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COMPARATIVE STUDY OF FREE RADICALLY SYNTHESIZED THERMAL STABLE POLYMERS OF N-(BROMO PHENYL) MALEIMIDE AND ITS ANTIMICROBIAL RESISTANCE

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ABSTRACT:
Synthesized 4- mono- and 2,4,6- tri- substituted bromo-phenyl maleimide monomers (N-PB1,N-TB2) were used for the synthesis of its homopolymer (H-PB1, H-TB2) and its copolymers (C-PB1,C-TB2) with Methyl methacrylate (MMA) by refluxing at 70°C in DMF and BPO as a free radical initiator. Thermogravimetric analysis (TGA) characterizes the thermal stability of all polymers. The initial decomposition temperature of homopolymers, H-PB1 and H-TB2 were at 200 °C and 180°C while copolymers C-PB1, C-TB2 were at 300 °C and 180°C. The non-isothermal dynamic parameters were computed by Kissinger method. Homopolymers, H-PB1 and H-TB2 have -9010.6 and -8646.8 J/mol and copolymers C-PB1 and C-TB2 have -10138.39 and -8646.8 J/mol, E_a, activation energy respectively. The homopolymer, H-TB2 and copolymer, C-PB1 has the highest molecular weight 4228.2 and 5177 obtained from Gel permeation chromatography (GPC). All synthesized monomers and polymers show excellent antimicrobial resistance against bacteria (*E. coli*, *B. subtilis*, S. *aureus*) and fungi (*A. niger*, *A. solani*).

Keywords:
Thermal stability; activation energy, antimicrobial resistance

INTRODUCTION

The Poly methyl methacrylate useful in resin applications is reformed by the influx of functional maleimide moiety results in the good thermal stable polymers [1-4]. N-substituted maleimides rank above among the group of useful monomers because of their unique and broad applications in functionalized monomers, conjugated linkers and high thermal stability of polymers. The rate of polymerization rate is influenced by solvent, initiators [5-6], temperature and additives [7]. Copolymers containing N-substituted maleimide moieties manifest reinforced thermal and mechanical properties [8-10]. The electron deficient maleimide group makes polymer with an alternative monomer for designing vinyl based polymers [11-15].The maleimide based polymers have high temperature applications up to 250 ^{O}C. Conventional Free radical polymerization methodologies is used for the preparation of thermally stable polymers. Aromatic polyimides polymers with imide group chain are considered to have thermo-oxidative stabilities [16-20].Modern study includes designing novel antimicrobial agent which have high thermal stability and have low toxicity. TGA analysis not only furnishes data on weight loss as a function of temperature but also provides a means to estimate kinetic parameters or thermal decomposition reactions. Recently, researchers has attempted to study the thermal degradation behavior of polymeric substrates [21], by studying the thermo-degradation kinetics data it could solved selection of thermally stable self-assemble polymers and can enhance the thermal stability of materials [22] for end-use applications and to improve the product quality. Therefore the polymeric antimicrobial agents are synthesized which are chemically and thermally stable [23]. These materials would withstand longer, very active too and releases biocidal materials in case of contamination at the end product [24-26].When designing polymers for pharmaceuticals and medicinal applications some properties especially biocompatibility, thermal properties and rate of degradation were considered primarily before further use. These thermo responsive bromo substituted poly maleimides polymers and copolymers with methylmethacrylate containing bromo as substituents and acrylates as unit can be very useful as antimicrobial agents in coating industries [27] and can be used in catheters, pacemakers and medical textiles, films, packaging materials, food stuffs, sanitary application, water purification on systems, contamination by microorganism is of great concern. Pathogenic microbial attack and polymers contamination by air can be prevented but use of coating of these antimicrobial polymers. The use of polymeric systems based on acrylic derivatives as biomaterials for clinical application has increased because of the excellent biocompatibility and long term stability [28-29].

