

## Kinetics of thermal decomposition and antimicrobial screening of terpolymer resins

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**Abstract** Polycondensation technique was employed to synthesize terpolymer resins of anthranilic acid, urea, and formaldehyde (AUF-I, II, and III) in dimethyl formamide medium with varying mole proportions. The terpolymer was characterized by infra-red, nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectroscopy, gel permeation chromatography (GPC), and scanning electron microscopy (SEM). The thermal decomposition pattern and the kinetics of thermal decomposition of the terpolymers were investigated by thermogravimetric analysis (TGA) in a static nitrogen atmosphere at a heating rate of 20 °C/min. Freeman–Carroll and Sharp–Wentworth methods have been adopted to evaluate the kinetic and thermodynamic parameters such as thermal activation energies ( $E_a$ ), order of the reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), and frequency factor ( $Z$ ). The thermal decomposition model for the terpolymers was also proposed using Phadnis–Deshpande method. The synthesized terpolymer resins were screened for antimicrobial activity against pathogenic bacteria and fungi. The resins show potent inhibition against bacteria such as *Escherichia coli*, *Klebsiella*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* and fungi viz. *Aspergillus flavus*, *Aspergillus niger*, *Penicillium species*, *Candida albicans*, *Cryptococcus neoformans*, and *Mucor species*.

**Keywords** Terpolymer · Thermal analysis · Kinetics · Degradation model · Antimicrobial screening

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## Introduction

Recently, much attention has been focused on the development of terpolymers which are rational alternative to conventional polymers [1, 2]. The biomedical applications of terpolymers have further provoked the researchers for the synthesis of new terpolymers with heteroatoms in their molecular structure. A survey of the literature reveals that the terpolymers with low molecular weight exert a pull on the concentration of synthetic chemists due to their varied biological activities [3]. A comparative study of mechanical and thermal behaviors of poly(propylene cyclohexene carbonate)s and poly(propylene carbonate) have been carried out, and the poly(propylene cyclohexene carbonate) possesses higher thermal stability and mechanical strength compared to the latter [4]. Thermal degradation kinetics of poly(methylphenylsiloxane) containing methacryloyl groups was investigated that different solid-state reaction mechanism was followed at different stages of degradation [5]. Methylvinylsilylene and styrene were copolymerized at different feed ratios. The thermal study reveals that the order of the reaction increases with the increase in the molar proportions of the monomer [6]. Terpolymer involving 8-hydroxyquinoline 5-sulfonic acid and melamine with formaldehyde was synthesized in the presence of an acid catalyst, and its thermal stability has also been reported. The high initial decomposition temperature of the terpolymer indicates the thermal stability of the terpolymer [7]. Kinetic parameters of the terpolymer involving 2,2-dihydroxybiphenyl, urea, and formaldehyde were calculated by the Freeman–Carroll (FC) and Sharp–Wentworth (SW) methods. From the results, it was reported that the terpolymers have good thermal stability, and the decomposition reaction follows the first order kinetics [8]. Terpolymer involving salicylic acid, guanidine, and formaldehyde was prepared, and its kinetic parameters evaluation was also carried out. The order of the reaction was found to be nearly one, and thermal activation energy was found to be very low [9]. Similarly, solution polymerization of three monomers involving 8-hydroxyquinoline, salicylic acid, and formaldehyde was carried out to obtain a terpolymer. From the TGA results, the terpolymer was thermally stable, and the order of reaction for the thermal decomposition was found to be nearly one [10]. Recently, our research group synthesized a terpolymer involving 8-hydroxyquinoline, anthranilic acid, and formaldehyde and its polychelates with few transition metals. The thermal stability and its kinetic parameters were calculated. The result of the study reveals that the polychelates possess higher thermal stability, low activation energy, and decreased order of reaction compared to their terpolymer ligand [11]. 2-hydroxy-4-ethoxybenzophenone–ethylene (HEBP–1,2-PG) resin was synthesized by the condensation of 2-hydroxy-4-ethoxybenzophenone and 1,2-propylene glycol in acidic medium, and its polychelates were synthesized. It was observed that the incorporation of the metal ion into the polymeric backbone decreases the thermal stability because of breaking of an intramolecular hydrogen bonding present in the polymeric ligand [12]. Urea and formaldehyde resin were synthesized, and it was reported for its potent application as effective antibacterial coating materials [13]. Thiosemicarbazide–formaldehyde resin was synthesized and reported for its higher inhibition characteristics against the chosen microbes [14]. Antimicrobial activity of

4-chloro-3-methyl phenyl methacrylate and its copolymers with butyl methacrylate possess effective antimicrobial activity due to the presence of chlorine atom in the polymeric ring [15].

