IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 11, Issue 5 Ver. II (May. 2018), PP 05-15
www.iosrjournals.org

Polymer Structures of N-[{4-(N'-Benzenesulphonicacid) Amino-Carbonyl} Phenyl] Maleimide: Synthesis, Thermal and Microbial Studies

Suamanjinger[1*], Jyoti Chaudhary[1], Supriya Dadhich[2]
*[1*123]Department of Polymer Science,MohanlalSukhadia University, Udaipur, Rajasthan, India*
Corresponding Author:Suamanjinger

Abstract: *Imido-functional group contenting N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide was prepared by reacting species of maleic anhydride, 4-amino benzoic acid and 4-amino sulphanilic acid via chlorination in the presence of Diphosphoruspentaoxide (P_2O_5) as a catalyst in medium of N, N'-dimethyl formamide (DMF). Homopolymer, copolymers[C1BSACPMI], [C2BSACPMI], [C3BSACPMI] and terpolymers [T1BSACPMI], [T2BSACPMI] were prepared by reaction of [BSACPMI] monomer with three different of acrylates, namely acrylonitrile (AN), acrylic acid (AA) and vinyl acetate (VA) in presence of tetrahydrofurane (THF) polar organic solvent. The structures of these compounds were confirmedby FT-IR, ^{1}H-NMR. The weight average molecular weight (Mw), number average molecular weight (Mn) and polydisperity (Mw/Mn ratio) of polymers were determined using Gel Permeation chromatography (GPC) technique. Thermal susceptibility of all polymers were studied by Thermo Gravimetric Analysis (TGA) and DSC techniques. All polymers wereevaluatedfrom biological activities against some bacterial and fungal species.*

Keywords*: Maleic acid, 4-amino benzoic acid, 4-amino sulphanilic acid, DMF, THF, acrylates, homopolymer, copolymers, terpolymers, TGA, DSC, GPC.*

Date of Submission: 05-05-2018 Date of acceptance: 21-05-2018

I. Introduction

Macromolecules containing imide functionality exhibit great electrical property, good water resistivity, anti-corrosive and good solubility in polar, organic media [1-4] and the most attractive thermal and oxidative stability properties. Due to their excellent properties many efforts have been made to synthesize high performing compounds containing imide functional group framed of one nitrogen atom sited between two carbonyl molecules in olefinic five hetero-membered ring. The imide group bearing monomer and their polymers are the examples of addition typed polymerization and that can be easily processes without any typical procedure and evolution of volatiles. However, the main disadvantage is their brittleness nature due to rigid structure of maleimide monomer[5-8]. Ether some flexible unsaturated acrylates inserted into monomer to form flexible, thermal stable polymeric chain[9-11].

With this context the present work deals with the synthesis of thermally high performance polymers and characterizations of homopolymer, copolymers and terpolymers made fromN-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide monomer using comonomers as acrylonitrile, acrylic acid and vinyl acetate.

II. Experimental

Materials

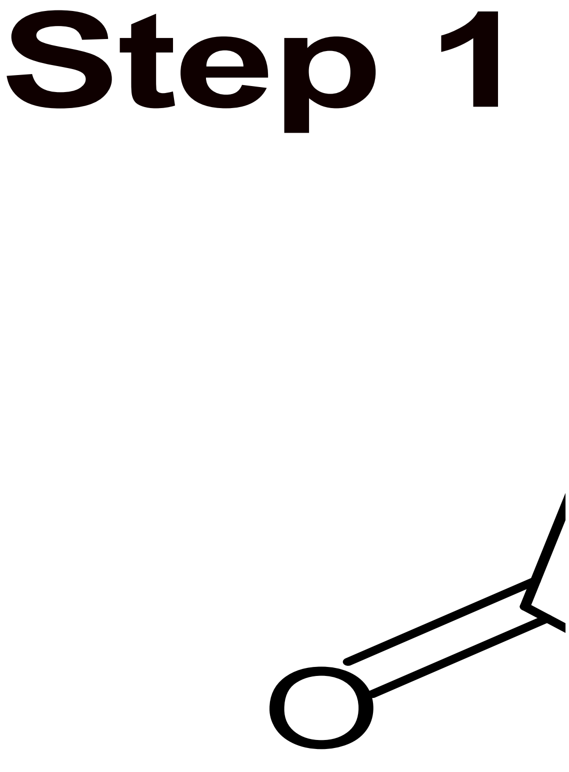
Maleic anhydride (LobaChemie, AR grade), 4-aminobenzoic acid (Sigma Aldrich), 4-amino sulphanilic acid, thionyl chloride (SO_2Cl), THF, DMF, Methanol (Sigma Aldrich) as solvent, P_2O_5 as a dehydrating agent and AIBN (Fisher Scientific) was used as initiator, acrylonitrile (central drug house, Mumbai), acrylic acid (Spectrochem, Mumbai) and vinyl acetate (LobaChemie, Mumbai) are used as comonomer units in polymerization.

