Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(12):5215-5224

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Novel Acrylic copolymers based on Schiff base: Synthesis, characterization and antimicrobial activity

Rajesh J. Patel[a*], Zarana R. Patel[b], Kirit H. Patel[b]

[a]*Department of Chemistry, Shri A. N. Patel P. G. Institute, c/o M. B. Patel Science college, Anand 388 001*
[b]*Department of Chemistry, Sardar Patel University, Vallabhvidyanagar 388 120*

ABSTRACT

Copolymers were prepared by using methylmethacrylate (MMA) and 4-{[4-chlorophenyl) imino] methyl} phenyl-2-methacrylate (MSB). The MSB monomer was synthesized using 4-[(1E)-2-aza-2-(4-chloro phenyl vinyl] phenol (SB) and methacryloylchloride. Homo and copolymers of MSB and methylmethacrylate were obtained with different feed ratios using N-N-di-methylformamide (DMF) as a solvent and 2-2'-azobis isobytyronitrile (AIBN) as an initiator at 70℃. IR Spectroscopy was employed to characterize the polymers thus obtained. The composition of the copolymers was found from proton NMR data. The MSB and MMA reactivity ratios were determined by applying the conversional linearization methods, of Fineman-Ross and Kelen-Tudos. The values of reactivity ratios obtained by above methods are comparable. Gel Permeation Chromatography (GPC) was used to determine average molecular weights and polydispersity of copolymers. Homo and copolymers were characterized for their thermal properties using Thermogravimetry (TG) and Differential thermal analysis (DTA). All polymers were tested for their antimicrobial properties against various microorganisms.

Keywords: copolymers, reactivity ratio, thermal analysis, antimicrobial properties.

INTRODUCTION

A wide range of acrylic materials is at present available with a broad property spectrum. Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties. Acrylate homopolymers along with their copolymers are used in various fields such as film, fibers, filament, coating, lithography, lacquers, adhesives, printing inks, binders, polymeric drug delivery and antimicrobial agents [**1-4**]. These properties allow acrylics to find use as binder vehicles in all type of paints [**5**] and improve the flowability [**6**]. Contamination by microorganism is of great concern in areas such as medical devices and healthcare product, biocidal coating [**7**] and ion-exchange study [**8**]. Copolymers of chlorophenyl acrylate and methacrylate were used as base coat for leather [**9**]. Soyakan and co-workers [**10**] prepared copolymers from N-(4-bromophenyl)-2-methacrylamide (BrPMMAm) and glycidyl methacrylate by free radical solution polymerization. The copolymers were characterized by FT-IR and ^{1}H-NMR. Patel and co-workers [**11**] proposed a method for determination of copolymer composition in the copolymer 4-methylcoumaryl acrylate and styrene from ^{1}H-NMR data. Lindsay and co-workers [**12**] synthesized the copolymerization of coumarin methacrylate with isobornyl methacrylate. These polymers showed tremendous non-linear optical properties. The present work incorporates the preparation and properties of homo and copolymers from 4-{[4-chlorophenyl) imino] methyl} phenyl-2-methacrylate (MSB) and methylmethacrylate (MMA). The copolymer composition was determined by proton NMR spectroscopy. The polydispersity of the copolymers was obtained from gel permeation chromatography. The thermal properties of various copolymers were investigated using thermogravimetry (TG) and differential thermal analysis (DTA). Antimicrobial properties of these homo copolymers were screened against various species of bacteria, fungi and yeast.

EXPERIMENTAL SECTION

Materials

Analytical grade solvents and reagents were used. Methacrylol chloride, p-hydroxy benzaldehyde, p-chloroaniline and hydroquinone were purchased from S. D. fine chemicals, 2-2' azobisisobutyronitrile (AIBN) was purchased from Aldrich.

Synthesis of 4-[(1E)-2-aza-2-(4-chloro phenyl) vinyl] phenol (SB)

SB was prepared by condensation of 4-hydroxy benzaldehyde and p-chloroaniline in ethanol achieved by boiling the mixture under reflux for 2-3 hours at 80°C. The precipitated SB was filtered, recrystallized from ethanol and dried. The melting point was 185°C.

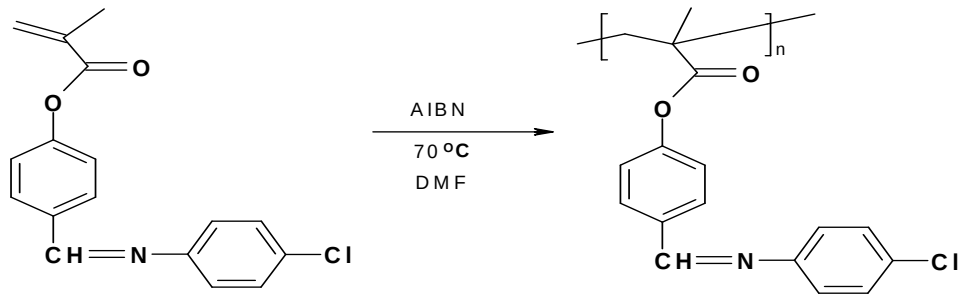
Synthesis of 4-{[(4-chlorophenyl) imino] methyl} phenyl-2-methacrylate (MSB): monomer

The esterification of 4-[(1E)-2-aza-2-(4-chlorophenyl) vinyl] phenol (SB) was performed with methacryloyl chloride. To a three necked flask, equipped with stirrer and condenser, absolute alcohol (200 ml) and NaOH (3.0 gm) were added and the contents were stirred until all the NaOH dissolved. To this SB was added and the mixture was stirred for about ten minutes. It was cooled at 0-5°C. Methacryloyl chloride was added dropwise to the reaction mixture, with the help of separating funnel. The temperature was maintained at 0-5°C and the contents were stirred for 2-3 hours. 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 and FT-IR [Figure-1 (a) and (b)].

