimide.

CONCLUSION

Synthesis, through free radically, homo polymer of NBMI and copolymer of NBMI with MMA has been investigated. The investigated homo and copolymaleimides show excellent solubility in THF, DMF, DMSO, CHCl₃, dichloromethane, acetone and Cyclohexanone. The copolymer shows higher intrinsic viscosity and molecular weight than homopolymer. The

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elemental analysis data and FT-IR and ¹H-NMR spectral data confirmed the structure of polymers. Homopolymer show excellent thermal stability then copolymer but other property is improved in copolymerization.

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