Instrumentation

FT-IR spectra were measured at room temperature using a Perkin Elmer mode RX-I spectrometer using KBr pellets for sample preparation. The spectrum information was collected in the range of 250-4000 cm^{-1}. The ^{1}H-NMR spectra were obtained from Bruker 400 MHz with TMS as an internal standard reference were used. CHN elements analysis were performed using ThermoFinnigan analyzer, calibrated by K-factor method. All sample was weighed by Gel Permeation chromatography (GPC) and soluble in DMF, THF and DMSO.Thermal properties were analyzed from TGA recorded on Perkin Elmer-Purix-TGA Thermal Analyzer and DSC recorded on NETZSCH DSC 204 Analyzer at a heating rate of 10 °C / min under oxygen atmosphere.

Synthesis of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide

N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [BSACPMI] monomer was synthesized by using maleic anhydride (0.01 mol) and 4-amino benzoic acid (0.01 mol). These reactantswere dissolved in DMF solvent and stirred continuously at magnetic stirrer for 3 hours at room temperature then 0.03 g P_2O_5 and 10 ml conc. H_2SO_4 mixed in same solution and stirred continuously at 70 °C for 4 hours. The dark pale-yellow coloured solution was precipitated in ice-water. The precipitate was filtered,washed and dried. In next step, this solid powder (0.01 mol) was refluxed with thionyl chloride (50 ml) for 4 hours and dried by air till that smell of thionyl chloride was gone and washed, driedand treated with 4-amino sulphanilic acid (1:1 ratio) in THF solvent at 40 °C for 4 hours. The dark pale-yellow coloured precipitate obtained in ice-water, filtered and recrystallized from 2-propanol and dried in vaccum oven at 40 °C for 8-10 hours.



Scheme 1: Synthesis of Monomer [BSACPMI]

Synthesis of homopolymer of N-[{4-(N'-benzene sulfonic acid) amino-carbonyl} phenyl] maleimide [HBSACPMI]

Homopolymer was synthesized by [BSACPMI] monomers (0.01 mol) using azobisisobutyronitrile (AIBN) (0.03 g) as a free radical initiator in the reaction medium of THF-solventthen the reaction mixture was refluxed at 70 ^{o}C for 24 hours and precipitated 10 % methanol-water solution and dried in vaccum oven at 40 ^{o}C for 8-10 hours.

Scheme 2: Synthesis of Homopolymer of [BSACPMI]

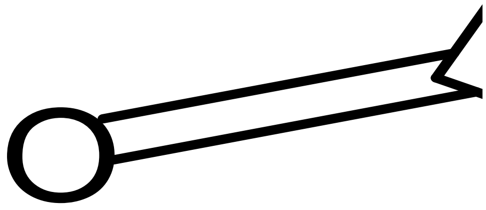
Synthesis of Copolymers of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [C1BSACPMI], [C2BSACPMI], [C3BSACPMI]

[BSACPMI] monomer (0.01mol) and acrylonitrile (AN) (0.01 mol) for [C1BSACPMI], acrylic acid (AA) (0.01 mol) for [C2BSACPMI] and vinyl acetate (VA) (0.01 mol) for [C3BSACPMI] were used in copolymerization. The AIBN, 0.03 g (0.00019 mol) was added in THF solution as an initiator, refluxed at 70 ^{o}C for 24 hours and precipitated 10 % methanol-water solution and dried in vaccum oven at 40 ^{o}C for 8-10 hours.

Scheme 3: Synthesis of Copolymers [C1BSACPMI], [C2BSACPMI], [C3BSACPMI]

Synthesis of Terpolymers of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [T1BSACPMI], [T2BSACPMI]

Monomer [BSACPMI] and comonomer units AN, AA, VA were used in equimolar amount (0.01 mol) for terpolymers preparation. Monomer [BSACPMI] and two comonomers, AN and VA used for [T1BSACPMI] and AA, VA was used for [T2BSACPMI], with 0.03 g (0.00019 mol) AIBN in THF solution and refluxed for 24 hours at 70 ^{o}C and precipitated 10 % methanol-water solution and dried in vaccum oven at 40 ^{o}C for 8-10 hours.



Scheme 4: Synthesis of Terpolymers of [T1BSACPMI], [T2BSACPMI]

III. Yield of Polymerization

The percentage yield was depends on the providing chemical environment. To get maximum yield of polymer products, applied different solvent-initiator pairs. Resultant, It was observed that the percentage yield in THF-AIBN system is high as compared to DMF, 1,4- Dioxane solvents and BPO initiator.

IV. Result and Discussion

MonomerN-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [BSACPMI]–

Yield 87%, melting point 156 oC; color yellow brown, FT-IR (KBr): 1715 cm-1 (C=O), 3064 cm-1 (N-H), 2883 cm-1(-OH) 1601 cm-1(C=O, amide), 1633 cm-1(CH=CH, C-C Stre.), 1318 cm-1(C-N-C), 1095, 1009 cm-1(S=O); 1H-NMR(400 MHz, CD3OD, DMSO): 7.19-7.76 (Aromatic), 6.96-7.25, (HC=CH of Maleimide), 10.06 (CO-NH), 2.53(SO3H).

Homopolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [HBSACPMI] –

Yield 87%, melting point 184 oC; color yellow brown, FT-IR (KBr): 1715 cm-1 (C=O), 3064 cm-1 (N-H), 2883 cm-1(-OH) 1601 cm-1(C=O, amide), 1633 cm-1(CH=CH, C-C Stre.), 1095, 1009 cm-1(S=O); 1H-NMR(400 MHz, CD3OD, DMSO): 7.11-7.89 (Aromatic), 6.96-7.31, (HC=CH of Maleimide), 9.98 (CO-NH), 2.533 (SO3H).

Copolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [C1BSACPMI]-

Yield 83%, melting point 206 oC; color yellow brown, FT-IR (KBr): 1719 cm-1 (C=O), 3063 cm-1 (N-H), 2883 cm-1(-OH) 1601 cm-1(C=O, amide), 1633 cm-1(CH=CH, C-C Stre.), 1388 cm-1(C-N-C), 1095, 1008 cm-1(S=O); 1H-NMR(400 MHz, CD3OD, DMSO): 7.11-7.93 (Aromatic), 6.92-7.63, (HC=CH of Maleimide), 9.84 (CO-NH), 3.02 (SO3H).

Copolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [C2BSACPMI]-

Yield 70%, melting point 241 oC; color yellow brown, FT-IR (KBr): 1718 cm-1 (C=O), 3065 cm-1 (N-H), 2983 cm-1(-OH) 1600 cm-1(C=O, amide), 1501 cm-1(CH=CH, C-C Stre.), 1388 cm-1(C-N-C), 1095, 1009 cm-1(S=O); 1H-NMR(400 MHz, CD3OD, DMSO): 7.18-7.96 (Aromatic), 6.26-7.63, (HC=CH of Maleimide), 9.84 (CO-NH), 2.57 (SO3H).

Copolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide [C3BSACPMI]-

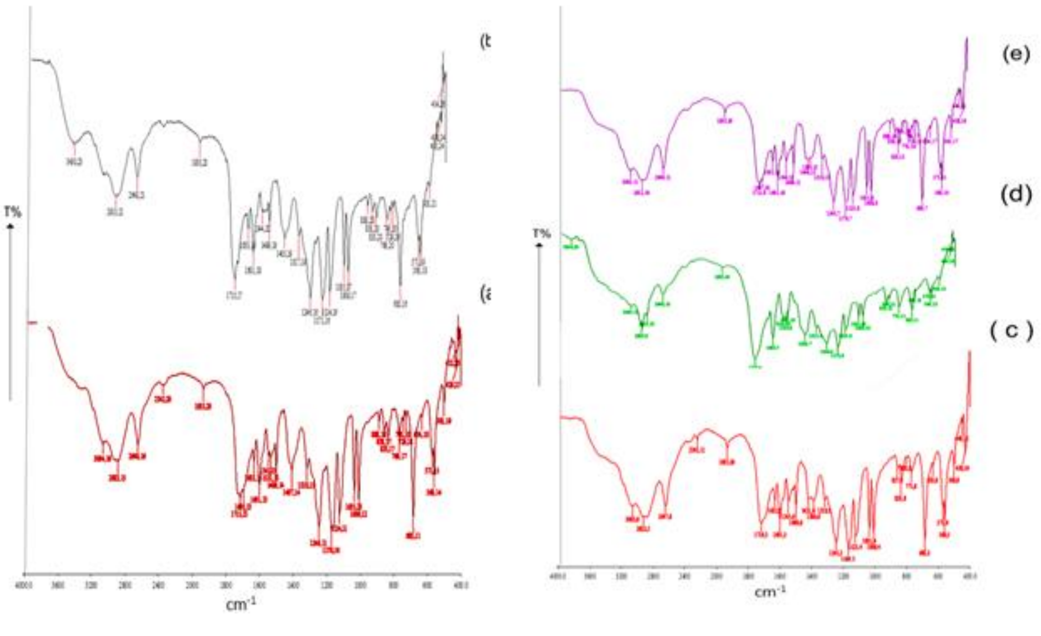
Yield 85%, melting point 255 oC; color yellow brown, FT-IR (KBr): 1715 cm-1 (C=O), 3063 cm-1 (N-H), 2883 cm-1(-OH) 1601 cm-1(C=O, amide), 1697 cm-1(CH=CH, C-C Stre.), 1396 cm-1(C-N-C), 1095, 1009 cm-1(S=O); 1H-NMR(400 MHz, CD3OD, DMSO): 7.11-7.96 (Aromatic), 6.25-7.67, (HC=CH of Maleimide), 10.38 (CO-NH), 3.03 (SO3H).

Terpolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide-acrylonitrile - vinyl acetate] [T1BSACPMI]-

Yield 87 %, melting point 258 oC; color dark brown, FT-IR (KBr): 1715 cm-1 (C=O), 3446 cm-1 (N-H, broad peak), 2928 cm-1 (CH=CH, C-H Stre.), 1604 cm-1(C=O, amide), 1383 cm-1(C-N-C), 1634 cm-1(CH=CH, C-C Stre.), 1116, 1034 cm-1(S=O); 1H-NMR (CD3OD): 7.14-7.96 (Aromatic), 7.10-7.30 (HC=CH of Maleimide), 3.76 {(CH-CH-)n}, 9.87(CO-NH).

Terpolymer of N-[{4-(N'-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide-acrylic acid - vinyl acetate] [T2BSACPMI]-

Yield 76 %, melting point 263 oC; color dark brown, FT-IR (KBr):1715 cm-1 (C=O), 3364 cm-1 (N-H, broad peak), 2990 cm-1 (CH=CH, C-H Stre.), 1601 cm-1(C=O, amide), 1389 cm-1(C-N-C), 1633 cm-1(CH=CH, C-C Stre.), 1035, 1009 cm-1(S=O); 1H-NMR(CD3OD): 7.15-7.67 (Aromatic), 7.02-7.48 (HC=CH of Maleimide), 3.64 {(CH-CH-)n}, 9.81 (CO-NH).