Synthesis of homo and copolymers

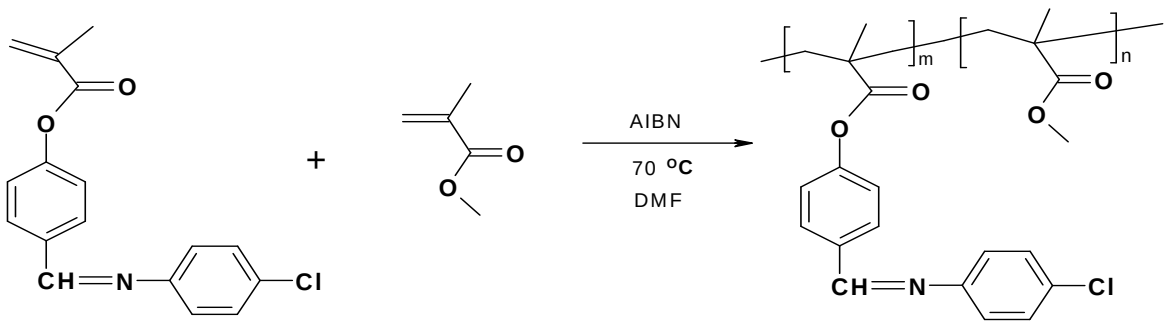
Homo and copolymerization were carried out in DMF using AIBN as an initiator, predetermined quantities of MSB, MMA, DMF and AIBN were mixed in a round bottom flask equipped with reflux condenser. The reaction mixture was heated at 70°C with constant stirring. The resulting polymer solution was slowly 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 MSB with MMA.

No. 1



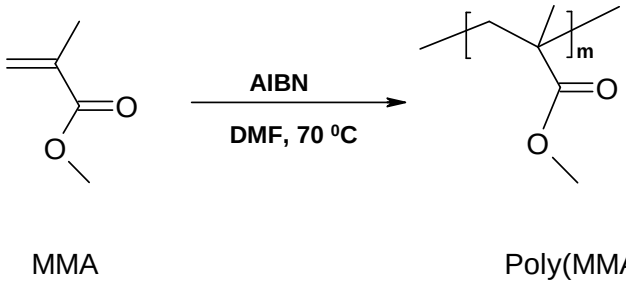
MSB Poly(MSB)

No. 2-6



MSB MMA Poly(MSB -co-MMA)

No. 7



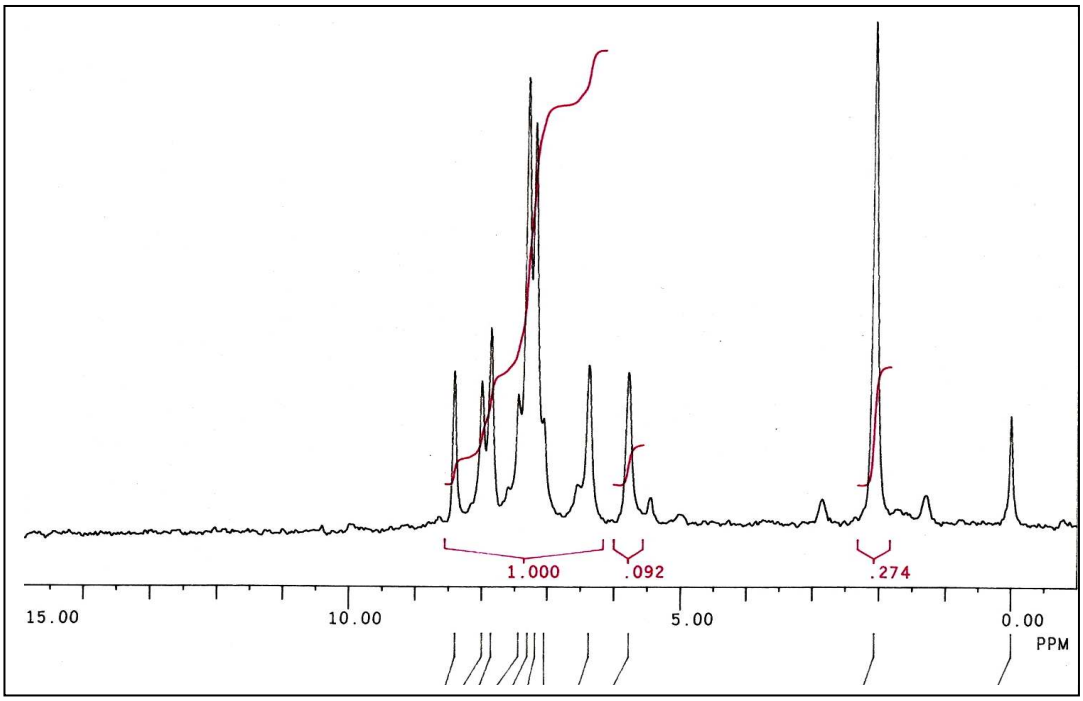
MMA Poly(MMA)

Reaction Scheme of (1) poly(MSB), (2-6) poly(MSB-co-MMA) and (7) poly(MMA).

