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Synthesis of acrylic copolymers and their antimicrobial screening

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ABSTRACT

Monomer vanillin methacrylate(VMA)was synthesized byreacting o-vanilline with methacryloylchloride. The monomercharacteristics was identified by Fourier transform infrared spectroscopy (FT-IR) and ^{1}H-NMR spectroscopy. Homo-polymer and co-polymers of VMA with hydroxyl ethyl methacrylate(HEMA) at different feedcomposition was prepared by free radical solution polymerization at 70 ±2°C using 2,2'-azobisisobutyronitrile(AIBN) as an initiator and N,N-dimethylformamide (DMF). Antimicrobial activity of the polymers was also investigated against various bacteria, fungi and yeast.

Keywords: vanillin methacrylate, copolymerization, characterization, antimicrobial activity.

INTRODUCTION

Currently the demand for MMA has increased as the hardness of acrylate copolymers can be adjusted when produced by emulsion and solution polymerization. These products initially found use in high quality finishes in the leather and textile industries. Sparkling crystal clarity, remarkable surface hardness together with excellent weather ability and good chemical resistance are characteristic properties of acrylic polymers. Commercial interest in the acrylic polymers began in the early 1930. In 1937, Bauer [1] in Germany prepared PMMA a non adhesive polymer. Yeon and co-workers [2] have synthesized p-(2,2,3-tricyno-4-carbomethoxycyclopropyl)phenoxyethylacrylate and polymerized via radical polymerization. Kim and co-workers [3] prepared methacrylate syrup by bulk polymerization. The method for producing a methacrylate syrup of this invention has such advantages that reaction run away does not occur, the control of molecular weight and conversion rate is possible even at low exothermic temperature with stirring, and a partially polymerized methacrylate syrup can also be prepared there from. Brar and co-workers [4] synthesized copolymers of 2-hydroxy ethyl methacrylate and methacrylate of different compositions were synthesized by free radical bulk polymerization using azobisisoobutyronitrile (AIBN) as an initiator under nitrogen atmosphere. Eroland Kolu [5] synthesized copolymers of a new methacrylate monomer bearing oxime ester and ether with methylmethacrylate. They have calculated the reactivity ratios of each monomer using Kelen-Tudos (K-T) and Fineman-Ross (F-R) methods. Soyakan and co-workers [6] prepared copolymers of N-(4-bromophenyl)-2-methacrylamide with glycidylmethacrylate in 1,4-dioxane solution at 70±1ºC using 2,2'-azobisisobutyronitrile as an initiator with different monomer ratios. In general, the rate of polymerization and the average molar mass must be controlled by the initiator and monomer concentration and the reaction temperature. Recently, the polymer/inorganic nanocomposites have gained great attention because of their potential applications in many surface-based technologies such as composite materials, biomaterials, adhesion and wetting, molecular recognition, microfluidics,

chemical sensing, and organic synthesis. What is more is that the polymer/inorganic nano composites have excellent properties, such as mechanical properties, thermal stability, and flame retardance, gas barrier properties, and biodegradation and abrasion resistance. The polymer/inorganic hybrid materials are generally prepared by surface modification of the inorganic particles. At present, there are many approaches for modifying solid surfaces with polymers, including physisorption, covalent attachment, and electrostatic adsorption [7]. The copolymers based on halogenated phenyl acrylate have been utilized for synthesizing electro active polymers for the preparation of polymeric reagents carrying piperazine and isonitrile functionalities. In last few decades, ^{1}H-NMR spectral analysis has been established as a powerful tool for determination of tacticity and sequence determination as well as for the estimation of copolymer composition because of its simplicity, rapidityand sensitivity [8-13].Free radical copolymerization of phenoxyethyl methacrylate and glycidyl methacrylate was carried out using AIBNin 2-butanone solution at 333°K by Anver et al.[14] Characterization of synthesized copolymers were done by FT-IR,^{1}H-NMR and ^{13}C-NMR spectroscopic methods. Thermal properties were also investigated. Monomer reactivity ratios were computed using F-R, K-T and RREVM methods. Acrylate homo-polymers along with their copolymersare used in various field such as films, fibers, filament, coating, lithography, lacquers, adhesives, printing inks and binders [15-17]. Patel and co-workers [18,19] prepared copolymer's 2,4-dichlorophenyl methacrylate with various vinyl monomers and reported that these polymers are useful as micro biocides and are thermally stable up to 250°C.

The present work describes the characterization of VMA and HEMA by FT-IR and ^{1}H-NMR spectroscopy. The formation of polymer has been established with the help of IR spectral data. Antimicrobial activity of the homo and copolymers was carried out against selected microorganisms like bacteria, fungi and yeast.

MATERIALS AND METHODS

2.1 Materials:

Analytical grade methacrylic acid, benzoyl chloride, hydroquinone, sodium hydroxide, vanillin were used. The solvent used for the reaction were fractionally distilled.

2.2 Synthesis of vanillin methacrylate(VMA) monomer

The esterification of o-vanillin was performed with methacryloylchloride. To a three necked flask, equipped with stirrer and condenser, absolute alcohol (200ml) and NaOH(3.0gm) were added and the contents were stirred until all the NaOH dissolved. To this VMA was added and the mixture was stirred for about ten minutes. It was cooled at 0-5°C. Methacryloyl chloride was added drop wise to the reaction mixture, with the help of separating funnel. The temperature was maintained at 0-5°C and the contents were stirred for 2-3hours. After that the mixture was poured in to crushed ice-water mixture. The product separated was filtered and purified. The formation of the monomer was confirmed by ^{1}H-NMR spectra(Figure-1) and FT-IR(Figure-2).