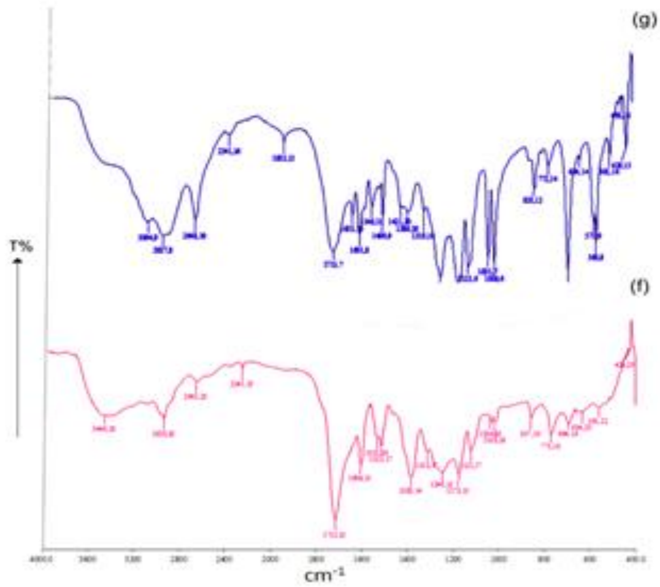
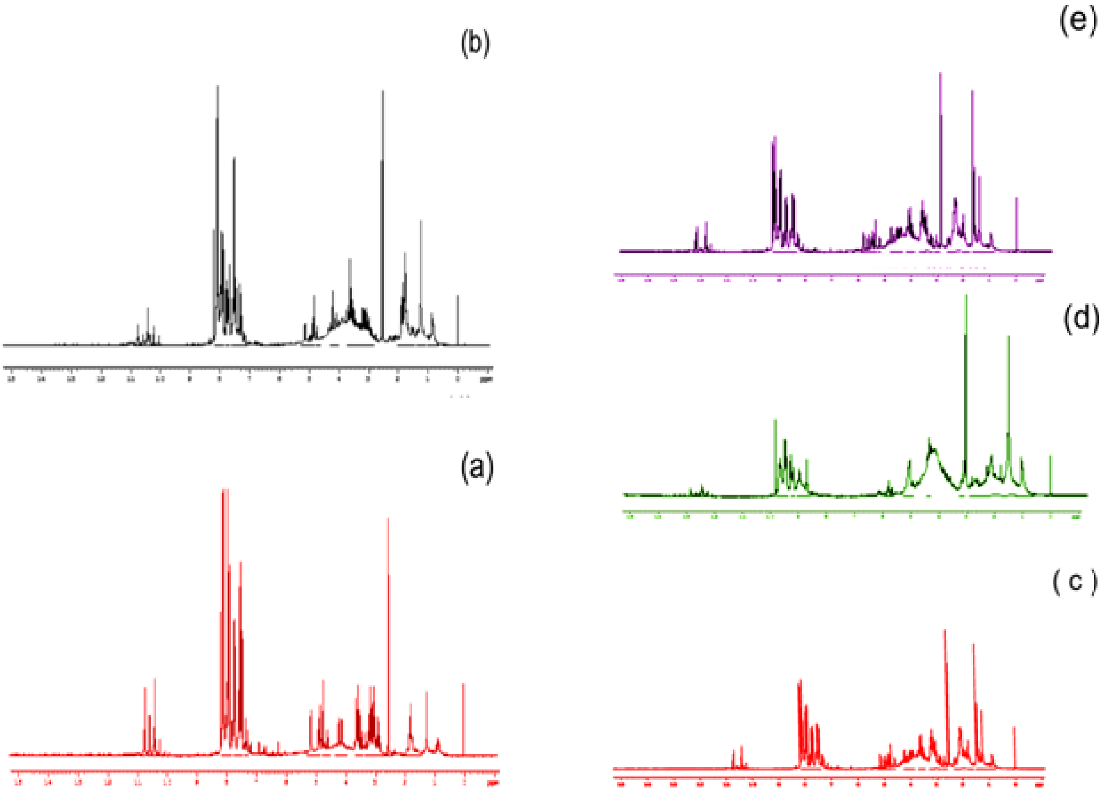


Figure 1: FTIR Spectra (a) BSACPMI (b) HBSACPMI (c) C1BSACPMI (d) C2BSACPMI (e) C3BSACPMI (f)T1BSACPMI(g)T2BSACPMI