Characterization

NICOLATE-400D FTIR was used to have Infra-Red spectra of MSB and polymers in KBr pellets. Copolymers composition and reactivity ratio were obtained from proton NMR data (HITACHI-R-1500, 60MHz, FT-NMR) using $CDCl3_{as}$ a solvent and tetramethylsillane as an internal standard. Average molecular weight of various homo and copolymers were determined using GPC instrument equipped with Jasco-PU 1580 pump, multisolvent delivery solvent system. Dimethylformamide (DMF) at 1.0 ml/min flow rate was used as mobile phase at 30℃. Thermogravimetric analyzer (TA-2960, USA) was used to record thermogram of polymers at a heating rate of $10℃/min$ in an inert atmosphere of nitrogen. DTA runs were performed with TA-2960(USA) instrument at a heating rate of $10℃/min$ in an inert atmosphere of nitrogen.

Figure1: Characterization of MSB (a) ^{1}H-NMR and (b) FT-IR spectra.



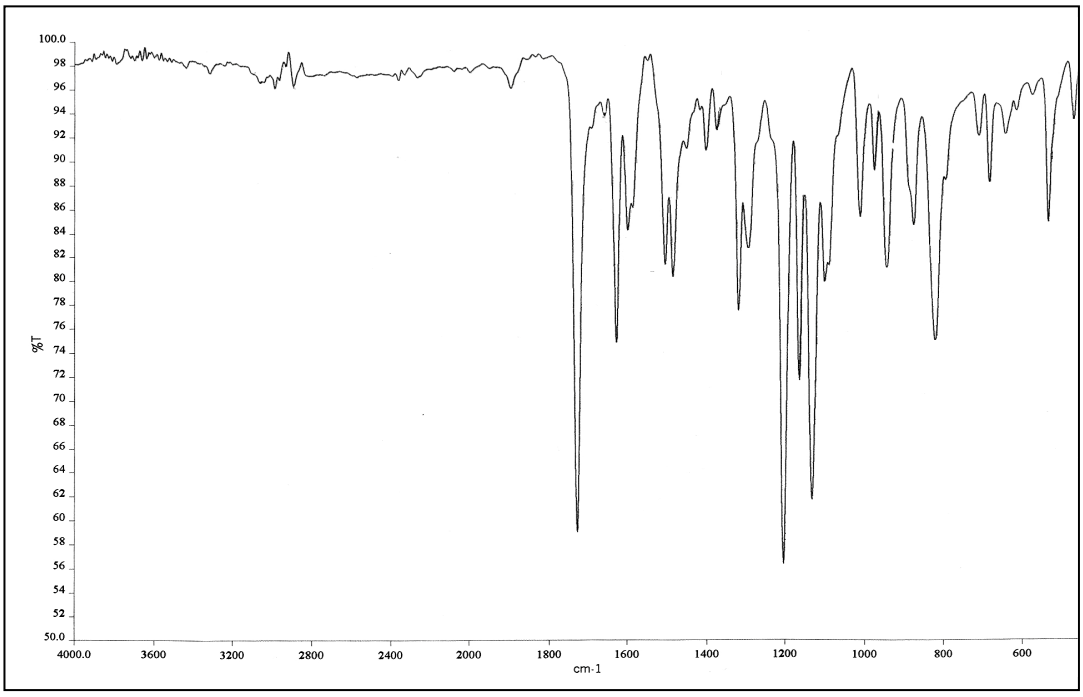
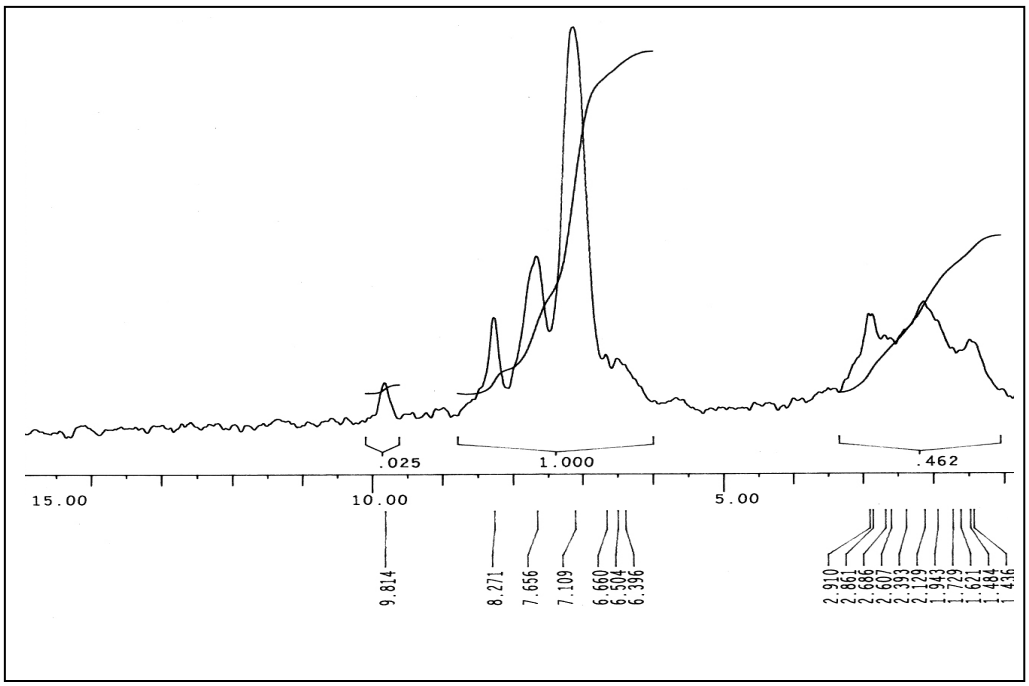
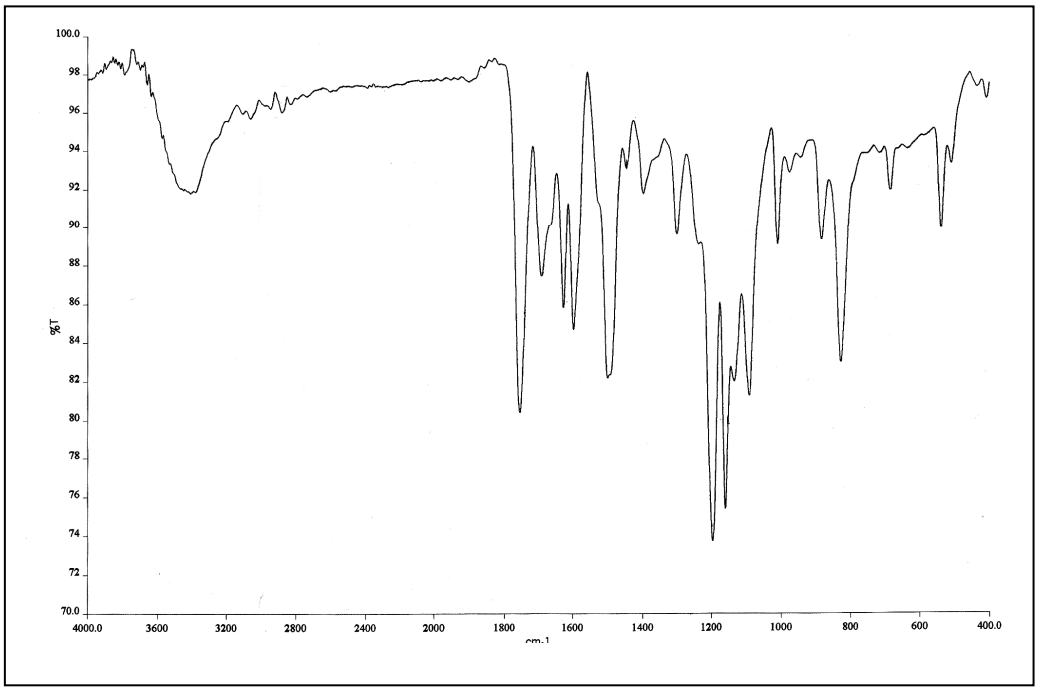