2.3 Synthesis of homo and copolymers:

Homo and copolymerization were carried out in DMF using AIBN as an initiator, predetermined quantities of VMA,HEMA, DMF and AIBN were mixed in a round bottom flask equipped with reflux condenser. The reaction mixture was heated at 70°C with constant stirring. The resulting polymer solution was slowly poured in to large volume of methanol with stirring when the polymer was precipitated out. It was filtered and washed with methanol. Solid polymers were purified by repeated precipitation by methanol from solution in DMF and finally dried under vacuum. The proposed reaction pathway described in reaction scheme describes the reaction leading to copolymerization of VMA with HEMA.

2.4 Characterization:

NICOLET 400D FT-IR spectrophotometer was used to record the infrared spectrum of homo and copolymers on solid KBr pellets. HITACHI-R-1500 permanent magnet FT-NMR spectrometer (60MHz) was used for recording the NMR spectrum.CDCl3 was used as a solvent and Tetra methylsilane (TMS) was used as an internal standard. Waters HPLC system, equipped with WATERS 510 multi-solvent delivery pump, auto injector, µ-bondapak C_{18} column, durable absorbance WATERS 486 detector, loaded with Aimil chromatography software, was used to determine the purity of monomer VMA. Methanol at 1ml/min flow rate was used as mobile phase. Concentration of the monomer sample was kept at 0.5 mg/ml and 20 µl of solution was injected during analysis.

2.5 Antimicrobial activity:
The homo and copolymers thus obtained were tested against different microorganism that is commonly employed for biodegradability tests. Bacterial strain (*Bacillus subtilis ,Eacherichia coli and Staphylococcus citreus*), fungal strain (*Aspergillus niger, Sportichum pulveruletum and Trichocerm lignorum*) and yeast strain (*Candida utilis, Saccharomyces cerevisial and Pichiastipitis*) were taken for the antimicrobial activity study. The details of theexperimental procedures have been reported in our earlier publication [20].

RESULTS AND DISCUSSION

Different homo and copolymers were obtained by the free radical solution polymerization technique. The molefraction of VMA ranging from 0.5 to 0.1 in the feed were studied in a wide composition interval.

3.1 Infrared spectra:
IR of VMA *(cm^{-1})*:3024(-CH stretching vibration of the aromatic ring), 1273(ν_{-CH3}),1691($\nu_{C=O}$), 1596,1506.75 and 1460.62($\nu_{C=C}$), 1273(asymmetric ν_{C-O-C}), 1207(symmetric ν_{C-O-C}), 890(-CH bending mode of vinyl group), 733.87 (orthodisubstituted benzene). The two absorption bands at 2747 and 2841.83 cm^{-1} may be assigned as the absorption due to –CH of aldehyde. Figure 1 shows the IR spectrum of monomer VMA. The main evidence of the polymer formation is certainly the disappearance of some characteristic signals of the double bond in the spectrum and this fact was effectively observed in the present investigation. Thus the absorption bands at 953 cm^{-1} and assigned respectively to the C-H bending of vinyl group and the stretching vibration band of C=C at 1634 cm^{-1} disappeared in the IR spectrum of poly (VMA). FT-IR spectra of monomer as well as homo-polymer of VMA are shown in Figure 2. In the spectrum of poly(VMA) figure 5, shows two sharp bands at 2736 cm^{-1} and 2849 cm^{-1} due to ϑ_{CHO} of aldehyde group observed, where as the band at 1702 cm^{-1} due to $\vartheta_{C=O}$ stretching for aldehyde and ketone double bond. The band at 1270 cm^{-1}may be due to C-O-C bending of CH_3-O aromatic ring. The sharp band at 732 cm^{-1} confirms the presence of ortho-disubstituted benzene. The spectrum of poly (VMA) shows three bands at 1465, 1503 and 1597 cm^{-1} which are characteristic absorptions of phenyl ring. The band at 1735 cm^{-1} may have contribution form ester-ketone group and interestingly the relative intensity of this band is decreased with decrease in VMA content in the copolymers. The band at 1390 cm^{-1} confirms the presence of methyl group and the strong absorption at 1465 cm^{-1} may be C-H bending vibrations of CH_3 group.

3.2^{1}H-NMR Spectrum:
^{1}H-NMR of VMA(δ ppm)(60MHz):5.931(1H, -CH=),6.307(1H)(non-equivalent methylene protons), 7.392-7.583 (3H, aromatic protons).In poly(VMA) the aromatic protons are assigned around 7.315-7.515 δppm. The formation of polymer is evident from the disappearance of signals at 5.931 (1H), 6.307 δppm (2H) of vinyl protons and the appearance of broad signals at 3.125 δppm (1H, -CH) and 2.736-2.894 δppm (2H, -CH_2). Spectrum of poly(VMA) is given in figure 3.

3.3 HPLC:
Figure 4 shows HPLC chromatogram of VMA. It is apparent from the chromatogram that the synthesized monomer is having 99.86 % purity.