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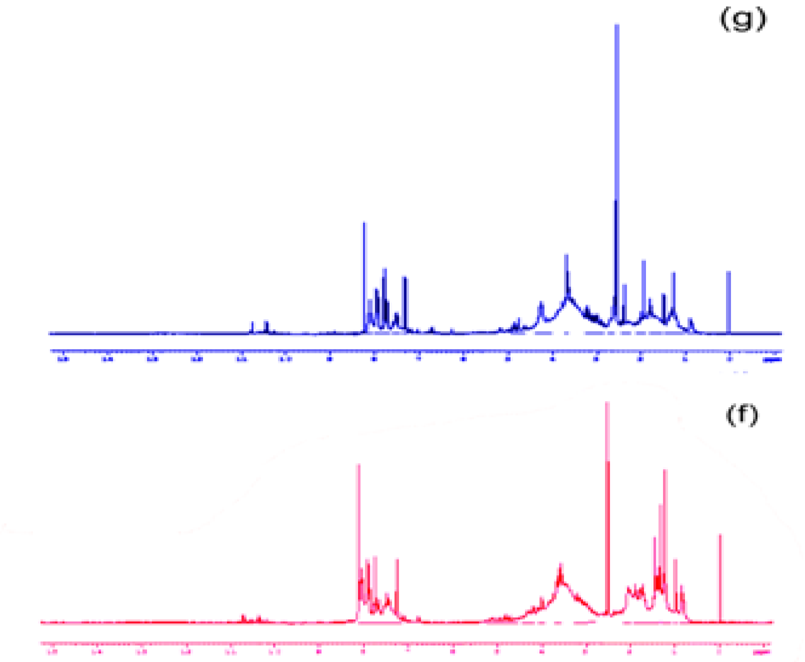


Figure 2: 1H-NMR Spectra (a) BSACPMI (b) HBSACPMI (c) C1BSACPMI (d) C2BSACPMI (e) C3BSACPMI (f) T1BSACPMI (g) T2BSACPMI

V. Molecular Weight

Molecular weight of all polymer were determined from GPC and values are given in Table 1. The GPC data for the homopolymer, copolymers and terpolymer were showed that the small alkyl group in acrylates and vinyls, increased and resultant the molecular weights of polymers decreases, due to branching in comonomer units. Polydispersity index (PDI) value ranging from 1.18 -1.75 clearly explain that the homopolymer, copolymers and terpolymer were aligned through radical polymerization process. The GPC-curvature’s area distribution were narrow i.e. illustrated the molecular weight of polymers occupy relatively high molecular weight fractionso it is assumed as the polymers bear high mechanical strength with good processing properties.

Table no 1: The weight average molecular weight (Mw), number average molecular weight (Mn) andpolydisperity (Mw/Mn) of polymers of BSACPMI

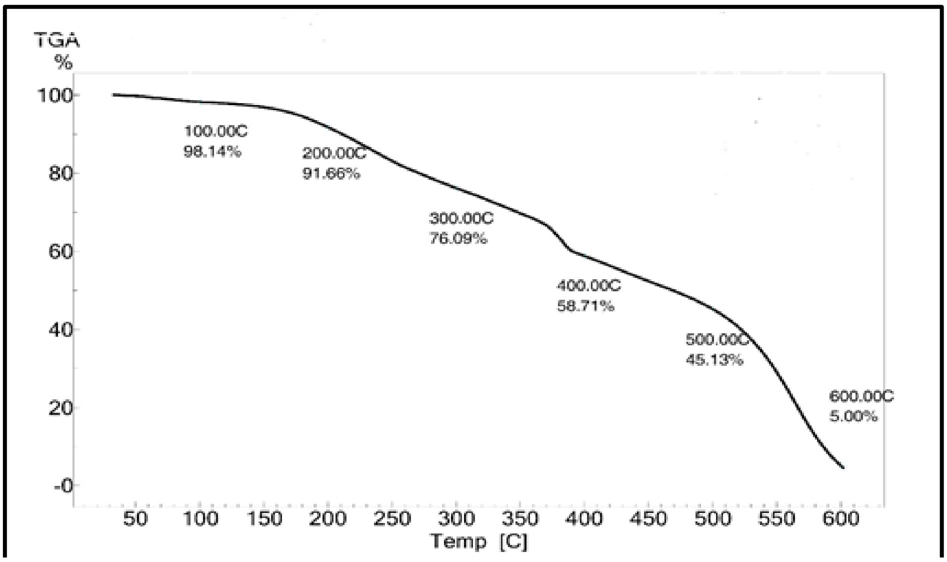
Polymer Code	Number Average (Mw) g/mol	Weight Average (Mn) g/mol	Poly Dispersity (Mw/Mn)	Start Mw
HBSACPMI	832.3	701.0	1.187	3723.3
C1BSACPMI	1102.4	818.5	1.346	4926.3
C2BSACPMI	1513.3	997.2	1.517	10456.9
C3BSACPMI	794.3	666.8	1.191	3318.8
T1BSACPMI	1505.7	856.5	1.616	17111.1
T2BSACPMI	1753.6	1084.9	1.757	18158.6

