

Conventional-Cum-Microwave Synthesis and Characterization Of Polymeric Structures Of N-Substituted Maleimide

Suman Jinger¹, Jyoti Chaudhary², Giriraj Tailor³

¹²³Department of Polymer Science, Mohanlal Sukhadia University, Udaipur, Rajasthan, India
Corresponding Author: Suman Jinger¹

Abstract: We described here at a convenient, fast and rapid process to synthesis of various imide class compounds; [4-N-phenylethanamideazo-3-N-(4-nitrophenyl) maleimide] [PANMI], [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide] [PABMI], N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide] [BSACPMI] and [N,N' bis(maleimide) benzene sulfonamide] [BMBS] using domestic microwave in small quantities of chemicals with small consumption of solvents and time. The compounds were prepared by the reaction of maleic anhydride with different amine-derivatives in the presence of ml volume of DMF to provide a homogenous solution for chemical transformation. The polymerization were also done under microwave heating is described and homopolymers, copolymers and terpolymers were prepared by using [PANMI], [PABMI], [BSACPMI] and [BMBS] monomers with three acrylates namely; acrylonitrile (AN), acrylic acid (AA) and vinyl acetate (VA) in presence of ml volume of DMF used with AIBN as free radical initiator. The structures of all compounds were confirmed by element CHN analysis, FT-IR, ¹H-NMR and molecular weight was determined by GPC.

Keywords: Microwave, Maleic anhydride, AIBN, DMF, acrylates, homopolymer, copolymers, terpolymers, FT-IR, ¹H-NMR and GPC.

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I. INTRODUCTION

The development of macromolecules containing imide functionality exhibit great electrical property, photostabilizing potency for thermoplastic [1-2] 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 processed 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]. Either some flexible unsaturated acrylates inserted into monomer to form flexible, thermal stable polymeric chain in the form of copolymers and terpolymers [9-11].

With this context the present work deals with the synthesis and characterizations of homopolymer, copolymers and terpolymers made from various maleimide monomer as; [4-N-phenylethanamideazo-3-N-(4-nitrophenyl) maleimide] [PANMI], [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide] [PABMI], N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide] [BSACPMI] and [N,N' bis(maleimide)benzene sulfonamide] [BMBS] and comonomers as acrylonitrile, acrylic acid and vinyl acetate.

II. EXPERIMENTAL

Materials

Maleic anhydride (LobaChemei, AR grade), 4-nitroaniline, 4-bromoaniline, 4-aminoacetanilide, 4-aminobenzoic acid (Sigma Aldrich), 4-amino sulphanilic acid, Sodium nitrite, thionyl chloride (SO₂Cl), THF, DMF, Methanol (Sigma Aldrich) as solvent, P₂O₅ as a dehydrating agent. AIBN (Fisher Scientific) was used as initiator. Acrylonitrile (central drug house, mumbai), acrylic acid (spectrochem, mumbai) and vinyl acetate (lobaChemie, Mumbai) were used as comonomer units in polymerization.

Instrumentation

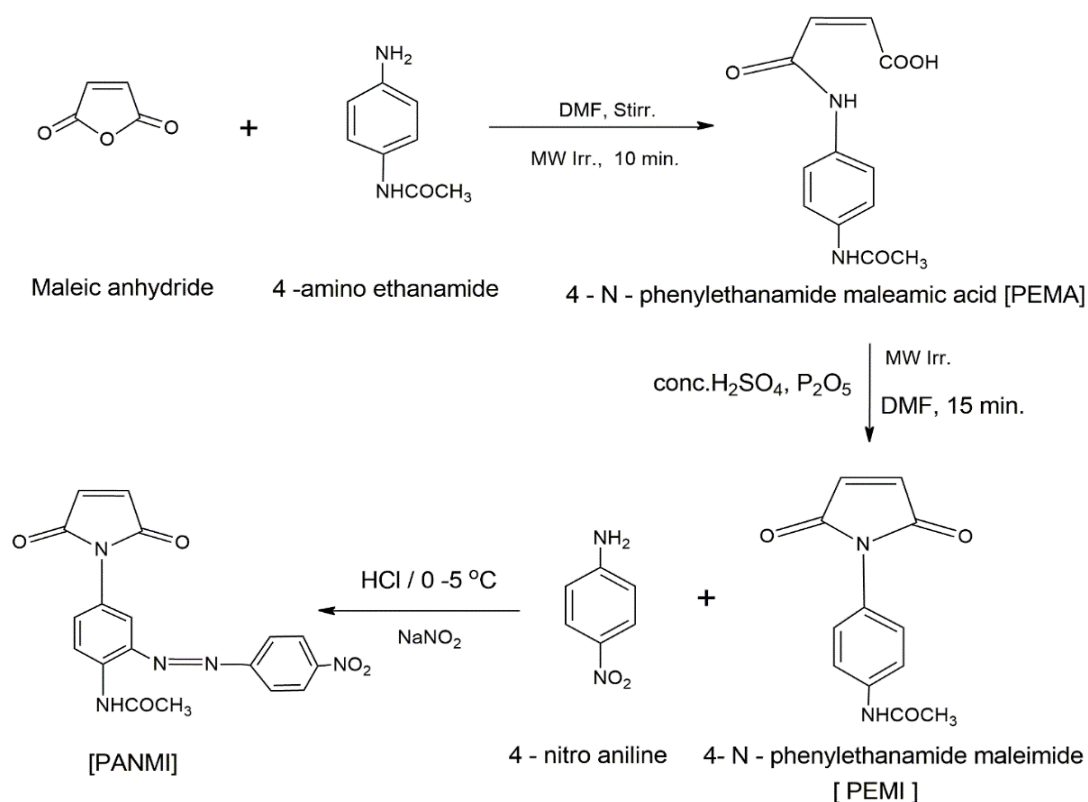
FT-IR spectra were measured at room temperature using a Perkin Elmer mode RX-I spectrometer using KBr pellets for sample preparation. The spectrum information was collected in the range of 250-4000 cm⁻¹. The ¹H-NMR was obtained from Bruker 400 MHz with TMS as an internal standard referenc. CHN elements

analysis were performed using ThermoFinnigan analyzer, calibrated by K-factor method. All polymer weremolecularly weighed by GPC and soluble in DMF, THF and DMSO.

Microwave synthesis of 4-N-phenylethanamideazo-3-N-(4-nitrophenyl) maleimide:

[4-N-Phenylethanamide Azo -3-N-(4-nitrophenyl) maleimide [PANMI] monomer was synthesized by maleic anhydride (0.1 mol) and 4-amino phenylethanamide (0.2mol) are dissolved 10 ml of N, N'-dimethyl formamide (DMF) and stirred for 10 min. and heated under microwave 10 min. Then this solution was precipitated out on crushed ice-water and filtered, washed and dried at 40 °C for 8 hours.