3.4Antimicrobial activity:
The antimicrobial activity of the homo and copolymers of VMA with HEMA was carried out. The obtained results are presented in Figures6 , 7 and 8 for bacteria, fungi and yeast respectively. Poly(VMA) shows 57% growth of *E. coli*. The copolymers of VMA with HEMA having different feed ratio exhibits 35-43% growth of *E .coli* respectively while homopolymer of HEMA shows 68% growth respectively. Poly(VMA) shows 62% growth of *B.cerus*. The copolymers of VMA with HEMA having different feed ratio exhibits 50-60% growth of *E .coli* respectively while homo-polymer of HEMA shows 74% growth respectively. Poly(VMA) shows 60% growth of *P.aeruginosa*. The copolymers of VMA with HEMA having different feed ratio exhibits 34-40% growth of *E .coli* respectively while homo-polymer of HEMA shows 69% growth respectively.

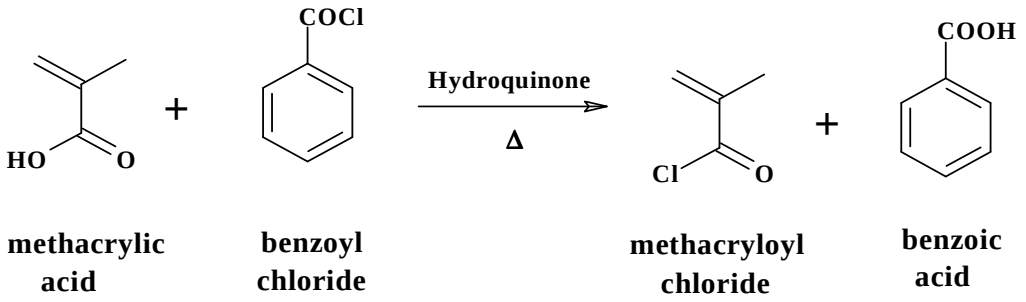
Figures 6 represents the comparative effect of acrylic copolymers on the growth of bacteria.

The homo-polymer of VMA shows 75% growth of *A.niger* .Different copolymer compositions of poly(VMA-*co*-HEMA) allows 62-72% growth respectively. The homo-polymers of HEMA registered 72%, growth of *B. subtilis*

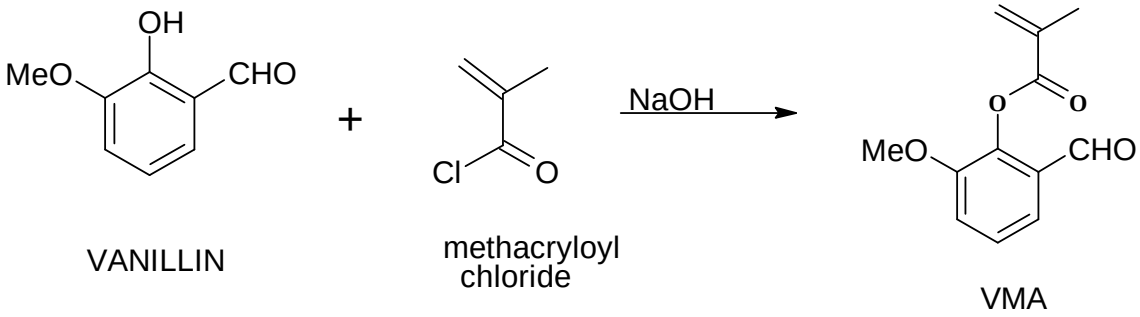
respectively. However, during this period control culture (without resin) exhibited maximum growth (100%). The main source of *E. coli* is in human stool. They are gram-positive and short rod shaped. They are aerobic in nature. Poly(VMA) shows 59% growth of Trichoderma. The copolymers of VMA with HEMA having different feed ratio exhibits 48-57% growth respectively while homo-polymer of HEMA shows 61% growth respectively. Poly(VMA) shows 54% growth of *F.oxysporum*. The copolymers of VMA with HEMA having different feed ratio exhibits 44-51% growth respectively while homo-polymer of HEMA shows 58% growth respectively. Poly(VMA) shows 66% growth of Penicillium. The copolymers of VMA with HEMA having different feed ratio exhibits 54-64% growth respectively while homo-polymer of HEMA shows 68% growth respectively.

Figures 7.represents the comparative effect of acrylic copolymers on the growth of fungi.

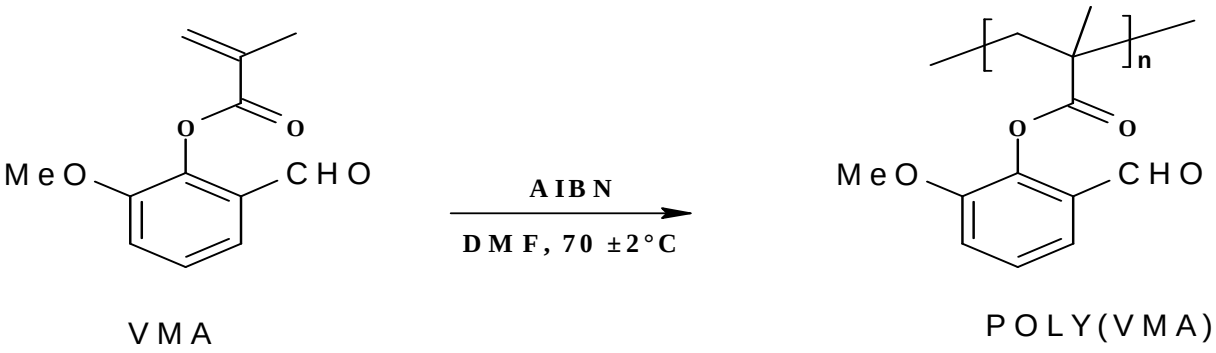
The homo-polymer of VMA shows 77% growth of *S. cerevisiae*. Different copolymer compositions of poly(VMA-*co*-HEMA) allows 61-68% growth of *S. cerevisiae* respectively. The homo-polymers of HEMA registered 68%, growth of *S. cerevisiae* respectively. It is shown in figure 8.