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Material and methods

Materials

N-Bromo substituted (phenyl) aniline (Spectrochem. S.D. Fine Chemical Pvt. Ltd, Mumbai) was used as received. Maleic anhydride (SRL, Mumbai) recrystallized from acetone. Methylmethacrylate (MMA) (SRL, Mumbai) were stirred for 10 minutes at 30 ± 0.1 °C with 5% NaOH to eliminate hydroquinone inhibitor [18]. It was then dried over anhydrous calcium chloride for 8 hours. The head and tail fractions were discarded before using the acrylate monomers. Benzoyl peroxide (BPO) (CDH, Mumbai) was used as received. Phosphorus pentoxide and concentrated H_2SO_4 (SRL, Mumbai) were used as received. N, N-Dimethylformamide (DMF), Tetrahydrofuran (THF), Dimethyl sulfoxide (DMSO), Acetone, 1, 4-dioxane used were of analytical grade and used as received.

Measurements

^{1}H NMR spectra of monomer and copolymer samples were recorded on a Bruker DPX-300 spectrometer at 300 MHz with $CDCl_3$ as a solvent. The internal reference used was TMS. FT-IR-spectra of monomer and copolymer samples were recorded on Perkin-Elmer model RXI (4000-450 cm^{-1}) FT-IR spectrophotometer by using KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.1 °C, using on Ubbelohde suspended level viscometer. Elemental analysis was made on Carlo-Erba Model NA 500 series analyzer. The number average molecular weight and polydispersity index of the copolymer was obtained using a water gel permeation chromatography (GPC) with 13082008 mix bead THF (30 to 1000 sec). Thermograms were obtained on a Mettler TA-3000 system at the scanning rate of 20°/min from 50 °C to 900 °C in air.

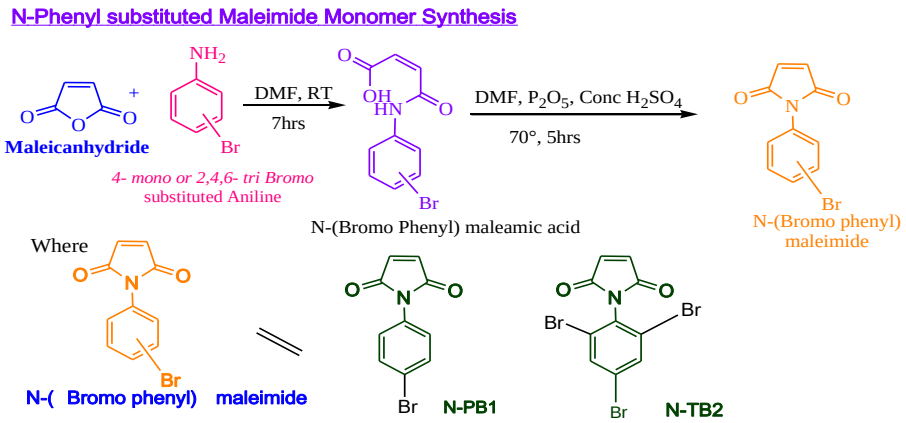
Experiment

Preparation of N- substituted bromo (phenyl) maleimide monomers (N-PB1, N-TB) (described below and shown in scheme-1)

Preparation of N- bromo (phenyl) maleimide monomer

4-mono and 2, 4, 6- tri substituted bromo (phenyl) maleimide monomers (N-PB1, N-TB3) are prepared from maleic anhydride (ME) and respective substituted aniline (described below and shown in Scheme 1). The solution of 0.1 moles of N- bromo substituted aniline in 40 mL DMF in a flat bottom flask was stirred well with solution of 9.8 g of maleic anhydride (0.1 moles) in 40 ml DMF in magnetic stirrer for 7 hours at room temperature. The resulting reaction mixture is cyclohydrated by adding 6 g P_2O_5 following 1 to 2 drops of concentrated H_2SO_4 into it stirred and refluxed for 5 hours at 70°C. The reaction mixture is cooled and poured into a crushed ice water to precipitate out the crude maleimide monomer. It is filtered and washed with 10% sodium bi-carbonate solution to remove any residue of N- substituted bromo phenyl maleamic acid. The remaining residue left behind is of crude maleimide monomer which was filtered and dried in vacuum for 8-9 hrs. On drying, it is recrystallized twice with 95% ethanol.