The present research article discusses the synthesis and the characterization of the terpolymer resins derived from anthranilic acid and urea with formaldehyde. The thermal behavior of the terpolymer resins was evaluated by TGA, and the kinetic and thermodynamic parameters such as activation energy ( $E_a$ ), order of the reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), and frequency factor ( $Z$ ) were determined by FC and SW methods [16, 17]. The thermal degradation model for the terpolymer was also proposed by Phadnis–Deshpande (PD) method [18]. In addition, the terpolymer resins were also screened for antimicrobial activity against pathogenic bacteria viz. *Escherichia coli*, *Klebsiella*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* and fungi viz. *Aspergillus flavus*, *Aspergillus niger*, *Penicillium species*, *Candida albicans*, *Cryptococcus neoformans*, and *Mucor species*.

## Experimental

### Materials

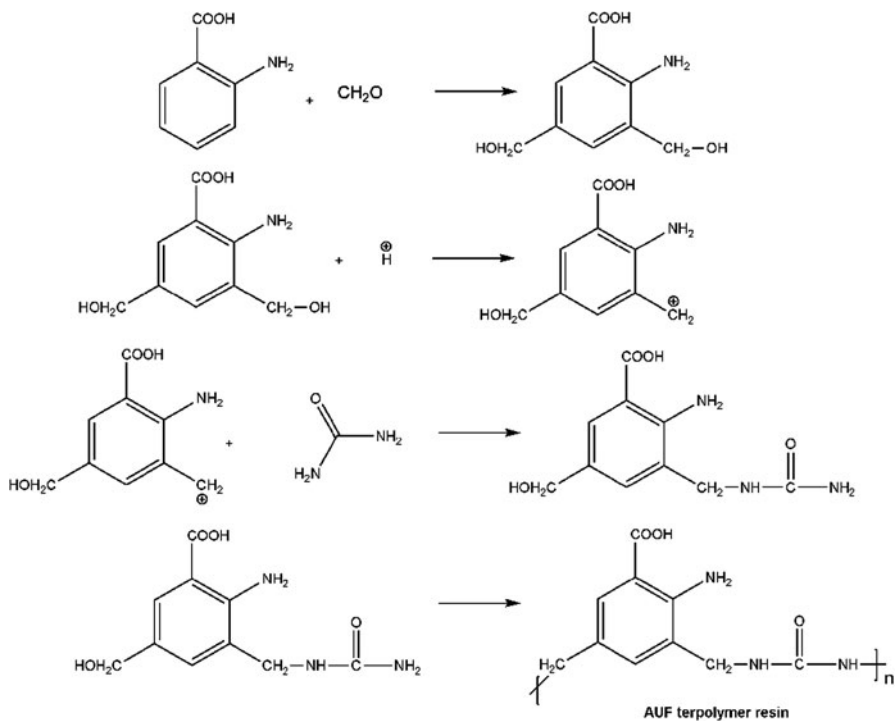
Anthranilic acid and urea were procured from Merck, India and purified by rectified spirit. Formaldehyde (37%) were of AR grade, Merck and used as received. Double distilled water was used for all the experiments. All other chemicals were of analytical grade and used without further purification.

### Solution polycondensation

The terpolymer resin (AUF-I) involving anthranilic acid (0.1 mol) and urea (0.1 mol) with formaldehyde (0.2 mol) was synthesized using glacial acetic acid as the reaction medium at  $140 \pm 2$  °C for 6 h [19]. The reaction mixture was then cooled, poured into crushed ice with constant stirring, and left overnight. The yellow colored resin obtained was then washed with warm water and methanol. It is then filtered off to remove unreacted monomers. Finally, the terpolymer resin was air dried. The yield of the terpolymer was found to be 80%. The dried resin sample was then dissolved in 8% NaOH and regenerated using 1:1 (v/v) HCl/water. It is then filtered off and cured in an air oven at 75 °C for 24 h. The same procedure was adopted for the synthesis of AUF-II and AUF-III terpolymer resins involving 1:1:3 and 2:3:5 molar proportions, respectively, with the monomers chosen for the preparation of the AUF-I terpolymer. The mechanism of the synthesis of terpolymer is shown in Scheme 1.

### Spectral analyses

The FTIR spectrum of the AUF-I terpolymer had been scanned in KBr pellets on a Bruker (Model Tensor 27) spectrophotometer, and the proton NMR spectrum of the



**Scheme 1** Reaction mechanism for the synthesis of AUF terpolymer

terpolymer resin was recorded in DMSO- $d_6$  solvent using Bruker 400 MHz.  $^{13}\text{C}$  NMR spectrum was recorded using Bruker 400 MHz.

### GPC and SEM analyses

The average molecular weights of the AUF terpolymers I, II, and III were determined by gel permeation chromatography (GPC) using Shimadzu (Model LC20AD) in DMSO column. The surface analysis of the AUF-I terpolymer resin was examined by scanning electron microscope (SEM) using Hitachi (Model S-3000H) at  $5000\times$  magnification.