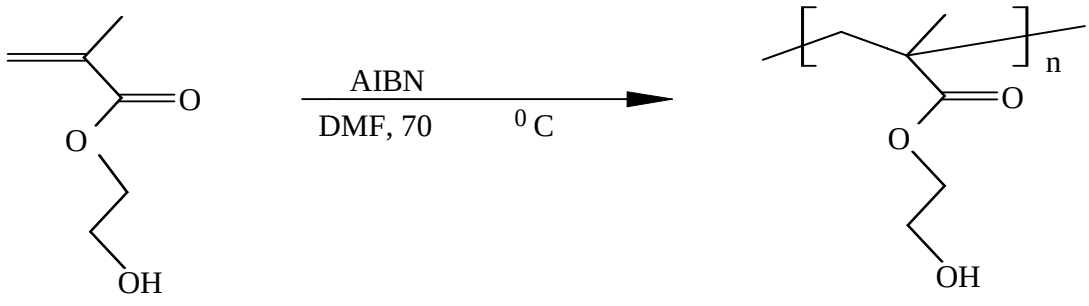
Scheme 1: Synthesis of methacryloyl chloride



Scheme 2: Synthesis of vanillinmethacrylate(VMA)

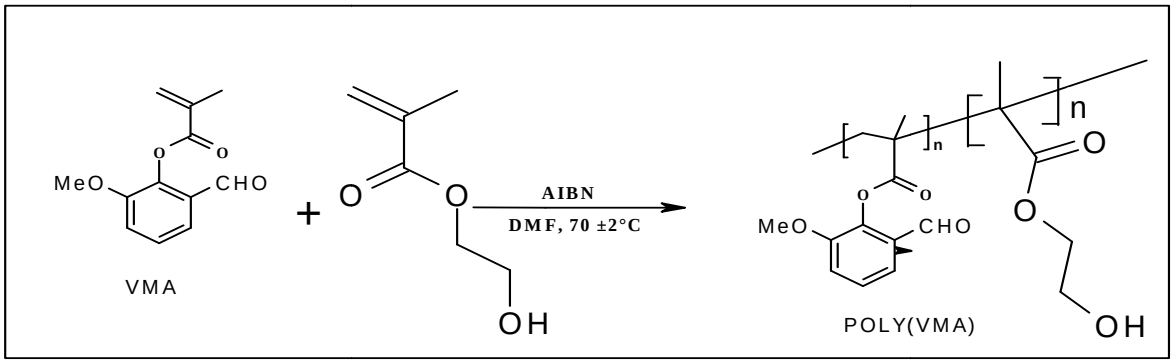


Scheme 3: Synthesis of poly(VMA)



HEMA **POLY(HEMA)**

Scheme 4: Synthesis of poly(HEMA)



Scheme 5: Synthesis of poly(VMA-co-HEMA)