The following **Scheme 1** to represent the synthesis process of N- bromo (phenyl) maleimide :



Scheme 1: The synthesis route for N-Bromo-substituted (phenyl) maleimide

Synthesis of homo and copolymerization of N-Bromo substituted (phenyl) maleimide (described below and shown in Scheme 2)

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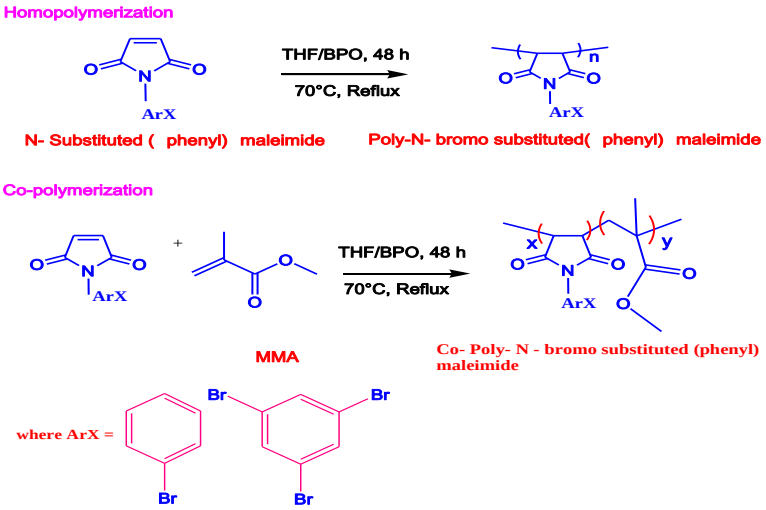
Homopolymerization : For 0.5 mol fraction, of n-substituted bromo(phenyl) maleimide monomer was mixed well in 80 ml DMF solvent in a round bottom flask. Then, 0.002 gm of BPO was added to the reaction mixture as a free radical initiator. It was then refluxed in a long spiral condensor at 70°C for 48 hrs. The homopolymer product obtained was in dissolved state in THF. This homopolymer product was precipitated in 5% methanol water mixture twice. It was then washed with methanol 2-3 times for purification. It was dried at 60°C under vacuum. The precipitate was brown in color.

Copolymerization: For 0.5 mol fraction, of n-substituted bromo(phenyl) maleimide monomer with 1.00 ml of methylmethacrylate (MMA) was mixed well in 80 ml DMF solvent in a round bottom flask. Then, 0.002 gm of BPO was added to the reaction mixture as a free radical initiator. It was then refluxed in a long spiral condensor at 70°C for 48 hrs. The copolymer product obtained was in dissolved state in THF. This copolymer product was precipitated in 5% methanol water mixture twice. It was then washed with methanol 2-3 times for purification. It was dried at 60°C under vacuum. The precipitate was brown in color.



Scheme-2: Free radical copolymerization of N-bromo substituted (phenyl)maleimide monomer with metha acrylate(MMA)

N-PB1: 3860 cm^{-1} (Ar C-H stretch.), 3122.6 cm^{-1} (Hetero C-H stretch.) , 1780.2 and 1708.1 cm^{-1} (sym. and asym. C=O in a five membered imide ring), 1586.7 1530.5 cm^{-1} (Ar. C=C stretch. of phenyl ring), 1396.4 cm^{-1} (Ar C-N stretch.), 852.6 and 677.0 cm^{-1} (Ar. C-Br in 1, 4 disubstituted benzene), 776.5 cm^{-1} para bromo stretching attached to phenyl ring stretching. 952.4 cm^{-1} (Hetero CH=CH deformation in imide ring). ^{1}H-NMR (300 MHz, TMS, $CDCl_3$, ppm), N-PB1: δ 7.26-7.27 ppm, d, 2H aromatic ortho to phenyl ring and δ 7.44-7.50 ppm, d, 2H aromatic in m-group in phenyl ring), δ 3.8 ppm S, 1H, CH=CH.

N-TB2: 3162.5 cm^{-1}(Ar C-H stretch.), 3021.5 cm^{-1} (Hetero C-H stretch.), 1780.4, and 1712.1 cm^{-1} (symmetric and asymmetric stretch of C=O in a five member imide ring), 1623.5 cm^{-1} and 1505.1 cm^{-1} (C=C Ar. Stretch. of phenyl ring), 1365.6 cm^{-1} (Ar. C-N stretch.), 1633.1 cm^{-1} (Hetreo C=C stretch.), 1042.1 cm-1 (Cl group ortho to phenyl ring), 930.1 cm^{-1} (Hetero CH=CH bending deformation), 895.4, 762.3 and 670.2 cm^{-1} (Ar. C-Br stretch.) and 1641.0 cm^{-1} (CH=CH of imide stretch).