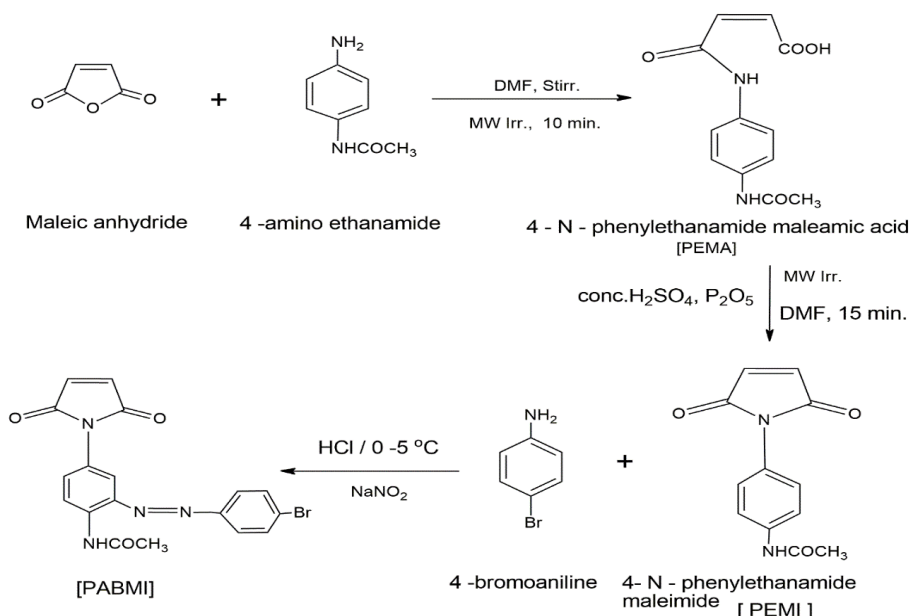
In second step, P₂O₅ was dissolved in H₂SO₄ (5 ml) and DMF (10 ml), added dropwise into solution of N-(4-phenylethanamide) maleamic acid (DMF) stirred and give temperature for 15 min. then precipitated in cold water. The obtained precipitate [PEMI] was vacuum filtered, washed and dried. Prepared 4-nitroaniline (0.01 mol), conc. HCl (5 ml) and water (5 ml) in 1:1 ratio and aqueous NaNO₂(10 ml) at 5°C and 4-nitroaniline solution added dropwise to NaNO₂ solution at 5 °C with continuous stirring. This mixture was then slowly added into the solution of [PEMI], which was prepared by dissolve in 10 ml 10% NaOH with maintain the same temperature and the final solution was cooled in the ice-bath and stirred continuously for 30 minutes. The precipitate formed was vacuum filtered, washed and recrystallized dried and the reaction scheme [1] illustrated below-



Scheme 1: Microwave synthesis of 4-N-phenylethanamideazo-3-N-(4-nitrophenyl) maleimide

Microwave synthesis of 4-N-phenylethanamideazo-3-N-(4-bromophenyl) maleimide:

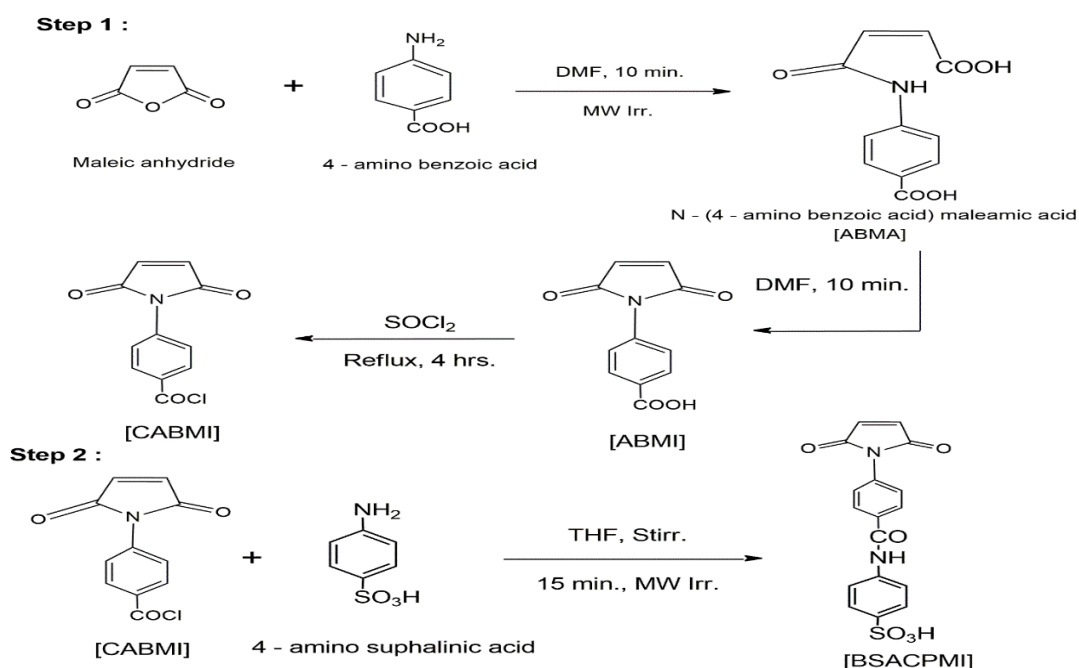
[4-N-Phenylethanamide Azo -3-N-(4-bromophenyl) maleimide [PABMI] monomer was synthesized by maleic anhydride (0.1 mol) and 4-amino phenylethanamide (0.2 mol) are dissolved 10 ml of N, N'-dimethyl formamide (DMF) and stirred for 10 min. and heated under microwave 10 min. Then this solution was precipitated out on crushed ice water and filtered, washed and dried at 40 °C for 8 hours. In second step, P₂O₅ was dissolved in H₂SO₄ (5 ml) and DMF (10 ml), added dropwise into solution of N-(4-phenylethanamide) maleamic acid (DMF) stirred and give temperature for 15 min. then precipitated in cold water. The obtained precipitate [PEMI] was vacuum filtered, washed and dried. Prepared 4-nitroaniline (0.01 mol), conc. HCl (5 ml) and water (5 ml) in 1:1 ratio and aqueous NaNO₂ (10 ml) at 5°C and 4-bromoaniline solution added dropwise to NaNO₂ solution at 5 °C with continuous stirring. This mixture was then slowly added into the solution of [PEMI], which was prepared by dissolve in 10 ml 10% NaOH with maintain the same temperature and the final solution was cooled in the ice-bath and stirred continuously for 30 minutes. The precipitate formed was vacuum filtered, washed and recrystallized dried and the reaction scheme [2] illustrated below-



Scheme 2: Microwave synthesis of 4-N-phenylethanamideazo-3-N-(4-bromophenyl) maleimide

Microwave synthesis of N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide [BSACPMI]-