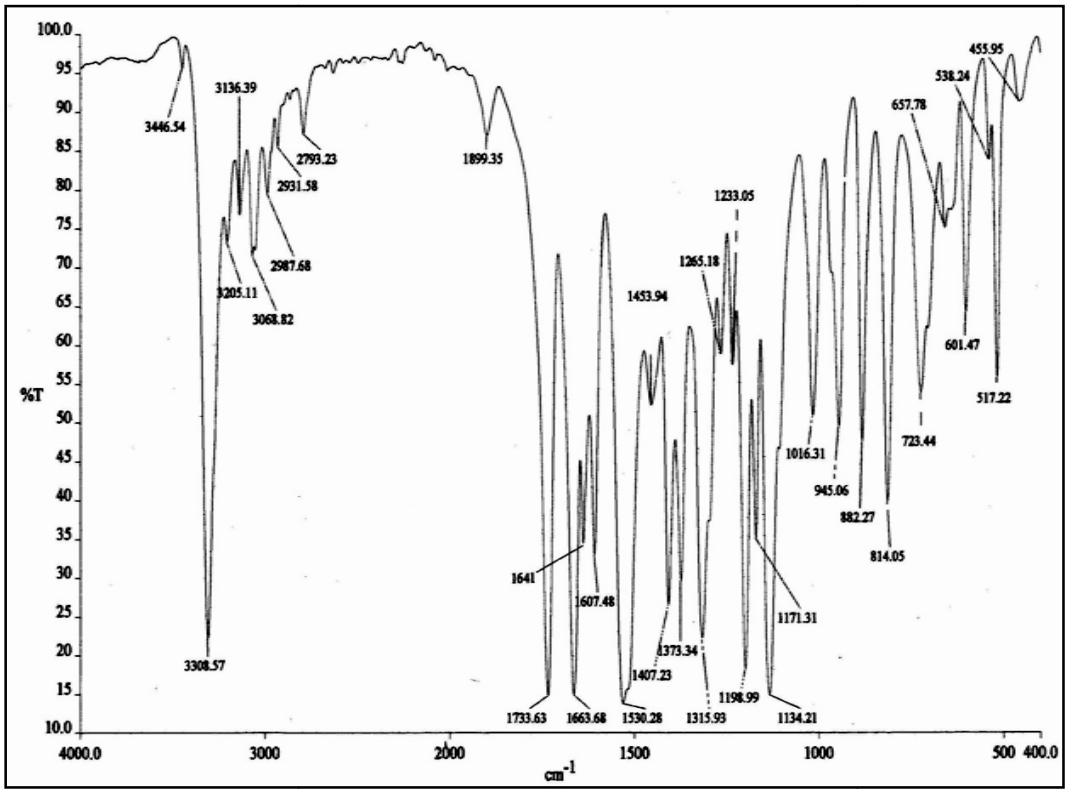


Figure 1: FT-IR spectra of VMA

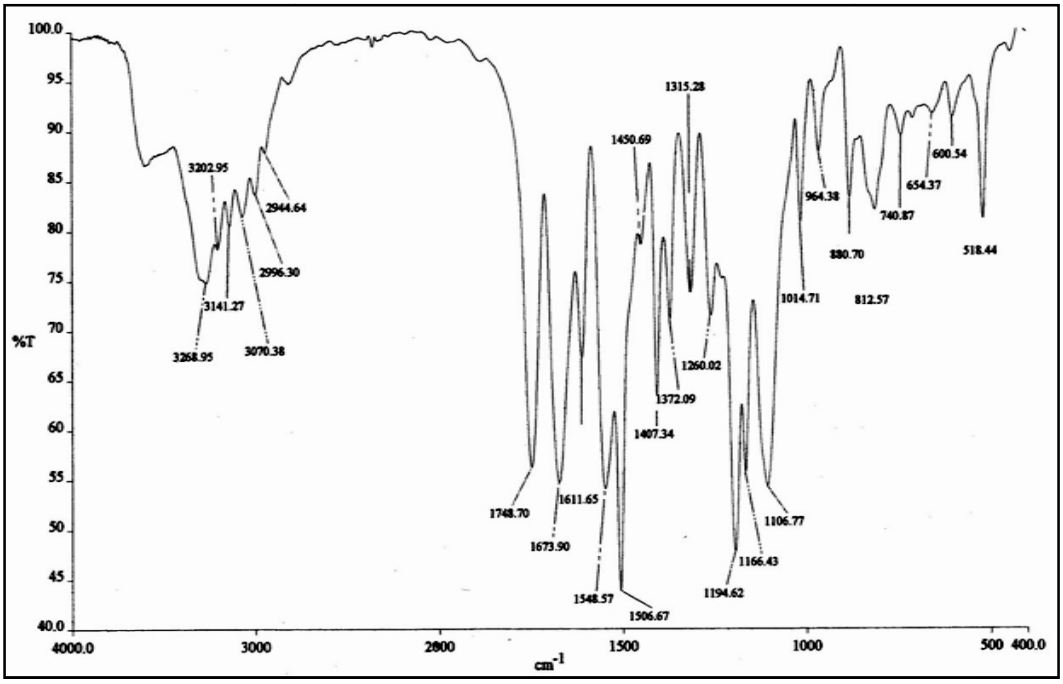


Figure 2: FT-IR spectra of poly(VMA)