^{1}H-NMR (300 MHz, TMS, $CDCl_3$, ppm) spectra N-TB2: 8.16 ppm (S, 2H in phenyl ring), 6.63 ppm (S, 2H, CH=CH imide ring).

H-PB: 3860 cm^{-1} (aromatic C-H stretching), 3122.6 cm^{-1} for alkene C-H stretch, , 1780.2 and 1708.1 cm^{-1} (C=O stretch. in a five membered imide ring), 1586.7 and 1530.5 $cm^{-}$for Ar. C=C stretch. 852.6 and 677.0 cm^{-1} (Ar. C-Br in 1, 4 disubstituted benzene), 776.5 cm^{-1} para Br stretch. 1396.4 cm^{-1} , (Ar C-N stretch.), 1165.3 cm^{-1} (C-N-C), 603.1 cm^{-1} (Heteroaromatic C-H deformation). ^{1}H-NMR spectra (300 MHz, TMS, $CDCl_3$, ppm) H-**PB1:** δ 7.26-7.27 ppm d, 2H-Ar. ortho to phenyl ring and δ 7.44-7.50 ppm d,2H-Ar. in phenyl ring). The peak at δ 3.8 ppm s 2H –(CH-CH)- in the polymer main chain.

C-PB1: 3061.2 cm^{-1} (Ar. C-H stretch.), 3123.1cm^{-1} C-H stretch for alkene,1716.2 cm^{-1} (C=O stretch. in a five membered imide ring), 1578.3 and 1542.4 $cm^{-}$for Ar. C=C stretch. 852.6 and 766.3 cm^{-1} (Ar. C-Br in 1, 4 disubstituted benzene), 776.5 cm^{-1} p- Br stretch. attached to phenyl ring. 1386.5 cm^{-1} (Ar C-N stretching),

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1180.1 cm^{-1} (C-N-C). ^{1}H-NMR (300 MHz, TMS, $CDCl_3$, ppm) C-PB1: δ 7.09-8.06 ppm d, 2-H Aromatic, ortho to phenyl ring and δ 7.44-7.50 ppm d, 2H- Aromatic in phenyl ring), δ 3.8 ppm S, 2H , –(CH-CH)- in the polymer main chain. δ 0.83-1.16 ppm (3H, CH_3) and at δ 1.83-2.01 ppm (2H , CH_2). δ 3.61 ppm s, 2H , –(CH-CH)- in the polymer main chain