Figure2: Characterization of Poly(MSB): (c) ^{1}H-NMR and (d) FT-IR spectra.





Microbial Screening:

Three bacteria, three fungi and three yeasts were used as test organisms. Those are: *Bacillus subtilis, Escherichia coli and Staphylococcus citreus* as bacteria, *Aspergillus niger, Sporotichum pulveruletum and Trichocerma lignorum* as fungi and Candida *utilis, Saccharomyces cerevisiac and Pichia stipitis* as yeast. Homo and copolymers were screened for their effect on growth of these microorganisms. The detail experimental procedure to measure antimicrobial activity was given in our earlier communication [**13**] and percentage inhibition of microbial were calculated using the following formula.

(I) The percentage inhibition for bacteria was calculated by following the formula:

Percentage inhibition = $\frac{100\,(X-Y)}{X}$

Where x= Optical density of bacterial suspension in control set
y= Optical density of bacterial suspension in test set.

(II) The percentage inhibition for fungi was obtained after 7 days as follows:

Percentage inhibition = $\frac{100\,(X-Y)}{X}$

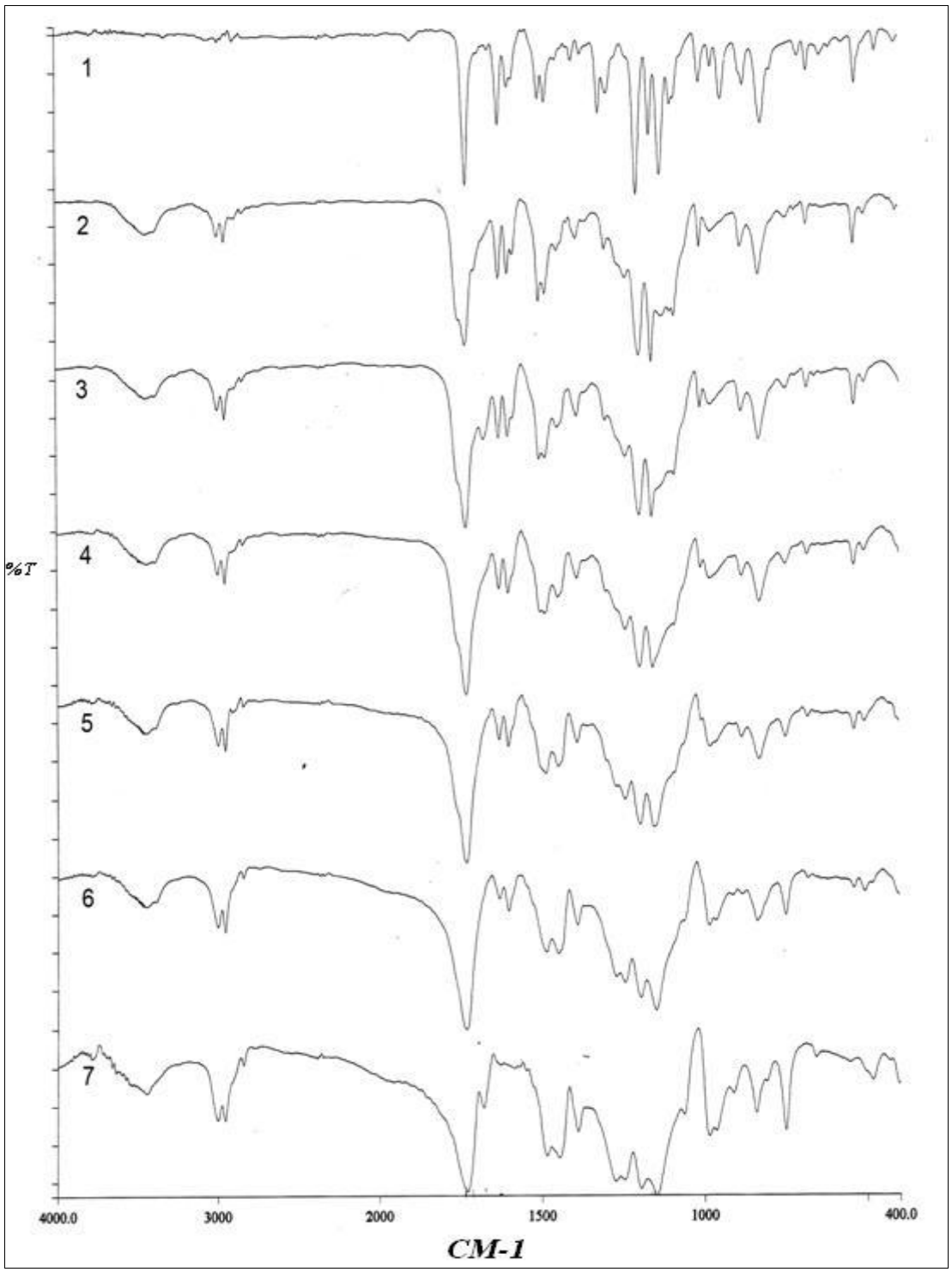
Where x= Weight of dry fungal cell mass in control set
y= Weight of dry fungal cell mass in test set.

(III) The percentage inhibition for yeast was calculated using the formula's

Percentage inhibition = $\frac{100\,(X-Y)}{X}$

Where x= Optical density of yeast suspension in control set
y= Optical density of yeast suspension in test set.

Figure 3: FT-IR spectra of (1) poly(MSB), (2-6) poly(MSB-co-MMA) and (7) poly(MMA).



RESULTS AND DISCUSSION

The synthesized monomer is light yellowish powder, soluble in acetone, methanol, di-methylformamide and insoluble in water.

Infrared Spectra

IR spectra of MSB and poly MSB shows all characteristic expected bands are shown in Figure 1b and Figure 2b respectively. A band at about 3071 cm^{-1} may be due to C-H stretching in aromatic ring. The band at about 1659 cm^{-1} is attributed to C=C stretching. The absorption band at 1400 cm^{-1} is assigned to symmetric banding of CH_3. After polymerization of MSB monomer, the C=C stretching at 1659 cm^{-1} is absent in polymer. The C-H out of plane

banding mode (709 cm^{-1} and 944 cm^{-1}) of vinyl group also disappears in polymers. The disappearance of band clearly indicates that polymerization has taken place involving C=C moiety.

^{1}H-NMR Spectra

The formation of monomer was also confirmed by ^{1}H-NMR techniques. Figure 1a and 2a show the ^{1}H-NMR of MSB and poly(MSB) respectively. 2.1(3H) (methyl protons), 6.4(1H) and 5.8 (1H) (Non-equivalent methylene protons), 7.2 to 8.0 (8H) (Aromatic proton). All the expected signals are observed but due to low sensitivity of the instrument (60 MHz) spin- spin coupling is not properly resolved. The signal at 6.3 and 5.7 for two non-equivalent methylene protons found in low field because both the protons are deshilded due to presence of phenyl ring.