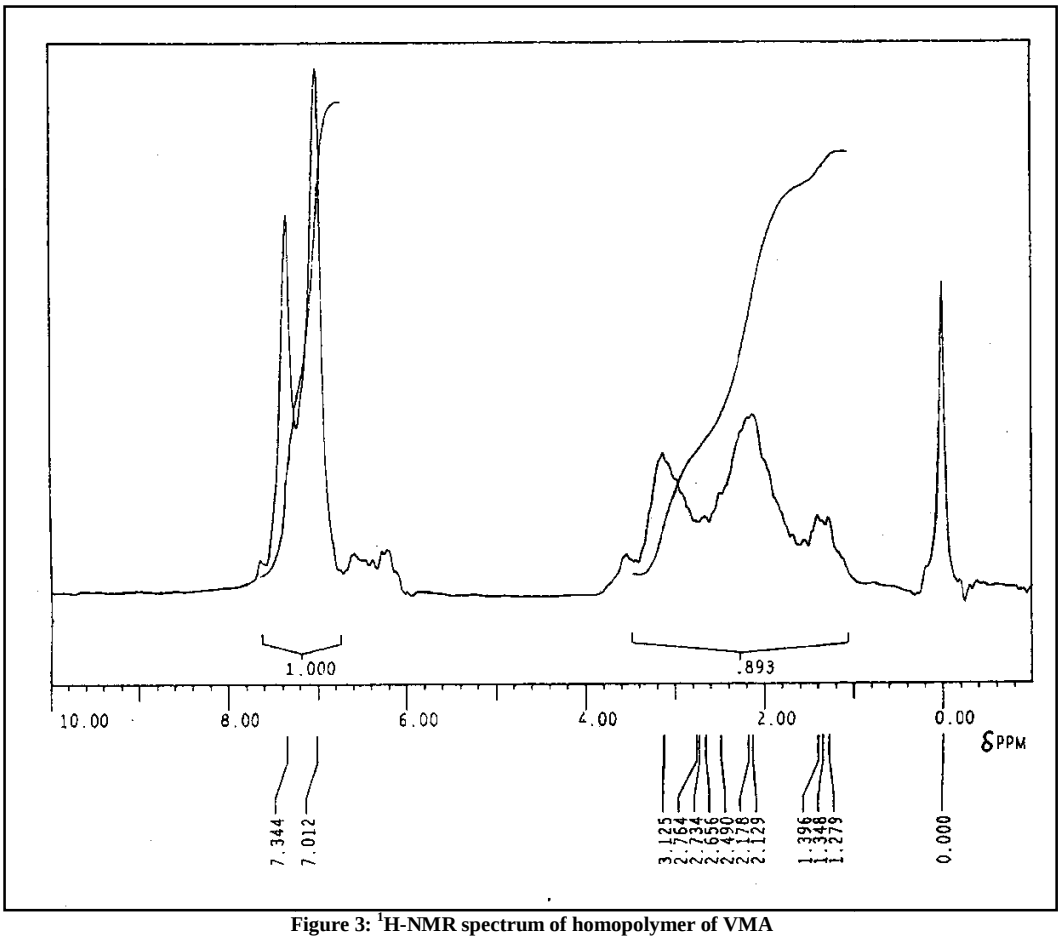


Figure 3: ^{1}H-NMR spectrum of homopolymer of VMA

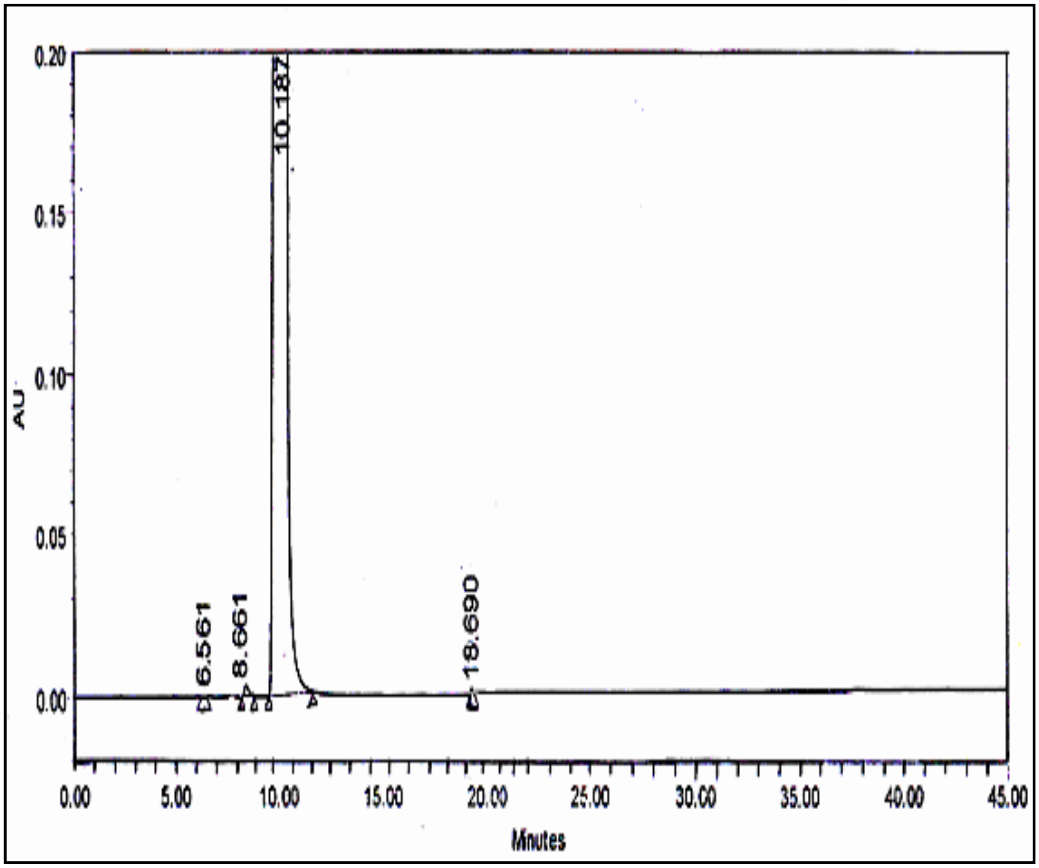


Figure 4: HPLC chromatogram of homopolymer of VMA

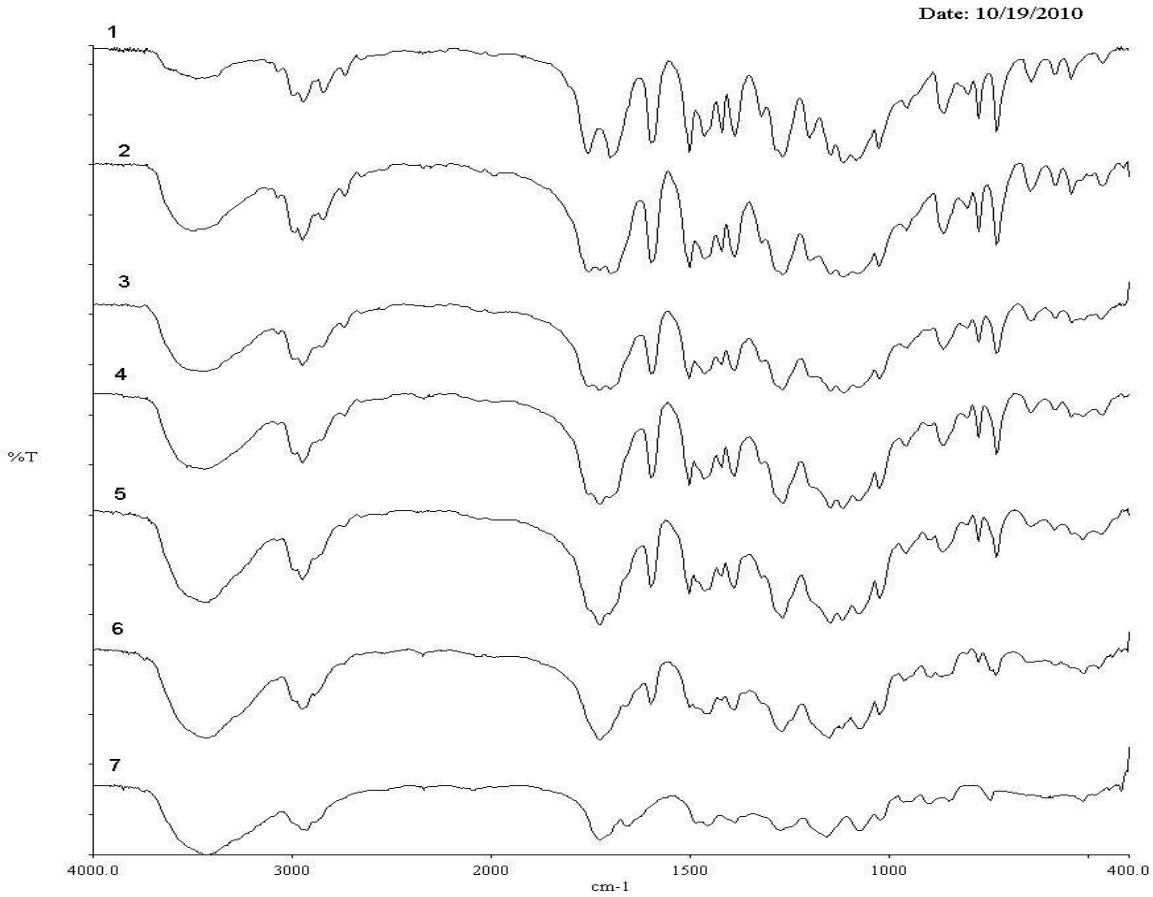