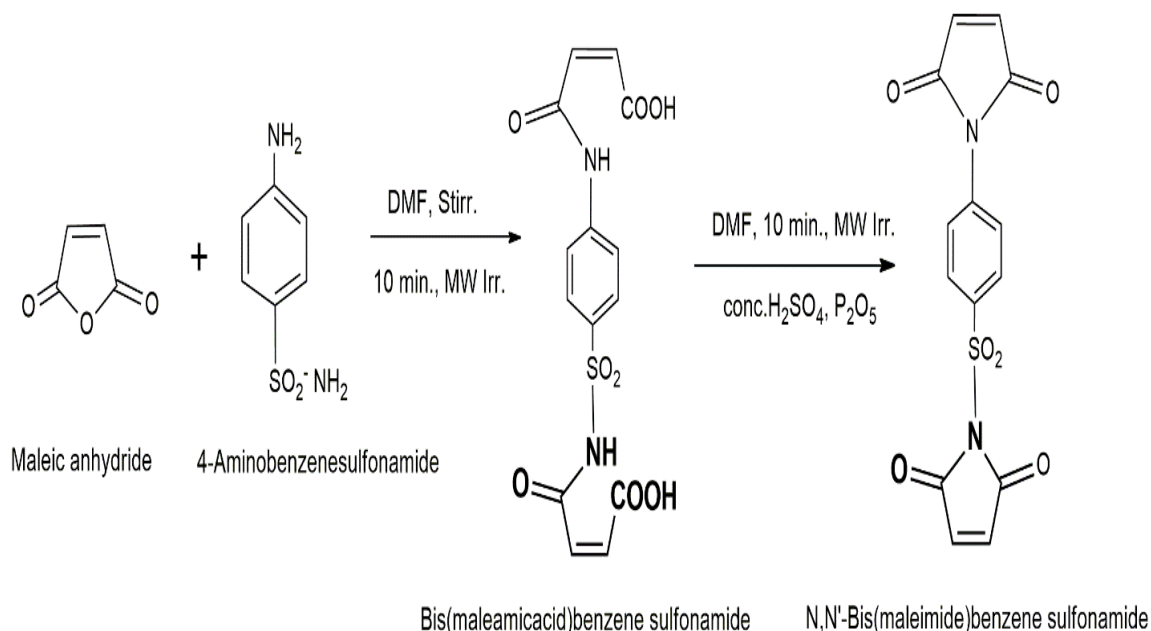
N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide [BSACPMI] monomer was synthesized by using maleic anhydride (0.01 mol) and 4-amino benzoic acid (0.01 mol) in DMF and stirred continuously at magnetic stirrer for 15 min. at room temperature. Then 0.03 g P₂O₅ and 10 ml conc. H₂SO₄ mixed in same solution and stirred 10 min. and put into microwave for 15 min.. The dark pale-yellow coloured solution was cooled down and precipitated in crushed ice water then filtered, washed and dried. Then this product was refluxed with thionyl chloride (10 ml) for 4 hours and the prepared solid compound was dried by air till that smell of thionyl chloride was gone and washed with distilled water and dried. After that this solid was treated with 4-amino sulphanic acid (1:1 ratio) in THF solvent in microwave for 15 min. then the dark pale-yellow coloured solution was precipitate, filtered, recrystallized and dried in vaccum oven at 40 °C for 8-10 hours. The detailed reaction scheme illustrated in scheme [3] at below-



Scheme 3: Microwave synthesis of N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide [BSACPMI]

2.6 Microwave synthesis of N, N' bis (maleimide) benzene sulfonamide [BMBS] monomer:

N, N' bis (maleimide) benzene sulfonamide [BMBS] monomer was synthesized using 4-amino sulfonamide and maleic anhydride. Maleic anhydride (0.02 mol) and 4-amino sulfonamide (0.01 mol) was dissolved in DMF (15 ml) in beaker and stirred for 10 min., then put in microwave for 10 min. Cyclization reaction of maleamic acid was carried out by adding 0.2 mol amount of fused sodium acetate and acetic anhydride, stirred and heated for 10 min. The reaction mixture was precipitated in water. The obtained precipitate was filtered, washed and air-dried.



Scheme 4: Microwave synthesis of N, N' bis (maleimide) benzene sulfonamide [BMBS] Polymerization

Microwave synthesis of homopolymers of [PANMI], [PABMI], [BSACPMI], [BMBS] monomers:

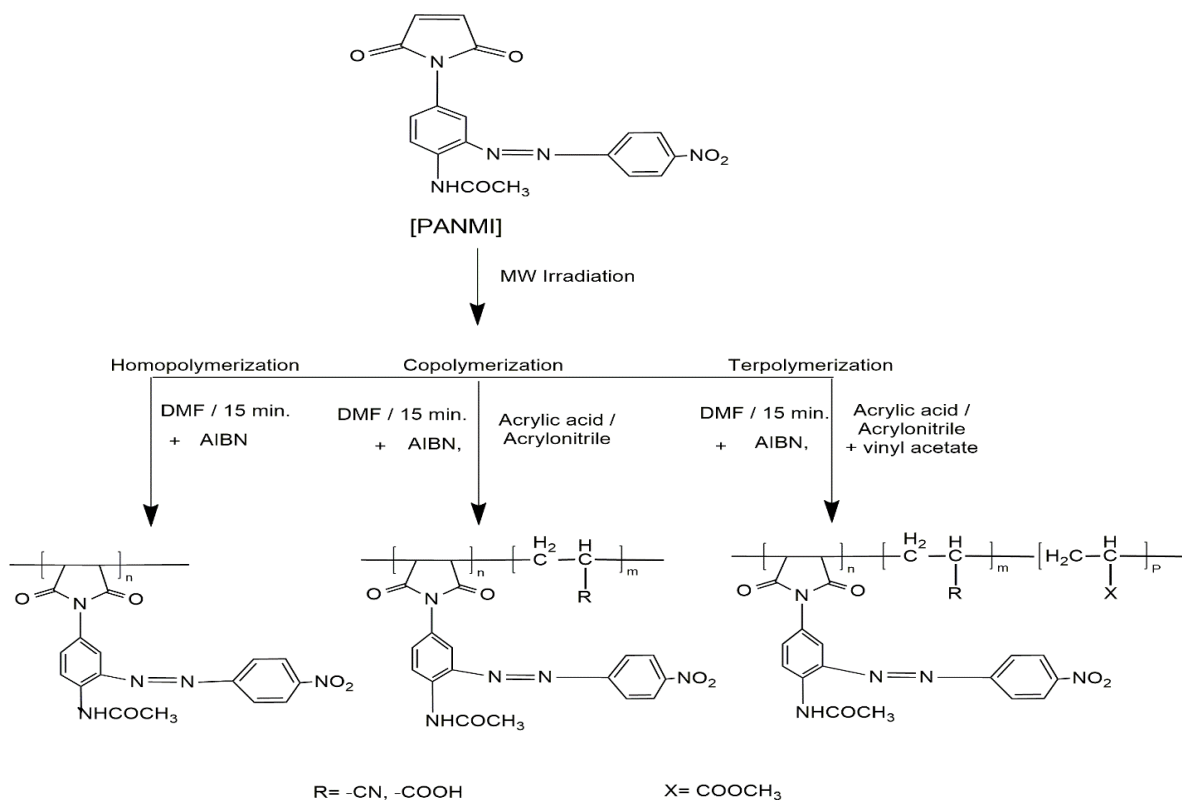
Homopolymers of [PANMI], [PABMI], [BSACPMI], [BMBS] monomers (0.01 mol) were synthesized by using azobisisobutyronitrile (AIBN) (0.02 g) as a free radical initiator in the small amount of DMF under microwave conditions for 15 min. The solution mixture was cooled at room temperature and poured into solvent mixture of methanol and distilled water (10 % methanol-water solution) for precipitation. The products were filtered using vacuum, washed with methanol and water, dried at 40 °C for 8-10 hours.