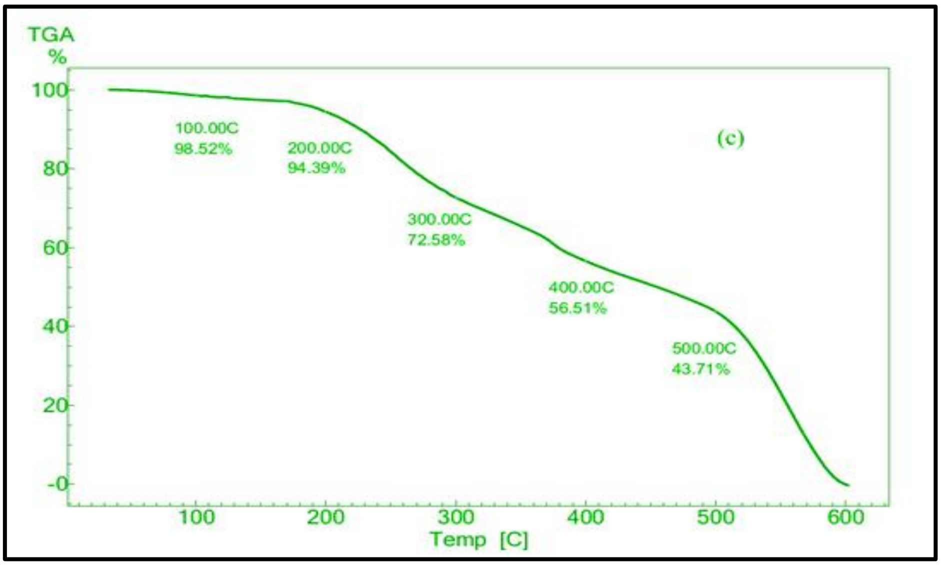
VI. Thermal Analysis

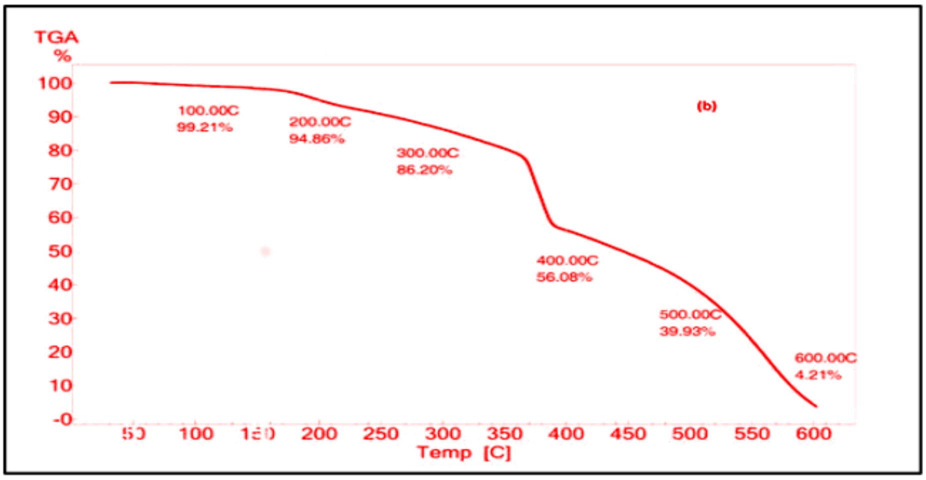
The TGA thermograms of homopolymer, copolymers and terpolymer of BSACPMImonomer are displayed. The measurement of weight differences in form of weight degradationwere referred to the function of temperature and time. TGA-curve gives the information about temperature stability / sustainability of polymeric or other materials.The analysis was typically carried out in milligrams by the sample size quantity with oxy-decomposition environment and with 10 ^{o}C / min heating rate from 100 ^{o}C to 800 ^{o}C. The polymer thermograms of HBSACPMI, C1BSACPMI, C2BSACPMI, C3BSACPMI, TBSACPMIand T2BSACPMI shown the major weight loss beginning from 200-300 ^{o}C and ending at 600-700 ^{o}C in single step. The reason of continuous degradation was followed eliminations of attached pendant small groups due to chain scission.The glass transition temperature (Tg) was determined from differential scattering colorimetric (DSC). The Tg value of homopolymer, copolymers and terpolymer HBSACPMI, C1BSACPMI, C2BSACPMI, C3BSACPMI, TBSACPMI and T2BSACPMI are respectively present in Table 2. From the analysis of Tg- temperatures, reflected that presence of acrylic acid (AA) and acrylonitrile (AN) groups in copolymers and terpolymer increases the Tg temperature then their homopolymer. The increased and moderate Tg-temperature bearing polymers are more applicable in various processing units in desired polymer industries and it may provide higer opportunity for many applications in related sectors.

Table no 2: Weight loss % of homopolymer, copolymers and terpolymer at various temperature and Tg temperature

Polymer Code	200^0C	300^0C	400^0C	500^0C	600^0C	Tg temperature in ^{0}C
	Weight loss (%)					
HBSACPMI	8.34	23.91	41.29	54.87	95.00	177.7
C1BSACPMI	5.14	13.80	43.92	60.10	95.79	140.2
C2BSACPMI	5.61	27.42	43.49	56.29	-	195.8
C3BSACPMI	7.59	18.22	50.93	69.41	-	118.7
T1BSACPMI	4.38	19.21	35.00	48.94	91.88	122.01
T2BSACPMI	5.53	20.20	49.91	72.07	-	139.2