Figure 5: FT-IR spectra of poly(VMA), poly(VMA-*co*-*HE*MA) and poly(HEMA)

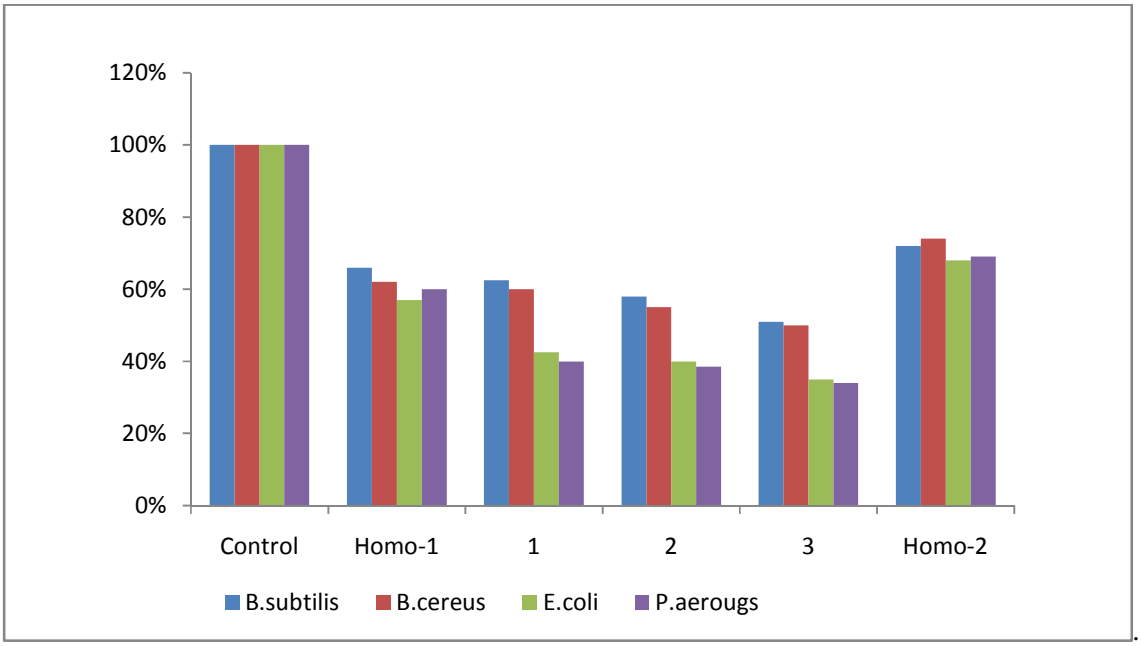


Figure 6: Effect of poly(VMA), poly(VMA-*co*-HEMA) and poly(HEMA) on growth (%) of bacteria