Microwave synthesis of copolymers of [PANMI], [PABMI], [BSACPMI], [BMBS] monomers:

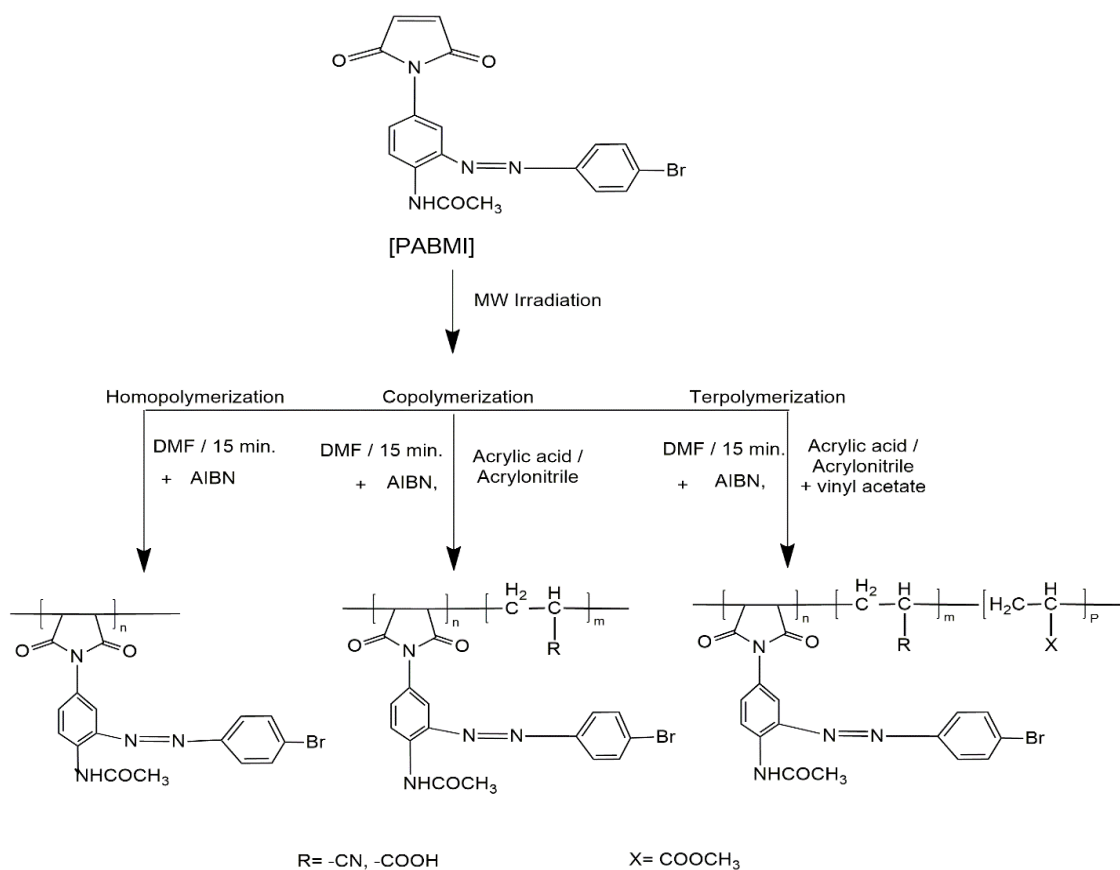
All monomer (0.01 mol) were copolymerized with acrylonitrile (AN) (0.01 mol), acrylic acid (AA) (0.01 mol) and vinyl acetate (VA) (0.01 mol) using AIBN, (0.02 g) as a free radical initiator in the small amount of DMF under microwave conditions for 15 min. The solution mixture was cooled at room temperature and poured into solvent mixture of methanol and distilled water (10 % methanol-water solution) for precipitation. The products were filtered using vacuum, washed with methanol and water, dried at 40 °C for 8-10 hours.

Microwave synthesis of terpolymers of [PANMI], [PABMI], [BSACPMI], [BMBS] monomers:

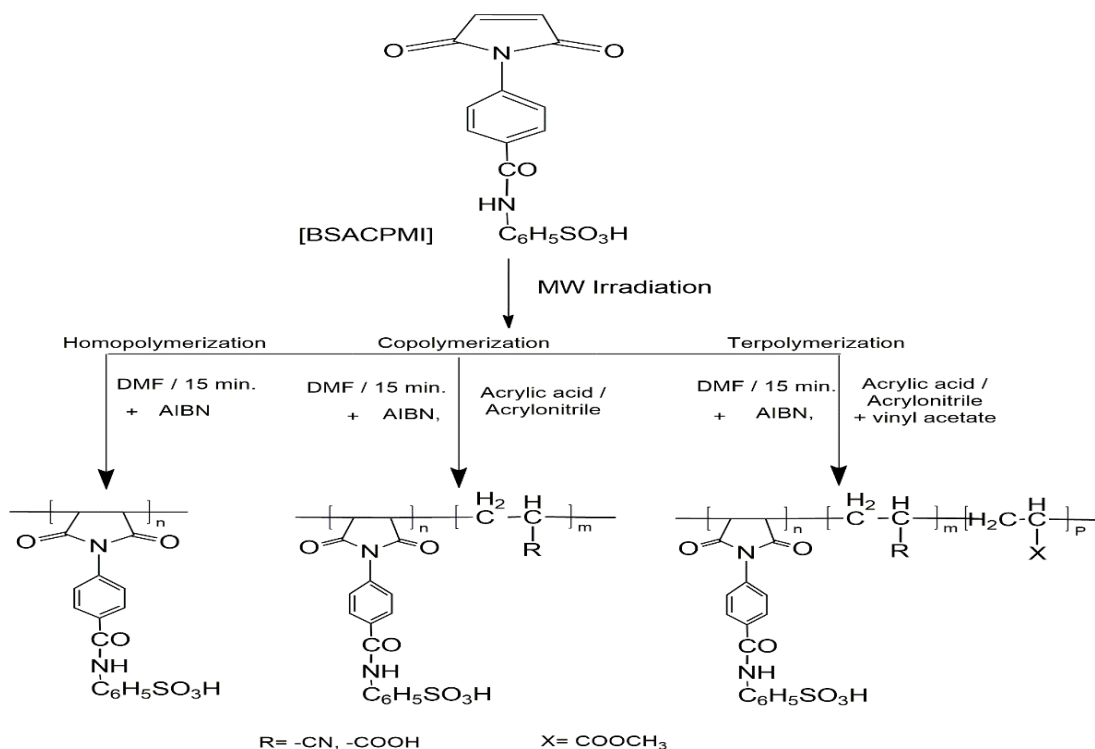
All monomer were terpolymerized with acrylonitrile (AN), acrylic acid (AA) and vinyl acetate (VA) in equimolar amount (0.01 mol). One monomer and two comonomers; AN and VA used for one type of terpolymer and another one monomer and AA, VA was used for second type of terpolymer. Terpolymerization were proceed by AIBN, (0.02 g) as a free radical initiator in the small amount of DMF under microwave conditions for 15 min. The solution mixture was cooled at room temperature and poured into solvent mixture of methanol and distilled water (10 % methanol-water solution) for precipitation. The products were filtered using vacuum, washed with methanol and water, dried at 40 °C for 8-10 hours.