H-TB2 : 3170.5 cm^{-1} (Ar. C-H stretch.), 3072.6 cm^{-1} (Hetero C-H stretch.), 1711.4, and 1781.3 cm^{-1} (C=O in a five membered imide ring), 1603.4 cm^{-1} 1587.7 cm^{-1} and 1498.1 cm^{-1} Ar. C=C stretch. phenyl ring), 1393.7 cm^{-1} (Ar. C-N stretching), 852.6 and 677.0 cm^{-1} (Ar. C- Br in 1, 4 disubstituted benzene) 762.9 and 673.2 cm^{-1} (Ar.C-Br stretch.), 617.1 cm^{-1} (Heteroaromatic C-H deformation) ^{1}H-
NMR(300 MHz, TMS, $CDCl_3$, ppm) H-TB2 : 8.13 ppm(singlet, 2H in phenyl ring), δ 3.47 ppm of 2H, s, CH-CH proton of imide in polymer.
FT-IR C-TB2: 3165 cm^{-1} (Ar. C-H stretch.), 3020 cm^{-1} (C-H stretch, hetero aromatic), 3110.1 cm^{-} (-CH=CH-,C-H stretching), 1784.6 and 1723.7 cm^{-1} (C=O stretch. in a five membered imide ring), 1623.4, 1500.2 and 1495.8 cm^{-1} Ar. C=C stretch. 1366.1 cm^{-1} (Ar. C-N stretching). 2977.3 cm^{-1} and 2957.1 cm^{-1} C-H stretch. in CH_3, CH_2 and 1426.0 cm^{-1} for –CH deformation in CH_2 of MMA showing that both the monomer units are present in copolymer sample 687.5 (aromatic CH=CH bending), 867.6 and 690.0 cm^{-1}(aromatic C- Br in benzene), 761.5 and 676.7 cm^{-1} (aromatic C-Br stretching)., 637.1 cm^{-1} (Heteroaromatic C-H deformation).
^{1}H-NMR(300 MHz, TMS, $CDCl_3$, δ ppm) spectra of C-TB2 : 8.13 ppm(S, 2H in phenyl ring), 0.96 (S, 2H in CH_2), 1.6-1.7 (S, 2H inCH_2), and 3.91 (S, 3H in OCH_3), 3.56 ppm,(2H Singlet, CH-CH proton of imide in polymer).
Antibacterial activity: Experimental Methodology for Bacteria
Agar- Well Assay/ Disk Diffusion Assay
Step: 1 Growth medium preparation**:** Nutrient agar medium was used to culture the bacteria. The composition of nutrient agar medium is as follows: Beef extract: 10 gram, Peptone: 10 gram, Sodium chloride: 5 gram, Agar-Agar medium: 15 gram, Distilled water: 1000 ml. The ingredients were weighed and dissolved in distilled water. pH was adjusted to 7.6, and then agar powder was added to it. The medium was dispensed in 25ml quantity in different testubes. The testubes were plugged by cotton wool and sterilized at 121.5 ° C and 15 psi pressure for 15 minutes. **Step 2:** Methodology for antibacterial susceptibility testing
In this method, 20ml nutrient agar medium [45-47] was poured in sterilized petriplates and control (streptomycin) was also added. And, the plates were dried over night. The freshly activated 100µL of indicator organisms (*Escherichia coli*, *Bacillus subtilis*, *stapylococcus aureus*) were spread with a sterile bent glass rod. Using sterile cork borer several cups or well were punched. Compounds of interest were then, inoculated in the well or cups, using sterile micropipette. The petriplates were incubated under optimum growth condition for various target microorganism and finally the diameter of zone of inhibition extending laterally around well was measured in mm. Control drug used were streptomycin.
Antifungal activity: **Experimental Methodology for Fungi**
Agar- Well Assay/ Disk Diffusion Assay Step: 1 Growth medium preparation: Sabouraud dextrose agar (SDA) medium [45-47] was used to culture the fungi. The composition of Sabouraud agar medium is as follows: Glucose: 20 gram, Peptone: 10 gram, Agar-Agar medium: 15 gram, Distilled water: 1000 ml. The ingredients were weighed and dissolved in distilled water. pH was adjusted to 7.6, and then agar powder was added to it. The medium was dispensed in 25ml quantity in different testubes. The testubes were plugged by cotton wool and sterilized at 121.5 ° C and 15 pound (psi) pressure for 15 minutes. **Step 2:** Methodology for antifungal susceptibility testing**:** In this method, 20ml nutrient agar medium was poured in sterilized petriplates and dried overnight. To prepare standardized control plates, SDA in one of the plates was mixed with Flucanazole as a control for fungi. Now, using sterile cork borer, the small disks (in mm) were cut from the old activated indicator organism culture plates. Here, fungi used were *Aspergillus niger* and *Alternaria solani* as an indicator organism. Over the sterilized petriplates the samples or compounds were spread properly using sterile bent glass rod. Then, the small disks of indicator fungi already cut were placed in middle of the petriplates. The plates were now inoculated with fungi. Same way, the plates of control was also inoculated. All the samples are placed in separate petriplates. The diameter of the inhibition zone was measured in millimeters (mm) for control plates as well as different samples plates.
Results and discussions
Gel permeation chromatography: Molecular weight usually decreases while the polydispersity index increases with increasing the maleimide content indicating higher rate of transfer to the maleimide monomer.

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GPC traces show that the copolymer contains no impurities. The molecular weight of H-PB1, H-TB2 and is 4156.1, 4228.2 and C-PB1, C-TB2 and is 5177.2, 4486.1. Since, polydispersity index is greater than 1, the process is free radical polymerization. The para substituted 4-Bromo (phenyl) maleimide copolymer with MMA (C-PB1) has the highest molecular weight.

