Acrylic copolymers based on Schiff base moiety: 
Synthesis and their antimicrobial properties

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ABSTRACT

Chlorine containing monomer 4-[(4-chlorophenyl) imino]methyl]phenyl-2-methacrylate (MSB) was synthesized by reacting 4-[(1E)-2-aza-2-(4-chlorophenyl) vinyl] phenol (SB) with methacryloylchloride. The monomer characteristics was identified by Fourier transform infrared spectroscopy (FT-IR) and ¹H-NMR spectroscopy to obtain copolymer composition. Homopolymer and copolymers of MSB with Styrene(ST) at different feed composition was prepared by free radical solution polymerization at 70 ±2°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator and dimethylformamide (DMF). The copolymer compositions were characterized using ¹H-NMR data. Fineman-Ross (F-R) and Kelen-Tudos (K-T) methods were used to find reactivity ratio. The molecular weight and polydispersity index of the polymer were obtained using gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of polymers carried out in a nitrogen atmosphere showed moderate thermal stability. Antimicrobial activity of the polymers was also investigated against various bacteria, fungi and yeast.

KEYWORDS: copolymerization, reactivity ratios, antimicrobial activity, thermal analysis.

INTRODUCTION

Chlorine containing phenyl(meth)acrylates and its polymers have received considerable attention in recent years. Chlorine containing phenol and its derivatives possess antimicrobial, antymycotic and ameobicidal properties. Three novel polymers incorporating Schiff bases were derived from condensation reaction of poly(acrylamide) with 5-chloro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde and 5-methyl-2-hydroxybenzaldehyde completes and Cu(II) and Ni(II) complex of them have been prepared by Sari and Ozcan [1]. Yeon and co-workers [2] have synthesized p-(2,2,3-tricyano-4-carboxmethoxycyclopropyl)phenoxycethyacrylate 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 therefrom. 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 azobisisobutyronitrile (AIBN) as an initiator under nitrogen atmosphere. Erol and 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 glycidyl methacrylate in 1,4-dioxane solution at 70±1°C using 2,2’-azobisobutyronitrile 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. Kadir and co-workers [7] prepared copolymers from phenyl methacrylate and methacrylate. The copolymers were characterized by IR, 1H-NMR and 13C-NMR techniques. 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, 1H-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, rapidity and sensitivity [8-13].

Free radical copolymerization of phenoxyethyl methacrylate and glycidyl methacrylate was carried out using AIBN in 2- butanone solution at 333°K by Anver et al.[14] Characterization of synthesized copolymers were done by FT-IR, 1H-NMR and 13C-NMR spectroscopic methods. Thermal properties were also investigated. Monomer reactivity ratios were computed using F-R, K-T and RREVM methods. Acrylate homopolymers along with their copolymers are used in various field such as films, fibers, 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 microbicicides and are thermally stable up to 250°C.

The present work describes the characterization of MSB and ST by FT-IR and 1H-NMR spectroscopy. Copolymer composition was obtained from 1H-NMR data and monomer reactivity ratios were determined by Fineman-Ross(F-R) [20] and Kelen-Tudos (K-T) [21] methods. The formation of polymer has been established with the help of IR spectral data. Gel permeation chromatography was employed to determine the molecular weights of the synthesized polymers. The thermal properties of the polymers were analyzed by TGA and DTA. Antimicrobial activity of the homo and copolymets was carried out against selected microorganisms like bacteria, fungi and yeast.

MATERIALS AND METHODS

2.1 Materials:
Methacrylic acid, benzoyl chloride, hydroquinone, 2,2’-azobisisobutyronitrile (AIBN) were analytical grade reagents. The solvents were purified by the conventional methods [22].

2.2 Synthesis of 4-[(1E)-2-aza-2-(4-chlorophenyl) 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.

2.3 Synthesis of homo and copolymers:
Homo and copolymerization were carried out in DMF using AIBN as an initiator, predetermined quantities of MSB, ST, 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 ST.