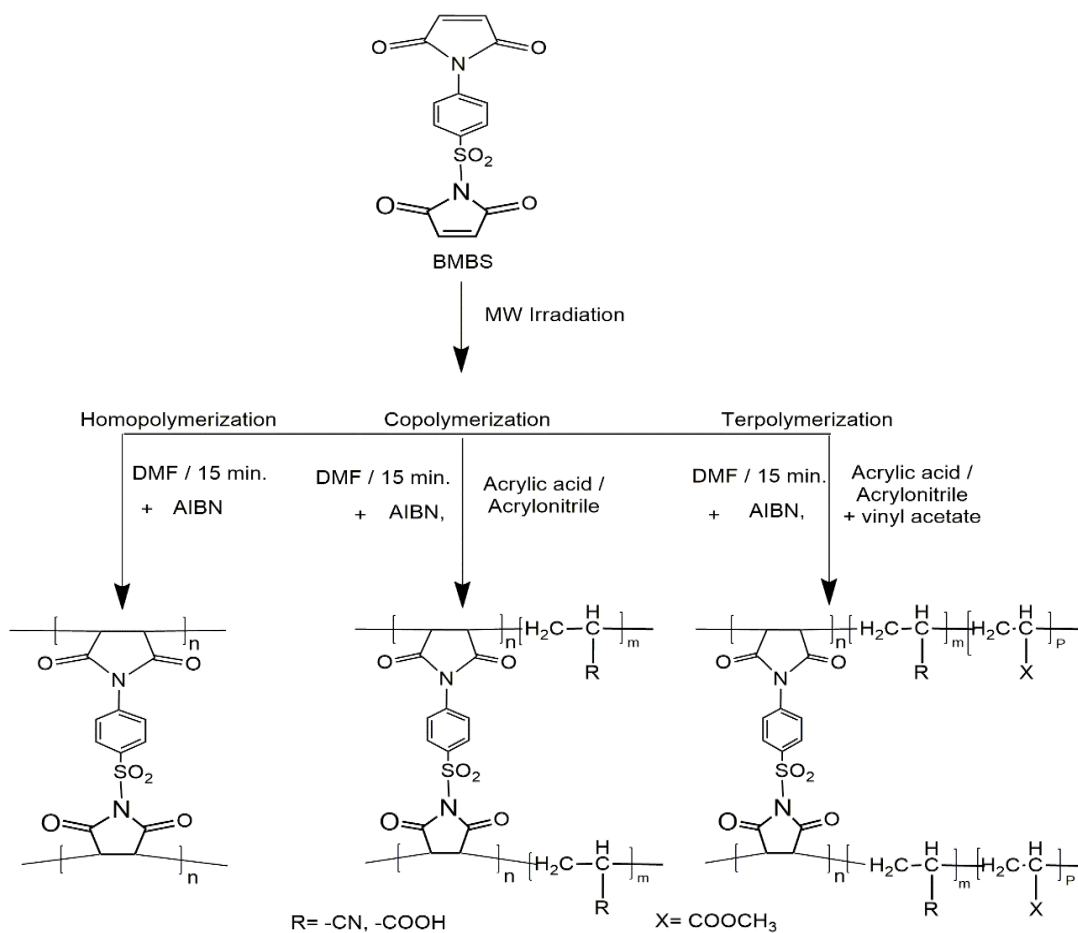
Scheme 5: Microwave polymerization of [4-N-phenylethanamideazo-3-N-(4-nitrophenyl) maleimide]



Scheme 6: Microwave polymerization of [4-N-phenylethanamideazo-3-N-(4-bromophenyl) maleimide]



Scheme 7: Microwave synthesis of N-[[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide



Scheme 8: Microwave synthesis of N, N' bis (maleimide) benzene sulfonamide

III. YIELD OF POLYMERIZATION

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

IV. RESULT AND DISCUSSION

Monomer [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl)Maleimide] [PANMI]-

Yield 80%, melting point 160.6 oC; color brick red, FT-IR (KBr): 1702 cm⁻¹ (C=O),3300 cm⁻¹ (N-H), 3095 cm⁻¹ (CH=CH, C-H Stre.), 1603 cm⁻¹(C=O, amide), 1666 cm⁻¹(CH=CH, C-C Stre.), 1372 cm⁻¹(C-N-C), 1534 cm⁻¹ (N=N), 1407 cm⁻¹(Ar-NO₂), 836 cm⁻¹ and 730cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.19-7.69 (Aromatic), 1.20-2.40 (HC=CH of Maleimide), 7.66 (Ortho-H of N=N-Ar), 7.69 (Meta -H of N=N-Ar), 10.07 (CO-NH) (ppm).

Homopolymer[4-N-Phenylethanamideazo-3-N-(4-nitrophenyl)Maleimide] [HPANMI]-

Yield 83%, melting point 168 oC; color brick red, FT-IR (KBr): 1713 cm⁻¹ (C=O),3363 cm⁻¹ (N-H), 3074 cm⁻¹ (CH=CH, C-H Stre.), 1603 cm⁻¹(C=O, amide), 1390 cm⁻¹(C-N-C), 1515 cm⁻¹(N=N), 523 cm⁻¹(Ar-NO₂), 836 cm⁻¹ and 741 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.91-7.68 (Aromatic), 1.20-2.45 (HC=CH of Maleimide), 8.19 (Ortho-H of N=N-Ar), 8.27 (Meta -H of N=N-Ar), 10.07 (CO-NH) (ppm).