Thermal analysis and Evaluation of Activation Thermodynamic Parameters

The thermodynamic activation parameters of decomposition processes for polymers such as activation energy (E*), entropy of activation (ΔS*), enthalpy of activation (ΔH*) and Gibbs free energy (ΔG*), are calculated with the help of DTA and TGA curves for polymers by using Kissinger method [30]. The TGA of homopolymers and copolymers are shown supporting file. The kinetic data processing was performed by applying Kissinger method which explains the influence of the heating speed and the dependence of activation energy on conversion degree. The method proposed by Kissinger is based on functional dependence of the heating rate (β) and variation of TG and DTA peak temperature (T_{max}) is in proportion to the maximum rate of reaction and equation:

$$\log \frac{\beta}{T_{\max}^2} = \log \frac{AR}{E_a} - \frac{E_a}{2.302 \times RT_{\max}} \qquad \text{Eq.(1)}$$

Plotting the left side of this equation against $\frac{1}{T_{\max}}$ should give a straight line of the slope $-\frac{E_a}{2.303 \times R}$ and intercept $\log \frac{AR}{E_a}$. By applying this method several thermal kinetic analysis of the same substance at different heating rate was performed, while, other non-isothermal parameters are calculated using following equation:

E* = - slope (2.303 R); Eq.(2)
ΔS* = 2.303[log(Ah/kT)]R; Eq.(3)
ΔH* =E*- RT; Eq.(4)
ΔG*= ΔH*- TΔS* Eq.(5)

where,

T_{max} is the peak Temperature,
h = Planck's constant (6.626×10^{-36} J-s),
k = Boltzman constant= 1.38×10^{-26} J K^{-1} mol^{-1}, R = Gas constant= 8.314 J K−1 mol,
A = Arrhenius factor

The data for homopolymer degradation in different heating rate at various temperature stages are summarized in Table 1. The high activation energy explains the thermal stability of the polymers. The entropy of activation has negative values which explain that the decomposition reactions proceed with a lower rate than normal ones.

TGA was carried out in air at heating rate of 20°C/min. The temperature for initial decomposition T_i, final decomposition T_f and maximum rate of weight loss T_{max} determined from TGA are summarized in Table 1 for both homopolymer and copolymer of Bromo substituted (phenyl) maleimide. The homopolymers H-PB1 and H-TB2 (Figure1&2) show two step degradation shows step-by-step degradation. The copolymer C-PB1 show two-step degradation shows step-by-step degradation and the other copolymer C-TB2 shows one step degradation. The activation energy, Ea for homopolymers (H-PB1, H-TB2) were -9010.6 J/mol and -8646.8 J/mol and copolymers (C-PB1, C-TB2) were -10138.39 J/mol and -8646.8 J/mol respectively.The non-isothermal kinetic parameters of the polymer were calculated by Kissinger method for homopolymers and copolymers. The initial T_i value for H-PB1 is 200 °C first step shows 18.3% percentage weight loss and second step initial T_i value is 400 °C shows upto 68.50 % weight loss .The initial T_i value for C-PB1 is 300°C for first step shows 23.1% percentage. weight loss and second step initial T_i value is 450 °C shows upto 58.3 % weight loss. Hence, from the data in Table 1 it is concluded that the copolymer C-PB1 is thermally more stable than homopolymer, H-PB1.The initial T_i value for H-TB2 is 198 °C first step shows 19.3% percentage weight loss and second step initial T_i value is 300 °C shows upto 45.60 % weight loss .The initial T_i value for C-TB2 is 180°C for first step shows 5.6% percentage weight loss. Hence, from the data in Table 2 it is concluded that the copolymer of 4- bromo (phenyl)maleimide (C-PB1) is thermally more stable than its homopolymer, H-PB1. The homopolymer of 2,4,6- tri bromo(phenyl)maleimide (C-TB2) is thermally more stable than its copolymer, C-TB2. Over all the copolymer of 4- bromo(phenyl)maleimide (C-PB1) is the most thermally stable polymer compared to other homopolymers and copolymers. Copoly- 4- bromo (phenyl) maleimide with MMA, (C-PB1) copolymer has the highest thermal stability it is due to the para substitution, which play a very important role in