TGA
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70
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10
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(b)
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99.21%
200.00C
94.86%
300.00C
86.20%
400.00C
56.08%
500.00C
39.93%
600.00C
4.21%
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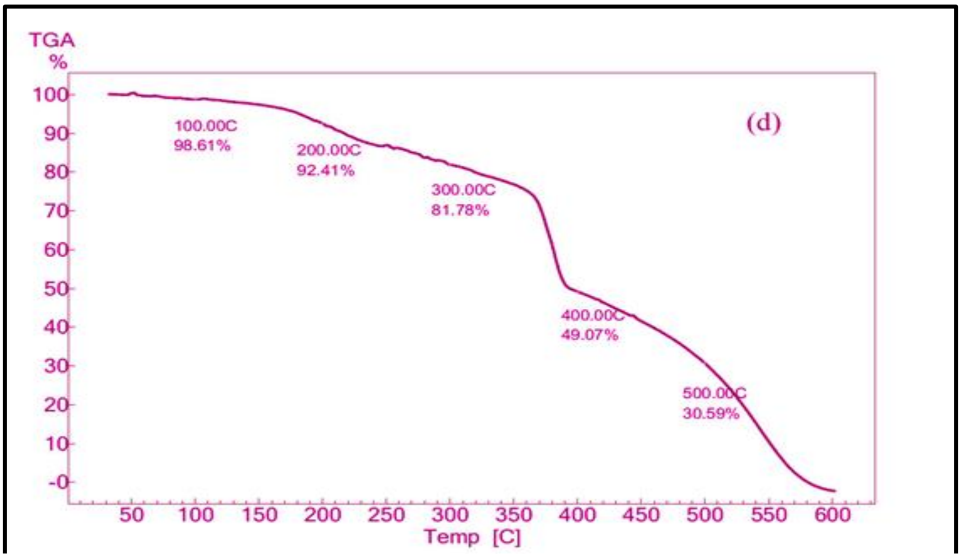
Temp [C]


TGA
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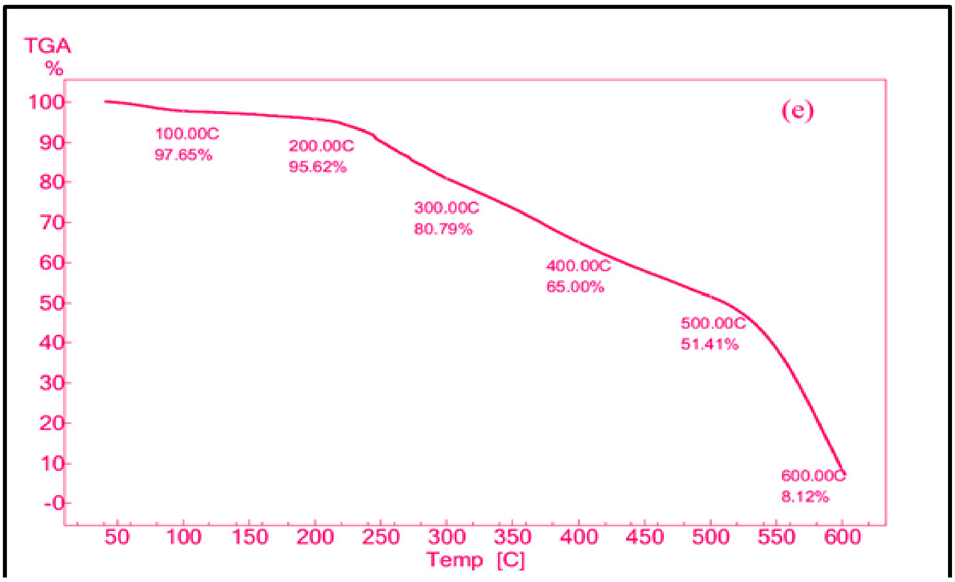
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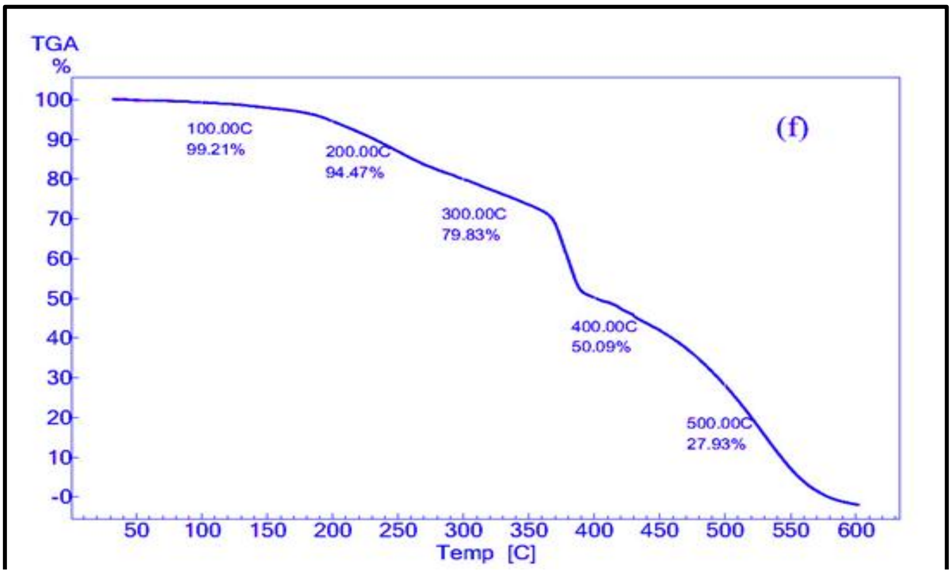

Figure 2: TGA Thermograms of (a) HBSACPMI (b) C1BSACPMI (c) C2BSACPMI (d) C3BSACPMI (e) T1BSACPMI (f) T2BSACPMI

VII. Microbial Activity

Microbial activity (antibacterial and antifungal activity) of monomer **BSACPMI**, homopolymer H**BSACPMI**and Copolymers C1**BSACPMI**, C2BSACPMI, C3BSACPMI and terpolymer T1BSACPMI and T2BSACPMI against bacteria’s and Fungus were carried out. Synthesized monomer and polymers were showed good antibacterial activity against bacteria **(Esherichiaaerogenes, Staphylocous aureus**) and antifungal activity against fungi (**Aspergillus niger, Alternariasolani**). The antimicrobial activity of polymers were due to presence of heteroatoms in polymeric structures.