In poly(MSB) the disappearance of signals at6.4 and 5.8 δ ppm (2H) of vinyl protons and the appearance of broad signals at 1.6-2.9 δ ppm (2H,-CH_2) shows the formation of the polymer.

Copolymer composition and reactivity ratios

Copolymer average monomer composition was determined from the corresponding proton NMR spectra using following procedure:

Let the reaction is

A + B → P ----------(1)

Where A is the monomeric unit-1 and B is the monomeric unit-2 while P is the resultant polymer.

The parameter C is the defined as

$$C = \frac{INTENSITY\ OF\ AROMATIC\ PROTONS}{INTENSITY\ OF\ ALIPHATIC\ PROTONS} \quad \text{---------- (2)}$$

$$C = (aM1 + bM2)/(cM1 + dM2) \quad \text{---------- (3)}$$

Where

M1 = mole fraction of monomer1

M2 = mole fraction of monomer2

a= number of aromatic protons in monomer1

b= number of aromatic protons in monomer2

c= number of aliphatic protons in monomer1

And

d= number of aliphatic protons in monomer2

But as we know that the sum of mole fraction of two monomers is always one. So we have,

M1 + M2 = 1 ---------- (4)

M2 = 1- M1 ----------(5)

From equation (3) and (5) we can write down as

$$M1 = \frac{b - Cd}{C(c-d) - (a-b)} \quad \text{---------- (6)}$$

The value of C is determined from the measuring the intensities of aromatic and aliphatic protons from the ^{1}H-NMR spectra. The composition of MSB in homo and copolymer were obtained with the help of the above equation (6) and converted into the appropriate units. The results are shown in table 1. The ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition, tacticity and sequence distribution because of its simplicity, rapidity and sensitivity [**14-17**].

The measurement of intensity of aliphatic and aromatic protons, allows the accurate evaluation of the content of each kind of monomeric unit incorporated into the polymer chains. From monomer feed ratio and copolymer compositions, the reactivity ratios (K-T) of MSB and MMA were determined by Fineman and Ross (F-R) [**18**] and Kelen and Tudos (K-T) [**19**] method and are shown in Table 1. The values of reactivity ratios of MSB (r_1) and MMA (r_2) are 1.61 and 1.09 respectively from F-R plot and 1.53 and 0.98 respectively from K-T plot. As the value of r_1 is more than r_2, in thus system MSB is more reactivity than MMA. The value of r_2 is nearly one and the products of r1r2 are also greater than one. This means that the distribution of monomeric units in copolymer chain is random.

Table 1: Reaction parameters for homo- and copolymers of MSB with MMA.

Sample Code No.	Monomer feed composition						Composition of MSB in copolymer	Reactivity Ratio			
	MSB			MMA				F-R Method		K-T Method	
	Mole	Gms.	%Wt.	Mole	Gms.	%Wt.		r_1	r_2	r_1	r_2
1	1.0	299.5	100	-	-	-	100.00	1.61	1.09	1.53	0.98
2	0.5	149.8	50	0.5	50.0	50	38.99				
3	0.4	119.8	40	0.6	60.0	60	53.63				
4	0.3	89.8	30	0.7	70.0	70	65.99				
5	0.2	69.9	20	0.8	80.0	80	79.77				
6	0.1	29.9	10	0.9	90.0	90	92.53				
7	-	-	-	1.0	100	-	-				

Molecular Weight Measurements:

Table 2 shows the number and weight average molecular weight of homo and copolymers of MSB and MMA, obtained from GPC. The value of number average and weight average molecular weight range from 10440 to 30150 gm/mole and from 20530 to 60530 gm/mole respectively. The polydispersity index ranges from 1.78 to 2.42. No specific trends are observed from GPC results.

Table 2: GPC data for homo & some copolymers.

SAMPLE CODE NO.	$\overline{Mn}$	$\overline{Mw}$	POLYDISPERSITY INDEX
1	30150	53800	1.8
2	27880	53765	1.9
4	27830	67420	2.4
6	10440	20530	2.0
7	32550	60525	1.9

Thermal analysis:

Thermal behavior of homo and copolymers was studied by TGA and DTA in nitrogen atmosphere. The TGA data shown in Table 3 indicates that the polymer underwent single step decomposition. Activation energy and integral procedural decomposition temperature (IPDT) were determine by Broido's [**20**] and doyle's [**21**] method, respectively. Thermal studies indicated that the mode of decomposition is affected by the composition of the copolymer, but no uniform trend was observed in the parameters obtained. From Broido and Doyle methods, the activation energy of degradation for the copolymers is found to in the range 57-67 KJ/mol. The IPDT value for copolymers is in the range 371-432°C. Differential thermal analysis (DTA) data of homo and copolymers were analyzed by Reich's [**22**] method. The activation energy of these polymers ranged from 57-68 KJ/mol and the degradation is first order reaction. DTA and TGA data indicates that the phase change is followed by degradation of polymers. It is also observed that presence of MMA monomer unit in polymer s backbone does not changes their thermal stability compared to the stability of individual homopolymers to any significant extent.