[4-N-Phenylethanamideazo-3-N-(4-nitrophenyl)Maleimide-co-Acrylonitrile] [C1PANMI]-

Yield 80%, melting point 168 oC; color brick red, FT-IR (KBr): 1713 cm⁻¹ (C=O),3363 cm⁻¹ (N-H), 3074 cm⁻¹ (CH=CH, C-H Stre.), 1603 cm⁻¹(C=O, amide), 1390 cm⁻¹(C-N-C), 1515 cm⁻¹(N=N), 523 cm⁻¹(Ar-NO₂), 836 cm⁻¹ and 741 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.91-7.68 (Aromatic), 1.20-2.45 (HC=CH of Maleimide), 8.19 (Ortho-H of N=N-Ar), 8.27 (Meta -H of N=N-Ar), 10.07 (CO-NH) (ppm).

[4-N-Phenylethanamide azo-3-N-(4-nitrophenyl)Maleimide-co-Acrylic acid] [C2PANMI]-

Yield 87 %, melting point 196.5 oC; color brick red, FT-IR (KBr): 1714 cm⁻¹ (C=O),3372 cm⁻¹ (N-H), 3070 cm⁻¹ (CH=CH, C-H Stre.), 1601 cm⁻¹(C=O, amide), 1379 cm⁻¹(C-N-C), 1510 cm⁻¹(N=N), 1445, 1351 cm⁻¹(Ar-NO₂), 836 cm⁻¹ and 751 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.93-7.66 (Aromatic), 1.20-2.40 (HC=CH of Maleimide), 8.24 (Ortho-H of N=N-Ar), 8.32 (Meta -H of N=N-Ar), 10.05 (CO-NH) (ppm).

[4-N-Phenylethanamideazo-3-N-(4-nitrophenyl)Maleimide-co-Vinyl acetate] [C3PANMI]-

Yield 78 %, melting point 167.8 oC; color brick red, FT-IR (KBr): 1713 cm⁻¹ (C=O),3353 cm⁻¹ (N-H), 3065 cm⁻¹ (CH=CH, C-H Stre.), 1601 cm⁻¹(C=O, amide), 1372 cm⁻¹(C-N-C), 1506 cm⁻¹(N=N), 1443, 1348 cm⁻¹(Ar-NO₂), 835 cm⁻¹ and 749 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.66-7.47 (Aromatic), 1.09-2.21 (HC=CH of Maleimide), 8.20 (Ortho-H of N=N-Ar), 8.28 (Meta -H of N=N-Ar), 10.03 (CO-NH) (ppm).

Terpolymer [4-N-Phenylethanamideazo-3-N-(4-nitrophenyl)Maleimide-Acrylonitrile -Vinyl acetate] [T1PANMI]-

Yield 80 %, melting point 202 oC; color brick red, FT-IR (KBr): 1714 cm⁻¹ (C=O), 3353 cm⁻¹ (N-H), 3071 cm⁻¹ (CH=CH, C-H Stre.), 1602 cm⁻¹(C=O, amide), 1392 cm⁻¹(C-N-C), 1515 cm⁻¹(N=N), 1447, 1314 cm⁻¹(Ar-NO₂), 837 cm⁻¹ and 752 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 8.29-7.09 (Aromatic), 1.09-2.17 (HC=CH of Maleimide), 8.29 (Ortho-H of N=N-Ar), 8.27 (Meta -H of N=N-Ar), 10.05 (CO-NH) (ppm).

Terpolymer[4-N-Phenylethanamideazo-3-N-(4-bromophenyl)Maleimide-Acrylicacid-Vinylacetate] [T2PABMI]-

Yield 85 %, melting point 252 oC; color brick red, FT-IR (KBr): 1716 cm⁻¹ (C=O), 3372 cm⁻¹ (N-H), 3070 cm⁻¹ (CH=CH, C-H Stre.), 1609 cm⁻¹(C=O, amide), 1390 cm⁻¹(C-N-C), 1513 cm⁻¹(N=N), 1445, 1397 cm⁻¹(Ar-NO₂), 835 cm⁻¹ and 745 cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 8.79-7.29 (Aromatic), 1.34-2.56 (HC=CH of Maleimide), 8.25 (Ortho-H of N=N-Ar), 8.31 (Meta -H of N=N-Ar), 10.02 (CO-NH) (ppm).

Monomer [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide] [PABMI]-

Yield 87%, melting point 148-50 oC; color dark brown, FT-IR (KBr): 1704 cm⁻¹ (C=O),3300 cm⁻¹ (N-H), 3095 cm⁻¹ (CH=CH, C-H Stre.), 1602 cm⁻¹(C=O, amide), 1666 cm⁻¹(CH=CH, C-C Stre.), 1372 cm⁻¹(C-N-C), 1532 cm⁻¹(N=N), 516 cm⁻¹(Ar-Br), 837 cm⁻¹ and 711cm⁻¹(Para, Ortho); 1H-NMR(CD3OD): 7.22-7.69 (Aromatic), 1.03-2.43 (HC=CH of Maleimide), 7.68 (Ortho-H of N=N-Ar), 7.67 (Meta -H of N=N-Ar), 10.06 (CO-NH) (ppm).

Homopolymer [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide] [HPABMI]-

Yield 85%, melting point 145-46 oC; color dark brown, FT-IR (KBr): 1708 cm⁻¹ (C=O), 3420 cm⁻¹ (N-H), 3063 cm⁻¹ (CH=CH, C-H Stre.), 1603 cm⁻¹ (C=O, amide), 1390 cm⁻¹ (C-N-C), 1515 cm⁻¹ (N=N), 523 cm⁻¹ (Ar-Br), 832 cm⁻¹ and 650 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.31-7.82 (Aromatic), 1.20-2.43 (HC=CH of Maleimide), 7.84 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 3.94 {(CH-CH)-n}, 10.06 (CO-NH) (ppm).

[4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide-co-Acrylonitrile] [C1PABMI]-

Yield 85%, melting point 145-46 oC; color dark brown, FT-IR (KBr): 1709 cm⁻¹ (C=O), 3428 cm⁻¹ (N-H), 3065 cm⁻¹ (CH=CH, C-H Stre.), 1606 cm⁻¹ (C=O, amide), 1395 cm⁻¹ (C-N-C), 1515 cm⁻¹ (N=N), 524 cm⁻¹ (Ar-Br), 832 cm⁻¹ and 652 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.31-7.82 (Aromatic), 1.04-2.51 (HC=CH of Maleimide), 7.84 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 3.94 {(CH-CH)-n}, 10.06 (CO-NH) (ppm).