2.5 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 Tetramethyl silane (TMS) was used as an internal standard. TA instrument (U.S.A) -2960 thermogravimetric analyzer was used to perform TGA at a heating rate of 10°C/min in nitrogen atmosphere. DTA trace was obtained with the TA instrument (U.S.A) -2960 differential analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

2.6 Antimicrobial activity:
The homo and copolymers thus obtained, were tested against different microorganism that is commonly employed for biodegradability tests. Bacterial strain (Bacillus subtilis, Echerichia coli and Staphylococcus citreus), fungal strain (Aspergillus niger, Sportichum pulveruletum and Trichocerm lignorum) and yeast strain (Candida utilis, Saccharomyces cerevisial and Pichia stipitis) were taken for the antimicrobial activity study. The details of the experimental procedures have been reported in our earlier publication [23].

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

\[
\text{Percentage inhibition} = \frac{100(X-Y)}{X}
\]

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

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

\[
\text{Percentage inhibition} = \frac{100(X-Y)}{X}
\]

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

(c) The percentage inhibition for yeast was calculated using the formula’s

\[
\text{Percentage inhibition} = \frac{100(X-Y)}{X}
\]

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

RESULTS AND DISCUSSION

Different homo and copolymers were obtained by the free radical solution polymerization technique. The mole fraction of MSB ranging from 0.5 to 0.1 in the feed were studied in a wide composition interval. Here the copolymerization was allowed to proceed only up to 10% conversion in order to satisfy the differential copolymerization equation for calculation of reactivity ratios. The data on the composition of the feed and copolymers are given in Table 1.

3.1 ¹H-NMR Spectrum:
The signal at 6.4 (1H) and 5.8 δ (1H) for two non-equivalent methylene proton found in low field because both the protons are deshielded due to presence of phenyl ring. In poly(MSB) the disappearance of signals at 6.4 and 5.8 ppm (2H) of vinyl protons and the appearance of broad signals at 1.6 - 2.9 δ ppm (2H,-CH2) shows the formation of the polymer. Figures 1 and 3, shows the ¹H-NMR of MSB and poly (MSB) respectively.

3.2 Infrared spectra:
The IR spectra confirm the structure of copolymers in all aspects. A band at 3071 cm⁻¹, which could be due to C-H stretching in the aromatic ring. The absorption at 1164 cm⁻¹ is traced to the symmetric ν-c-o-c stretching mode and C-Cl [24] is attributed to the peak at 682 cm⁻¹. The absorption bands at 1400 cm⁻¹ due to symmetric bending of -CH3.
group. The peak at 944 cm\(^{-1}\) is assigned to \(-\text{CH}\) out of plane banding mode of vinyl moiety. The absorption bands at 1627 cm\(^{-1}\) and 1659 cm\(^{-1}\) are due to stretching -C=\(\text{N}\) and -C=\(\text{C}\) respectively and in poly(MSB) -C=\(\text{C}\) stretching of monomer is absent. The band between 3100-3000 cm\(^{-1}\) assigned to the stretching vibration of aromatic ring and the bands at 1448 and 1603 cm\(^{-1}\) due to -C=\(\text{C}\) stretching vibration of aromatic ring for poly(ST). The band at 763 cm\(^{-1}\) due to \(-\text{C-H}\) out of plane bending vibration of mono-substituted aromatic ring and the IR spectra of homo and copolymers are shown in Figure 4.

### 3.3 Copolymer composition and reactivity ratios:

The monomer compositions of the copolymer samples were determined by \(^1\)H-NMR spectra. The assignment of the resonance peaks in the \(^1\)H-NMR spectrum leads to accurate evaluation of each monomer unit incorporated into the copolymer chains. The molefraction of MSB in the copolymer was calculated by measuring the integrated peak height of aromatic protons of MSB to that of total aliphatic protons in the copolymer as using the following equation.

\[
\text{C} = \frac{\text{INTENSITY OF AROMATIC PROTONS}}{\text{INTENSITY OF ALIPHATIC PROTONS}}
\]
\[
= \frac{\text{M}_1}{\text{M}_2} = \frac{(3\text{C} - 5)/(8 - \text{C})}{(4\text{M}_1 + 3\text{M}_2)/(3\text{M}_1 + 5\text{M}_2)}
\]

Where \(\text{M}_1\) is the mole fraction of MSB in the copolymer. \(\text{M}_2\) is the molefraction of styrene in the copolymer. Based on equation (2), the mole fraction of MSB in copolymer was determined by measuring the integral peak height of signals due to aromatic and aliphatic protons. Here, the corresponding mole fractions of MSB in the copolymers are shown in Table 1.