Sample Code No.	% Weight loss at various temperature (°C)					Decomposition Temperature Range (°C)	T_{max} [a] (°C)	T_{50} [b] (°C)	IPDT [c] (°C)	Activation Energy [d] (E_A) (KJ.mole^{-1})
	200	300	400	500	600					
1	2	12	90	97	100	270-449	310	350	377	37
2	-	8	73	90	100	240-360	305	342	371	35
4	2	10	82	87	100	228-385	330	360	405	39
6	3	8	68	84	100	255-410	335	370	432	45
7	3	49	97	99	99	193-383	325	304	414	38

Microbial Screening

All the homo and copolymers of MSB and MMA were screened for antimicrobial activity against various microbial. The results related to antimicrobial activity are presented in Figure 4, 5 and 6 respectively for bacteria, fungi and yeast. Poly MSB allows less than 40% growth of bacteria and as the incorporation of MMA in copolymer increases, the percentage growth of bacteria increases. From the plot it is clear that the activity of the copolymers depends upon the relative percentage of both monomers in copolymers. Homopolymer of MSB shows good antimicrobial properties compared to copolymers. Homopolymer of MSB shows maximum activity against both fungi and yeast. From results above it is obvious that presence of chlorine in copolymers plays important role for the inhibition of microbials growth.

Figure 4: Effect of poly(MSB-co-MMA) homo and copolymers on growth (%) of Bacteria.

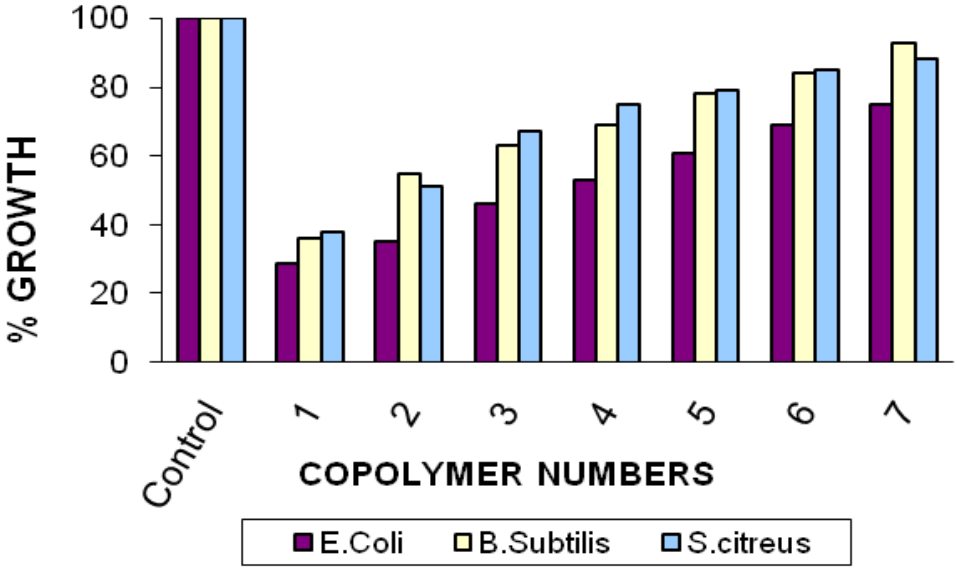


Figure 5: Effect of poly(MSB-co-MMA) homo and copolymers on growth (%) of Fungi.

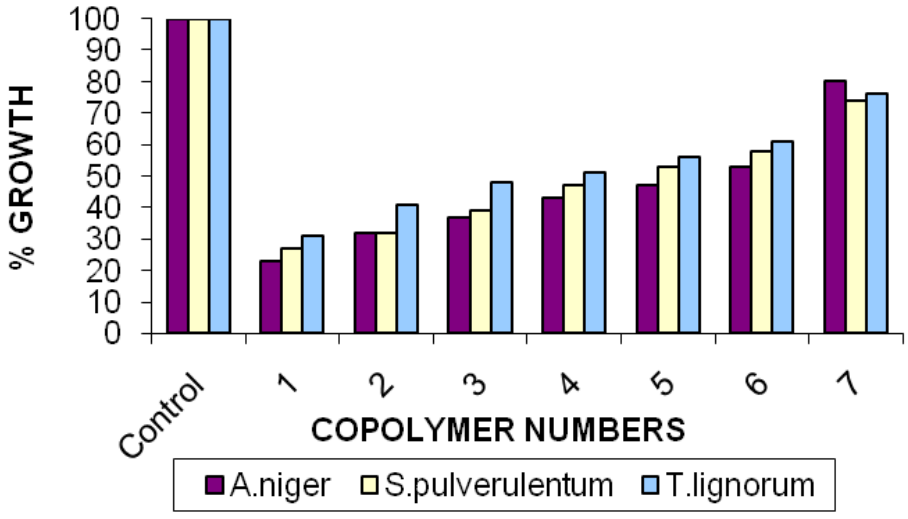
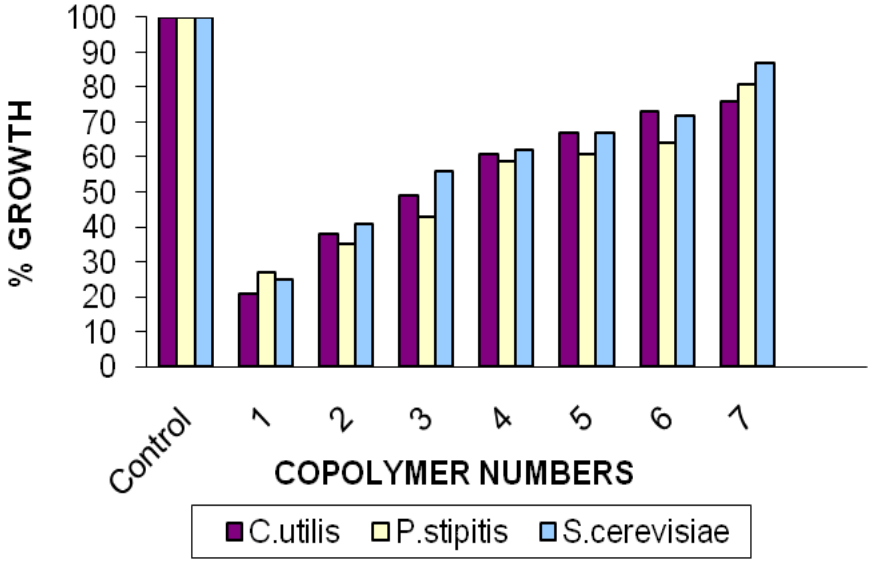