[4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide-co-Acrylicacid] [C2PABMI]-

Yield 80 %, melting point 193-95 oC; color dark brown, FT-IR (KBr): 1707 cm⁻¹ (C=O), 3353 cm⁻¹ (N-H), 3069 cm⁻¹ (CH=CH, C-H Stre.), 1605 cm⁻¹ (C=O, amide), 1398 cm⁻¹ (C-N-C), 1515 cm⁻¹ (N=N), 526 cm⁻¹ (Ar-Br), 834 cm⁻¹ and 744 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.15-7.66 (Aromatic), 1.09-2.73 (HC=CH of Maleimide), 8.12 (Ortho-H of N=N-Ar), 8.19 (Meta -H of N=N-Ar), 1.20-3.03 {(CH-CH)-n}, 10.43 (CO-NH) (ppm).

[4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)Maleimide-co-Vinylacetate] [C3PABMI]-

Yield 78 %, melting point 154 oC; color dark brown, FT-IR (KBr): 1712 cm⁻¹ (C=O), 3364 cm⁻¹ (N-H), 3064 cm⁻¹ (CH=CH, C-H Stre.), 1606 cm⁻¹ (C=O, amide), 1394 cm⁻¹ (C-N-C), 1515 cm⁻¹ (N=N), 527 cm⁻¹ (Ar-Br), 833 cm⁻¹ and 743 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.14-7.68 (Aromatic), 1.03-2.56 (HC=CH of Maleimide), 7.55 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 1.03-3.04{(CH-CH)-n}, 10.05 (CO-NH) (ppm).

Terpolymer [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide-Acrylonitrile-Vinylacetate] [T1PABMI]-

Yield 80 %, melting point 154 oC; color dark brown, FT-IR (KBr): 1713 cm⁻¹ (C=O), 3344 cm⁻¹ (N-H, broad peak), 3064 cm⁻¹ (CH=CH, C-H Stre.), 1607 cm⁻¹ (C=O, amide), 1393 cm⁻¹ (C-N-C), 1514 cm⁻¹ (N=N), 524 cm⁻¹ (Ar-Br), 833 cm⁻¹ and 650 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.16-7.76 (Aromatic), 0.98-2.83 (HC=CH of Maleimide), 8.18 (Ortho-H of N=N-Ar), 8.35 (Meta -H of N=N-Ar), 1.07-3.20 {(CH-CH)-n}, 10.07 (CO-NH) (ppm).

Terpolymer [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide - Acrylic acid - Vinyl acetate] [T2PABMI]-

Yield 85 %, 1709 cm⁻¹ (C=O), 3448 cm⁻¹ (N-H, broad peak), 2990 cm⁻¹ (CH=CH, C-H Stre.), 1606 cm⁻¹ (C=O, amide), 1396 cm⁻¹ (C-N-C), 1515 cm⁻¹ (N=N), 528 cm⁻¹ (Ar-Br), 832 cm⁻¹ and 648 cm⁻¹ (Para, Ortho); 1H-NMR(CD3OD): 7.15-7.67 (Aromatic), 1.07-2.97 (HC=CH of Maleimide), 7.31 (Ortho-H of N=N-Ar), 8.14 (Meta -H of N=N-Ar), 3.66 {(CH-CH)-n}, 10.01 (CO-NH) (ppm).

Monomer N-[[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), 0.96-1.90, (HC=CH of Maleimide), 10.06 (CO-NH), 2.53 (SO3H) (ppm).

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), 0.95-1.78, (HC=CH of Maleimide), 9.98 (CO-NH), 2.53 (SO3H) (ppm).

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), 3204 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), 0.92-2.63, (HC=CH of Maleimide), 9.84 (CO-NH), 3.02 (SO₃H) (ppm).

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), 3125 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), 1.26-2.63, (HC=CH of Maleimide), 9.84 (CO-NH), 2.57 (SO₃H) (ppm).

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), 3183 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), 0.85-2.67, (HC=CH of Maleimide), 10.38 (CO-NH), 3.03 (SO₃H) (ppm)

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), 1.32-3.76 {(CH-CH)-n}, 9.87(CO-NH)(ppm).

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), 3190 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), 1.03-3.01{(CH-CH)-n}, 9.81 (CO-NH) (ppm).

Monomer N,N'-bis(maleimido)Sulfanalimide [BMBS]-

Yield 82%, melting point 216.7 oC; color camel yellow, FT-IR (KBr): 1722 cm⁻¹ (C=O),3366, 3263 cm⁻¹ (N-H stre.), 3100 cm⁻¹ (CH=CH, C-H Stre.), 1597 cm⁻¹(CH=CH, C-C Stre.), 1304 cm⁻¹(C-N-C), 1336 cm⁻¹ asym. and 1162 cm⁻¹ sym.(S=O stre., Sulfonamide), 909 cm⁻¹ (C-H bending), 837 cm⁻¹(C-H bending, Ar for 1,4 disubstitutions); ¹H-NMR(CD₃OD): 7.96-7.56 (Aromatic), 7.40-7.11 (HC=CH of Maleimide) (ppm).

Homopolymer N,N'-bis(maleimido)Sulfanalimide [HBMBS]-

Yield 89%, melting point 250 °C; color dark camel yellow, FT-IR (KBr): 1714 cm⁻¹ (C=O),3351, 3261 cm⁻¹ (N-H stre.), 3103 cm⁻¹ (CH=CH, C-H Stre.), 1336 cm⁻¹(C-N-C), 1304 cm⁻¹ asym. and 1159 cm⁻¹ sym.(S=O stre., Sulfonamide), 912 cm⁻¹ (C-H bending), 838 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 7.96-7.40 (Aromatic), 1.03-2.23 [HC-CH]_n of Maleimide (ppm).

Copolymer N,N'-bis(maleimido)Sulfanalimide [C1BMBS]-

Yield 92%, melting point 258 °C; color dark brown yellow, FT-IR (KBr): 1714 cm⁻¹ (C=O),3356, 3264 cm⁻¹ (N-H stre.), 3110 cm⁻¹ (CH=CH, C-H Stre.),1365 cm⁻¹(C-N-C), 1332 cm⁻¹ asym. and 1160 cm⁻¹ sym.(S=O stre., Sulfonamide), 901 cm⁻¹ (C-H bending), 838 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 8.21-7.41 (Aromatic), 1.07-2.93 [HC-CH]_n of Maleimide) (ppm).

Copolymer N,N'-bis(maleimido)Sulfanalimide [C2BMBS] –

Yield 90%, melting point 255 °C; color light brown, FT-IR (KBr): 1714 cm⁻¹ (C=O),3351, 3261 cm⁻¹ (N-H stre.), 3103 cm⁻¹ (CH=CH, C-H Stre.), 1336 cm⁻¹(C-N-C), 1304 cm⁻¹ asym. and 1159 cm⁻¹ sym.(S=O stre., Sulfonamide), 912 cm⁻¹ (C-H bending), 838 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 8.17-7.40 (Aromatic), 1.02-2.67 [HC-CH]_n of Maleimide), 11.24 (-COOH of acrylic acid) (ppm).