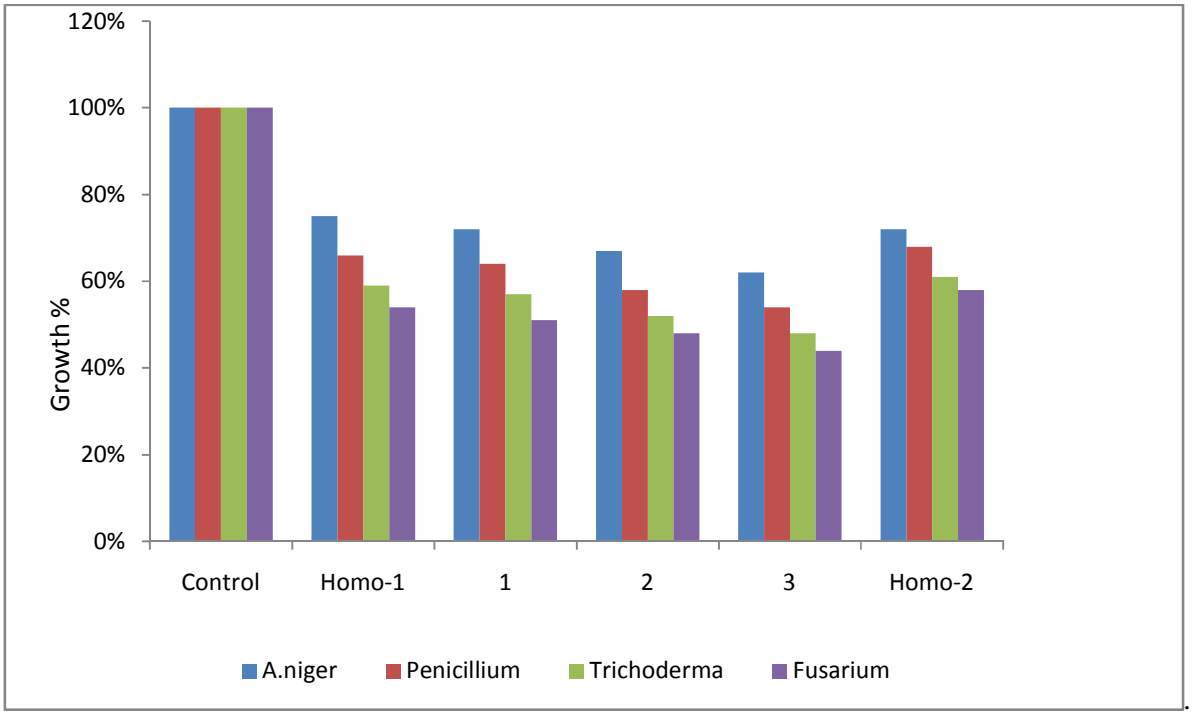


Figure 7: Effect of poly(VMA), poly(VMA-*co*-HEMA) and poly(HEMA) on growth (%) of Fungi

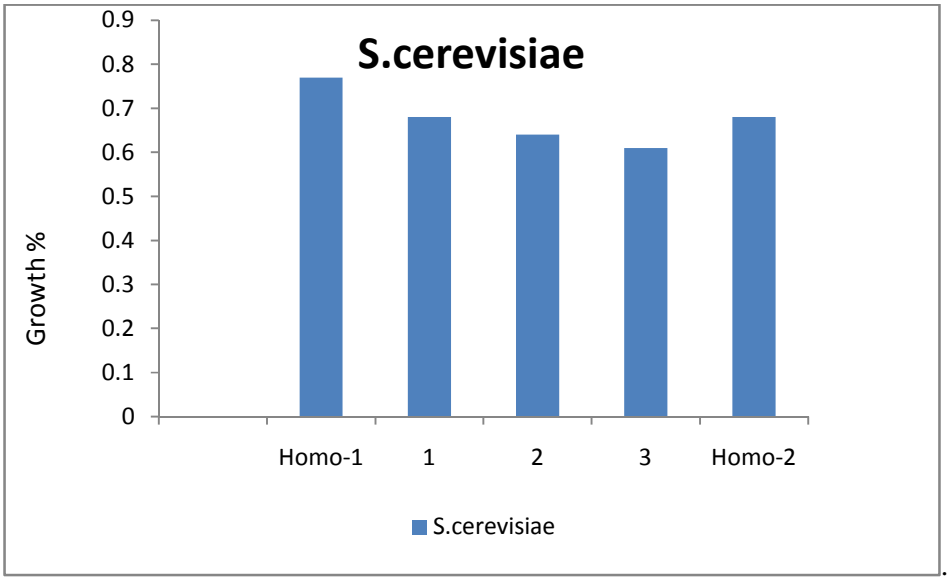


Figure 8: Effect of poly(VMA), poly(VMA-*co*-HEMA) and poly(HEMA) on growth (%) of Yeast

CONCLUSION

The monomer VMA was synthesized, characterized and copolymerized with styrene by free radical solutionpolymerization using different feed ratios. Conventional methods were employed to characterize the polymers. The homo and copolymers were characterizedby FT-IR. The GPC results show that molecular weight increases as the VMA content decreases in the copolymer.This study suggests that of VMA containing acryliccopolymers are good antimicrobial agent.

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