The monomer reactivity ratios were calculated by the application of linearization methods, such as F-R and K-T methods. The F-R and K-T parameters for the copolymers are presented in Table 1. The \(r_1\) and \(r_2\) values obtained from F-R and K-T methods are in well agreement with each other. Since the value of \(r_1\) is less than \(r_2\), the product of \(r_1\) and \(r_2\) is less than 1. The system gives rise to azeotropic polymerization at particular composition of monomer, the value of \(N_1\) is 0.85, so the copolymer formed will be richer in MSB monomeric unit. The product \(r_1/r_2\) is less than 1, which indicates that the system follows a random distribution.

### 3.4 Molecular weight:

The number and weight average molecular weight of homo and copolymers of MSB with styrene were obtained from gel permeation chromatography. The values of number average and weight average molecular weight ranges from 9360 to 30150 gm/mole and 21350 to 53800 gm/mole respectively where as polydispersity index ranges from 1.8 to 1.9 respectively. Molecular weight data are presented in Table 2. It is observed from the results that molecular weight increases as MSB content decreases in the copolymer. The value of polydispersity index suggests that the chain termination of polymers takes place predominantly by disproportionation rather than coupling [25].

### 3.5 Thermogravimetric analysis:

Thermal behaviors of polymers were studied using TG and DTA traces. The measured results are shown in Tables 3 and 4 respectively. Poly (MSB) and poly (ST) shows single step degradation, while poly(MSB-co-ST) undergo two step degradation. The copolymers undergo decomposition in the range 260-449°C. The activation energy calculated by Broido’s method [26] lies in the range 37-66 KJ/mole and as the MSB content in the polymer decreases the activation energy increases. The integral procedural decomposition temperature (IPDT) calculated by Doyle’s method [27]. The value of IPDT represents an overall thermal stability of the polymers and it varies from 377 to 543°C.

From DTA traces the decomposition of polymers occurs at around 394 to 522°C. The activation energy for thermal degradation and reaction order were determined by Reich’s method [28]. Activation energy of polymers ranged between 34 and 61 KJ mol\(^{-1}\) where as the reaction order for all the polymers was being one.

### 3.6 Antimicrobial activity:

The antimicrobial activity of the homo and copolymers of MSB with ST was carried out. The obtained results are presented in Figures 5, 6 and 7 for bacteria, fungi and yeast respectively. Poly(MSB) allows about 37% growth of

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bacteria, where as its copolymers favored 34-89% growth, poly(ST) allows 90% growth of bacteria. Fungi shows 27% growth for poly(MSB), 72% growth for poly(ST) and 33-62% growth for copolymers. Yeast shows 25% growth for poly(MSB), 75% growth for poly(ST) and 30-74% growth for its copolymers. It was observed that polymer prepared using styrene shows strong inhibitor effect towards the microorganisms tested. A MSB content in the copolymer increase, inhibition to the growth of microorganisms also increases.

**TABLE 1: Composition data for free radical copolymerization of MSB with ST.**

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>Monomer feed composition</th>
<th>Composition of</th>
<th>Reactivity ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MSB ST</td>
<td>MSB in copolymer</td>
<td>F-R method</td>
</tr>
<tr>
<td>1</td>
<td>1.0 299.5 100</td>
<td>-</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>0.5 194.8 50</td>
<td>0.5 52.1 50</td>
<td>0.78</td>
</tr>
<tr>
<td>3</td>
<td>0.4 119.8 40</td>
<td>0.6 62.5 60</td>
<td>0.80</td>
</tr>
<tr>
<td>4</td>
<td>0.3 89.8 30</td>
<td>0.7 72.9 70</td>
<td>0.82</td>
</tr>
<tr>
<td>5</td>
<td>0.2 69.9 20</td>
<td>0.8 83.3 80</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1 29.9 10</td>
<td>0.9 93.7 90</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>- - -</td>
<td>1 104.2 100</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2: GPC data for poly (MSB), poly (ST) and poly (MSB-co-ST)**