Copolymer N,N'-bis(maleimido)Sulfanalimide [C3BMBS]-

Yield 90%, melting point 255 °C; color light brown, FT-IR (KBr): 1714 cm⁻¹ (C=O), 3351, 3261 cm⁻¹ (N-H stre.), 3103 cm⁻¹ (CH=CH, C-H Stre.), 1336 cm⁻¹(C-N-C), 1304 cm⁻¹ asym. and 1159 cm⁻¹ sym.(S=O stre., Sulfonamide), 912 cm⁻¹ (C-H bending), 838 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 8.17-7.40 (Aromatic), 1.02-2.67 [HC-CH]_n of Maleimide) (ppm).

Terpolymer N,N'-bis(maleimido)Sulfanalimide-AN-VA [T1BMBS]-

Yield 83%, melting point 267 °C; color light brown, FT-IR (KBr): 1720 cm⁻¹ (C=O), 3358, 3267 cm⁻¹ (N-H stre.), 3129 cm⁻¹ (CH=CH, C-H Stre.), 1342 cm⁻¹(C-N-C), 1130 cm⁻¹ asym. and 1155 cm⁻¹ sym.(S=O stre., Sulfonamide), 911 cm⁻¹ (C-H bending), 835 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 8.12-7.48 (Aromatic), 0.89-3.27 [HC-CH]_n of Maleimide) (ppm).

Terpolymer N,N'-bis(maleimido)Sulfanalimide-AA-VA [T2BMBS]-

Yield 89%, melting point 305°C; color light brown, FT-IR (KBr): 1720 cm⁻¹ (C=O), 3352, 3266 cm⁻¹ (N-H stre.), 3029 cm⁻¹ (CH=CH, C-H Stre.), 1367 cm⁻¹(C-N-C), 1137 cm⁻¹ asym. and 1163 cm⁻¹ sym.(S=O stre., Sulfonamide), 917 cm⁻¹ (C-H bending), 838 cm⁻¹(C-H bending, Ar for 1,4 di-substitutions); ¹H-NMR(CD₃OD): 8.04-7.45 (Aromatic), 0.92-3.25 [HC-CH]_n of Maleimide), 11.04 (-COOH of acrylic acid) (ppm).

Physical properties

Solubility of homopolymers, copolymers and terpolymers of all monomers were examined by using solvents of varying parameters and it was seems that these were perfectly soluble in THF, DMF, DMSO due to presence of polarity and partially soluble in acetone, 1, 4- dioxane and ethyl acetate. Molecular weight of all polymers were determined by Gel Permeation Chromatography (GPC) technique. The molecular weight distribution in polymers varies from very low to very high range of molecular weight reavled in broad area distribution curves. Polydispersity index of all polymers were also determined by same technique. Terpolymers revealed high molecular weight due to presence of three comonomer units to furnished dense molecular structure. The number average molecular weight (M_n), weight average molecular weight (M_w) and Polydispersity (M_w/M_n) are given in Table 1.

Table no 1: Number average molecular weight (M_n), weight average molecular weight (M_w) and Polydispersity (M_w/M_n) of polymers-

Polymer Code	M _w	M _n	PDI (Poly Dispersity Index)
MW-HPANMI	1134.8	958.9	1.183
MW-C1PANMI	1278.9	989.2	1.292
MW-C2PANMI	1275.1	1080.8	1.179
MW-C3PANMI	1298.7	974.7	1.332
MW-T1PANMI	1465.2	1298.7	1.128
MW-T2PANMI	1565.2	1346.6	1.162
MW-HPABMI	1059.3	945.2	1.120
MW-C1PABMI	1195.5	1095.4	1.091
MW-C2PABMI	1477.5	1289.8	1.145
MW-C3PABMI	1087.3	997.2	1.090
MW-T1PABMI	1498.6	1269.5	1.180
MW-T2PABMI	1567.6	1289.8	1.215
MW-HBSACPMI	1178.8	1021.2	1.154
MW-C1BSACPMI	1134.3	967.9	1.171
MW-C2BSACPMI	1345.9	1098.4	1.225
MW-C3BSACPMI	1167.8	1032.1	1.131
MW-T1BSACPMI	1278.5	1069.9	1.194
MW-T2BSACPMI	1302.5	1099.5	1.209
MW-HBMBS	1189.7	1024.6	1.161
MW-C1BMBS	1209.5	1048.8	1.153
MW-C2BMBS	1348.2	1120.2	1.203
MW-C3BMBS	1199.6	1037.7	1.156
MW-T1BMBS	1418.9	1167.3	1.215
MW-T2BMBS	1498.4	1198.3	1.250

V. MICROBIAL PERFORMANCE

Microbial activities conducted by Disk diffusion experimental method in department of botany and department of biotechnology, MLSU, Udaipur.

In sequence to explore and investigated microbial properties of homopolymer, copolymers and terpolymer of all monomers, were evaluated against various microorganism such as *Esherichiaaerogenes*, *Staphylocous aureus*

bacteria and *Aspergillus nizer*, *Alternariasolanifungi* with DMSO as solvent with sample concentration was 500 µg/ml. Synthesized Polymers revealed good antimicrobial activity against used bacteria and fungi. The antimicrobial activity of homopolymers, Copolymers and terpolymers were showed due to presence of heteroatoms as a nitrogen, oxygen and sulphur matrix in polymers. These heteroatomic atoms served as antimicrobial agents in synthesized polymers. Resultant, sulphur containing all polymers and especially terpolymer with acrylic acid showed highest antimicrobial properties against applied microbial species. Overall and comparative results are showed as:

Terpolymers and copolymers of [BSACPMI] > Polymers of bismaleimide [BMBS] > Terpolymers and copolymers of [PANMI] > Terpolymers and copolymers of [PABMI]

VI. CONCLUSIONS

Four monomers and twelve different copolymer compounds and eight terpolymer compounds based on [4-N-Phenylethanamideazo-3-N-(4-nitrophenyl)Maleimide, [4-N-Phenylethanamideazo-3-N-(4-bromophenyl)Maleimide, N-[4-(N'-benzenesulphonicacid) amino-carbonyl] phenyl] maleimide, N,N'-bis(maleimido)Sulfanalimide have been successfully synthesized in microwave conditions and characterized.

In these studies, synthesis of polymers from microwave irradiation technique is compared with conventional heating method. Time and yield % were considered as experimental parameters. The results revealed that the achieved yield % of monomers, homopolymers, copolymers and terpolymers were greater in microwave heating method [MWM] compared to conventional heating method that have published previously various journals with least investment of energy and time comparatively and the other hand, consumption of raw chemicals and solvents were also reduced in MWM, hence it become economic and environment-friendly. Resultant, on the behalf of evaluations with all significances, microwave heating method for synthesis of polymers, is more compatible and feasible than the conventional heating method.

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