Figure 6: Effect of poly(MSB-co-MMA) homo and copolymers on growth (%) of Yeast.



CONCLUSION

Homopolymer and copolymers of MSB and MMA were prepared by free radical polymerization using different feed ration. Conventional methods were employed to characterize the polymers. Reactivity ratio indicated that the distribution of monomeric unit in copolymers chain is random. TGA data indicated that the homo and copolymers undergoes single step degradation. Microbial activity of homo and copolymers of MSB is higher. As MSB monomeric unit in copolymer decreases, the percentage growth of microbial increases. This clearly indicated that the presence of chlorine is responsible for antimicrobial activity.

REFERENCES

[1] D. Silvestri, M. Gagliardi, N. Barbani, C. Cristallini, P. Giusti, *Drug Delivery*, **2009**, 16(2), 116-124.
[2] KA. Shaffei, AB. Moustafa, AI. Hamed, *International journal of polymer science*, **2009.**
[3] Z. Czech, A. Butwin, E. Herko, B. Hetcyze, J. Zawadiak, *express poly. Let.*, **2008**, 2(4), 277-283.
[4] J. T. Tan, C. H. Goh, K. C. Tam, *Eur. J pharm. Sci.*, **2007**, 32(4), 340-348.
[5] C. S. Chuang, Tsai, M. K. Wang et al, *Wood science and technology*, **2008**, 42, 593-607.
[6] H. I. Al-Shafey, A. I. Hashem, R. S. Abdel Hameed, E. A. Dawood, *Advances in applied science research*, **2011**, 2(5), 476-489.
[7] S. K. Singh, A. Jain, D. Sharma, A. Dubey, *Der chemical sinica*, **2011**, 2(1), 111.
[8] D. T. Masram, K. P. Kariya, N. S. Bhave, *Advances in applied science research*, **2011**, 2(4), 156-165.
[9] S. Thamizharasi, G. Srinivas, N. Sulochana, B. S. R. Reddy, *J Appl Poly Sci*, **1999**, 73, 1153-1160.
[10] C. Soyakan, A. Dilibus, R. Coskun, *Reactive and functional polymer*, **2008**, 68,114-124.
[11] J. R. Patel, K. H. Patel, R. M. Patel, *Colloid polymer science*, **2009**, 287, 89-95.
[12] G. A. Lindsay, R. A. Henry, J. M. Hoover, *Poly Prepr AmeChe Soc Div Poly Chem*., **1993**, 34, 771.
[13] A. K. Patel, R. J. Patel, K. H. Patel, R. M. Patel, *J. chil. Chem. Soc.*, **2009**, 54, N3.
[14] K. J. Ivin, S. Ptichumani, C. R. Reddy, S. Rajadurai, *Polymer science chem.*, **1982**, 20, 277-281.
[15] R. Balaji, D. Grande, S. Nanjundan, *polymer*, **2004**, 45(2), 1089-1099.
[16] A. S. Brar, D. Khausik, *Euro. Poly. J.*, **1988**, 34(11), 1585-1593.
[17] U. Senthikumar, R. Balaji, A. R. Prasath, S. Nanjundan, *J. macromol. Sci. pure appl. Chem.*, **2002,** A38, 1312-1319.
[18] M. Fineman, S. D. Ross, *J. poly. Science.*, **1950**, 5(2), 259-262.
[19] T. Kelen, F. Tudos, *J. macro. Science chem.*, **1975**, A 9(1).
[20] A. Broido, *J. polym. Science.*, **1969**, A 2(7), 1761-1773.
[21] C. D. Doyle, *Anal. Chem.*, **1961**, 33, 77-79.
[22] L. Reich, *Die macromol. Chem.*, **1969**, 123, 42-45.