Table no 3: Antibacterial and antifungal activity of BSACPMI, HBSACPMI and C1BSACPMI, C2BSACPMI, C3BSACPMI, T1BSACPMI and T2BSACPMI

Code	**Antibacterial activity (Inhibition Zone in mm) 100(µg/ml) Concentration of compound taken**		**Antifungal activity (Inhibition Zone in mm) 100(µg/ml) Concentration of compound taken**	
	Zone of Inhibition for *E.aerogenes*	**Zone of Inhibition for *S. aureus***	**Zone of Inhibition for *A.niger***	**Zone of Inhibition for *A.solani***
HBSACPMI	12	12.6	11.8	12.4
C1BSACPMI	13.5	12.8	13.1	12.8
C2BSACPMI	17.3	16.8	17.6	16.3
C3BSACPMI	13.1	14.4	14.1	13.5
T1BSACPMI	18	16.2	16.4	17.2
T2BSACPMI	19.2	20.2	18.4	18.9

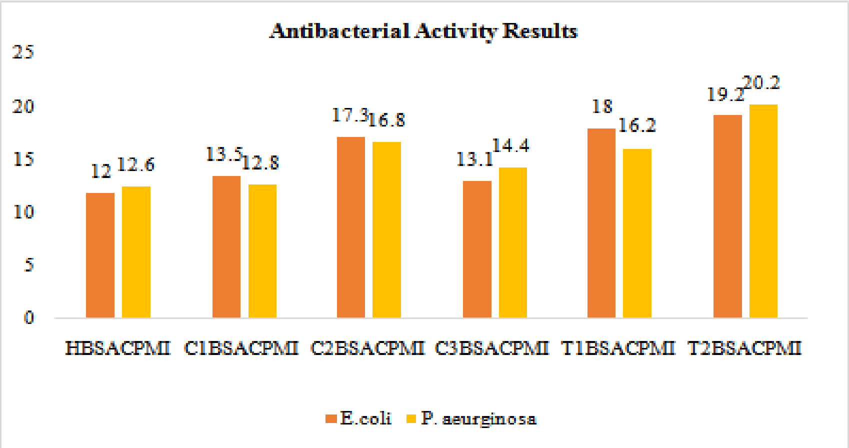

Figure 3: Antibacterial activity of [BSACPMI] polymers

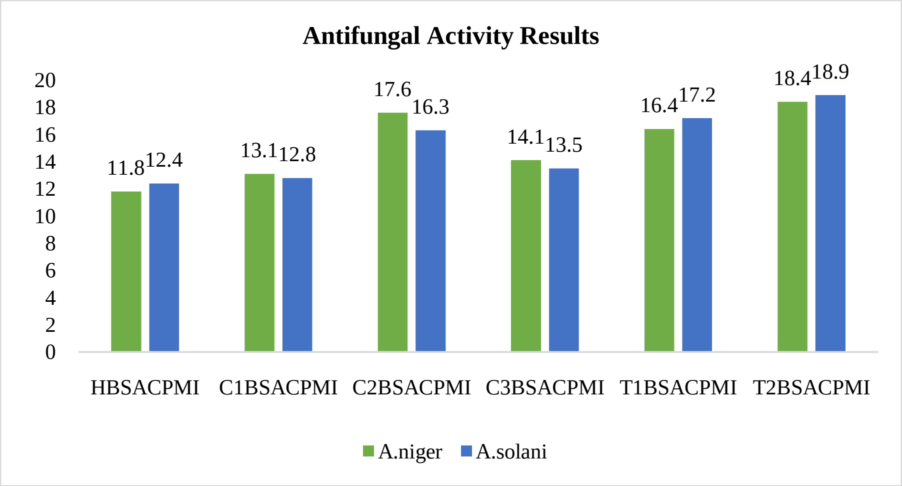

Figure 4: Antifungal activity of [BSACPMI] polymers

VIII. Conclusion

One monomer and six different polymer compounds based onN-[{4-(N’-benzenesulphonicacid) amino-carbonyl} phenyl] maleimide have been successfully synthesized and characterized. The use of phosphorus pentaoxide (P_2O_5) as a catalyst has decreased the reaction temperature and reaction time from 300 ^oC to 70-80 ^oC and given high yield of products.

Acknowledgements

The authors would like to thank UGC-Delhi for the financial assistance from fellowship scheme and department of Polymer Science, MLSU, Udaipur for research assistance.

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Suamanjinger "Polymer Structures of N-[{4-(N’-Benzenesulphonicacid) Amino-Carbonyl} Phenyl] Maleimide: Synthesis, Thermal and Microbial Studies." IOSR Journal of Applied Chemistry (IOSR-JAC) 11.5 (2018): 05-15.