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giving stability to it. While, the copolymer is Poly- 2, 4, 6- tribromo (phenyl) maleimide with MMA, C-TB2 is the least stable due to steric hindrance. Percentage weight loss of homopolymers per 100 ^{o}C raise of temperature is higher for para substituted bromo phenyl maleimide homopolymer, H-PB1 than 2,4,6-tri bromo substituted phenyl maleimide homopolymer. The percentage weight loss reaches 75.5 % at 500 ^{o}C for homopolymer, H-PB. While for the copolymers, C-PB1 and C-TB2 degrades gradually at an interval of 100 ^{o}C raise of temperature .and 75 % weight loss at 600 ^{o}C. The activation energy value shows the decomposition starts with an exothermic process and activation energy at a heating rate of 20 °C/min decreases as temperature increases gradually in next step. The entropy of transition state was found negative in both steps in polymers. The decrease in enthalpy value may be due to weak bond breaking between first stage and second stage of polymer degradation. The Gibbs free energy, $\Delta G^{\ddagger}$ is negative and value decreases shows the process is more spontaneous.

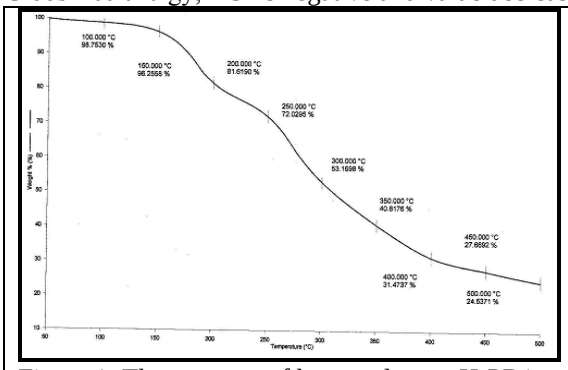

Figure 1: Thermogram of homopolymer, H-PB1

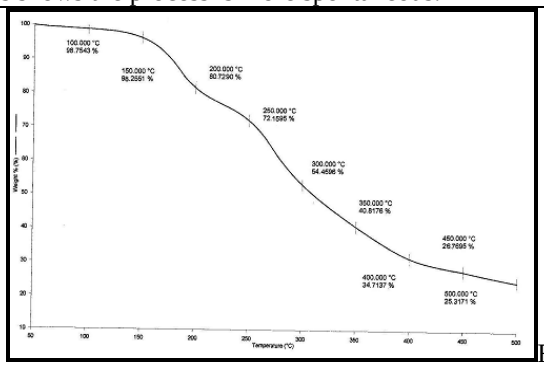

Figure 2 : Thermogram of homopolymer, H-TB2

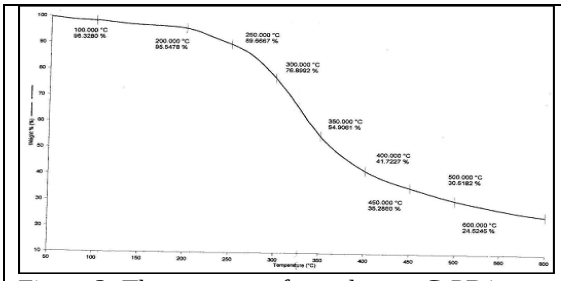

Figure 3: Thermogram of copolymer, C-PB1

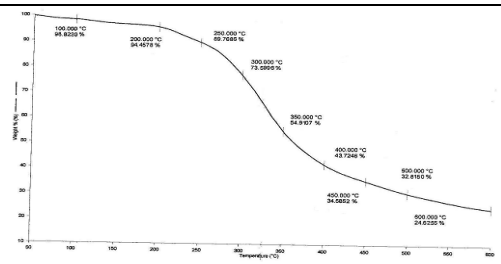

Figure 4: Thermogram of copolymer, C-TB2

Table 1: Non-isothermal characterization of homopolymers and copolymers

Non-Isothermal kinetic parameters using Kissinger method						
H-PB1 : Para-(bromo phenyl)maleimide homopolymer						
Heating rate	Thermal decompostion temperature range/^{o}C	Non-isothermal kinetic parameter				
		E_a* (Jmol^{-1})	A	ΔS (Jmol^{-1})	ΔH* (Jmol^{-1})	ΔG* (Jmol^{-1})
20^{0}C/min	1st step: 200-350	-9010.6	0.0099	-1.287	-11920.5	-11469.8
	2nd step: 350-500	-11526.5	0.0077	-1.265	-15683.5	-15050.8
H-TB2 : Tri-(bromo phenyl)maleimide homopolymer						
20^{0}C/min	1st step: 200-300	-8646.85	0.0101	-1.295	-11141.1	-10752.4
	2nd step: 300-500	-11045.9	0.0081	-1.267	-15202.9	-14569.4
C-PB1 : Para-(bromo phenyl)maleimide with MMA copolymer						
20^{0}C/min	1st step: 300-400	-10318.4	0.0072	-1.271	-13643.9	-13135.4
	2nd step: 400-600	-13200.04	0.0068	-1.254	-18188.4	-17435.9
C-TB2 : Tri-(bromo phenyl)maleimide with MMA copolymer						
20^{0}C/min	180-300	-8646.85	0.011	-1.296	-10953.4	-10564.6