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_z$</th>
<th>Polydispersity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30150</td>
<td>53800</td>
<td>79350</td>
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<tr>
<td>2</td>
<td>9360</td>
<td>21350</td>
<td>37130</td>
<td>1.9</td>
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<td>4</td>
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<td>24230</td>
<td>35070</td>
<td>1.8</td>
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<tr>
<td>6</td>
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<td>24430</td>
<td>39180</td>
<td>1.8</td>
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<tr>
<td>7</td>
<td>15360</td>
<td>27400</td>
<td>42830</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**BLE 3: TGA data for homo and copolymers of MSB with ST**

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>% Weight loss at various temperature (°C)</th>
<th>Decomposition Temperature Range (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
<th>IPDT (°C)</th>
<th>Activation Energy $a$ (kJ/mole $b$)</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>- 12 90 97 98</td>
<td>270-449</td>
<td>310 350 377</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>- 5 55 81 95</td>
<td>295-520</td>
<td>350 290 408</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>- 4 52 82 90</td>
<td>270-530</td>
<td>383 300 422</td>
<td>42</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>- 5 60 89 95</td>
<td>290-510</td>
<td>340 390 410</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>- 3 94 99 99</td>
<td>267-450</td>
<td>397 343 543</td>
<td>66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Temperature for maximum rate of decomposition
$^b$Temperature for 50% weight loss
$^c$Integral procedural decomposition temperature
$^d$By Broido’s method

**TABLE 4: DTA data for homo and copolymers of MSB with ST**

<table>
<thead>
<tr>
<th>Sample Code No.</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
<th>$T_3$ (°C)</th>
<th>Activation Energy $a$ (kJ/mole $b$)</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>385 440 412</td>
<td>34</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>388 466 416</td>
<td>39</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>378 463 398</td>
<td>45</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>377 458 394</td>
<td>51</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>374 586 522</td>
<td>61</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Starting Temperature of DTA trace
$^b$Ending Temperature of DTA trace
$^c$Peak maxima Temperature of DTA trace
$^d$Activation Energy by Reich’s method
Reaction Scheme of (1) poly(MSB), (2-6) poly(MSB-co-ST) and (7) poly(ST).
FIGURE 1: $^1$H-NMR Spectrum of monomer MSB.

FIGURE 2: FT-IR Spectrum of monomer MSB.
FIGURE 3: $^1$H-NMR Spectrum of poly (MSB).

FIGURE 5: Effect of poly(MSB), poly(MSB-co-ST) and poly(ST) on (%) growth of bacteria.
FIGURE 4: FT-IR Spectra of (1) poly(MSB), (2-6) poly(MSB-co-ST) and (7) poly(ST).
CONCLUSION

The monomer MSB was synthesized, characterized and copolymerized with styrene by free radical solution polymerization using different feed ratios. Conventional methods were employed to characterize the polymers. The copolymer composition was determined by $^1$H-NMR data. The reactivity ratio of the monomer obtained from F-R and K-T methods and the $r_1$ value is less than $r_2$ and the product of $r_1$ and $r_2$ is less than one, this shows the
copolymers are random distribution of monomeric unit in the chain. The homo and copolymers were characterized by FT-IR. The GPC results show that molecular weight increases as the MSB content decreases in the copolymer. TGA data reveal that the poly(MSB) and poly(ST) undergoes single step decomposition where as poly(MSB-co-ST) undergoes double step decomposition. All the polymers showed moderate thermal stability. Chlorine content is important to impart antimicrobial property in these polymers. This study suggests that of MSB containing acrylic copolymers are good antimicrobial agent.

REFERENCES