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ANTIMICROBIAL ACTIVITY

Antimicrobial activity of monomer, homopolymers and copolymers against bacteria and fungi was carried out. It has been observed that the presence of bromo group in synthesized molecules imparts antimicrobial activity in it. The antimicrobial activity of monomer and homopolymers and copolymers against bacteria (***Escherichia coli, Bacillus subtilis,*** and ***staphylococcus aureus***) and fungi **(*Aspergillus niger, Alternaria solani*)** .

The synthesized monomers impart better antimicrobial activity than synthesized homopolymers and copolymers. Tri- bromo(phenyl) maleimide (N-TB2) monomer shows the best antimicrobial activity against all the bacteria compared to other synthesized *para*- bromo(phenyl) maleimide (N-PB1) and polymers.N-TB2 monomers screens the best against *Escherichia coli* bacteria and the least screening effect against *Bacillus subtilis* while its homopolymer, H-TB2 its copolymer, C-TB2 with MMA imparts good antibacterial activity against *staphylococcus aureus.* The antifungal activity was also carried out for synthesized monomers (N-PB1, N-TB2), homopolymers (H-PB1, H-TB2) and copolymers (C-PB1, C-TB2) against fungi, *Alternaria solani* and *Aspergillus niger*. It is concluded that the both the synthesized para- and tri– substituted bromo (phenyl) maleimide monomers(N-PB1, N-TB2) and homopolymers (H-PB1,H-TB2) imparts 100% inhibition against the growth of both the fungi, *Alternaria solani* and *Aspergillus niger*. While the copolymer C-TB2 has shown 88.7% inhibition against *Aspergillus niger* and shown 89.1% inhibition against *Alternaria solani*, at 1000 µg/mL concentration of the compound taken. Thus over all we concluded that the monomers imparts better activity against both bacteria and fungi.

CONCLUSION

Free radical polymerization process was used for the synthesis of homopolymer of N-bromo substituted (phenyl) maleimide and its copolymers with MMA. The homopolymers show two step degradation shows step-by-step degradation The copolymer C-PBPMI two-step degradation shows step-by-step degradation while C-TBPMI shows one strep degradation. The initial decomposition temperature of homopolymers H-PB1, H-TB2 was 200 °C and 198°C. and copolymers C-PB1, C-TB2 were 300 °C and 180°C. The non isothermal kinetic parameters of the polymer were calculated by Kissinger method for homopolymer and copolymer. The activation energy, Ea for homopolymers (H-PB1, H-TB2) were -9010.6 J/mol and -8646.0 J/mol and copolymers (C-PB1, C-TB2) were -10138.39 J/mol and -8646.8 J/mol respectively. Gel permeation chromatography (GPC) determines the molecular weight and polydispersity index (PDI) as for H-PB1, H-TB2 are 4156.1, 4228.2 and 2.15, 2.01 and for C-PB1, C-TB2 are 5177.2, 4486.1 and 1.30, 1.29 shows higher molecular weight poly chain. Halogen group such as bromo content is important to impart antimicrobial activity in the synthesized monomers, homopolymers and copolymers. The monomers impart better antimicrobial activity against both bacteria and fungi. Tri- bromo (phenyl) maleimide (N-TB2) monomer shows the best antimicrobial activity against all the bacteria compared to other synthesized *para*- bromo(phenyl) maleimide (N-PB1) and polymers. The synthesized para- and tri– substituted bromo (phenyl) maleimide monomers (N-PB1, N-TB2) and homopolymers (H-PB1,H-TB2) imparts 100% inhibition against the growth of both the fungi, *Aspergillus niger* and *Alterneria solani* than synthesized copolymers with methyl metha acrylate, MMA (C-PB1,C-TB2).

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