### Thermogravimetric analysis (TGA)

The modes of thermal degradation of the terpolymers AUF-I, II, and III were analyzed using thermogravimetric analyzer (TA Instruments Model SDT Q600) at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  in a static nitrogen atmosphere. Based on the results obtained, the degradation pattern, activation energy ( $E_a$ ), order of the reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), and frequency factor ( $Z$ ) were calculated by FC and SW methods. The thermal degradation model for the decomposition reaction was proposed using PD method.

## Antimicrobial screening

Antimicrobial activity was tested by the filter paper disk diffusion technique involving the cultures of the selected organisms for 24 h [20]. The test solutions of AUF-I, II, and III terpolymers were prepared in sterile dimethyl sulphoxide solvent for the study. The compounds were tested at different concentrations ranging from 50 to 1000 ppm to find out the minimum concentration of the sample required to inhibit the microbial growth. Ciprofloxacin (100  $\mu\text{g}/\text{mL}$ ) was taken as the standard for antibacterial activity. The organisms were seeded into sterile nutrient agar medium by mixing 1 mL of inoculum with 20 mL sterile-melted nutrient agar kept at 48–50 °C in a sterile petri dish. The medium was allowed to solidify first. Then, the test solutions, the standard drugs as well as the blank were impregnated in Whatmann filter paper disks and placed on the solidified medium in the petri dish and left undisturbed for 2 h at room temperature. The petri dishes were then incubated at 37 °C for 24 h, and the zone of inhibition for the test samples, standard, and the control (DMSO) was measured.

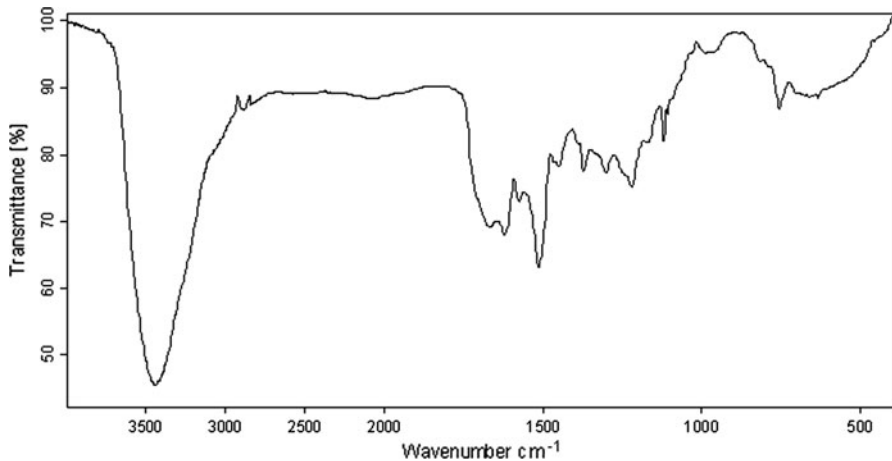
Sterile yeast nitrogen base (HI Media) with 2% agar was inoculated by a rotating swab (soaked in standard inoculum suspension) over the surface of the media. Fluconazole (100 mcg/ml) was taken as the standard for antifungal activity. The test solution impregnated disks were placed on the agar and incubated at 37 °C for 18 h. The zone of inhibition was measured by measuring the minimum dimension of the zone of fungal growth around the filter paper disk.

## Results and discussion

The AUF terpolymer resins (I, II, and III) were soluble in solvents like *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and aqueous NaOH and KOH solutions, whereas the resins were insoluble in benzene, xylene, toluene, and water.

### FTIR spectra

The FTIR spectrum of the AUF-I terpolymer resin is shown in Fig. 1, and the spectral data are presented in Table 1. A strong band at 1293.1  $\text{cm}^{-1}$  is due to (C–N) stretching of (Ar–NH<sub>2</sub>) [21]. A broad band appeared in the region 3442.5  $\text{cm}^{-1}$  may be assigned to the hydroxyl group of –COOH [21, 22]. A peak appeared at 2884.7  $\text{cm}^{-1}$  may be assigned to aromatic ring stretching modes [23]. The 1,2,3,5 tetra substitution of aromatic benzene ring by sharp, medium/weak absorption bands appeared between 1200 and 800  $\text{cm}^{-1}$  [23]. The band appeared at 1622.7  $\text{cm}^{-1}$  may be due to –C=O (carboxylic ketone and amide moiety) stretching vibrations [24]. The presence of –NH bridge in the terpolymer is confirmed by the absorption band at 3442.5  $\text{cm}^{-1}$  [21]. This band seems to be merged with a broad band of –OH of –COOH group. A band appeared at 2837.6  $\text{cm}^{-1}$  may be attributed to –CH<sub>2</sub> linkage present in the terpolymer resin [25].



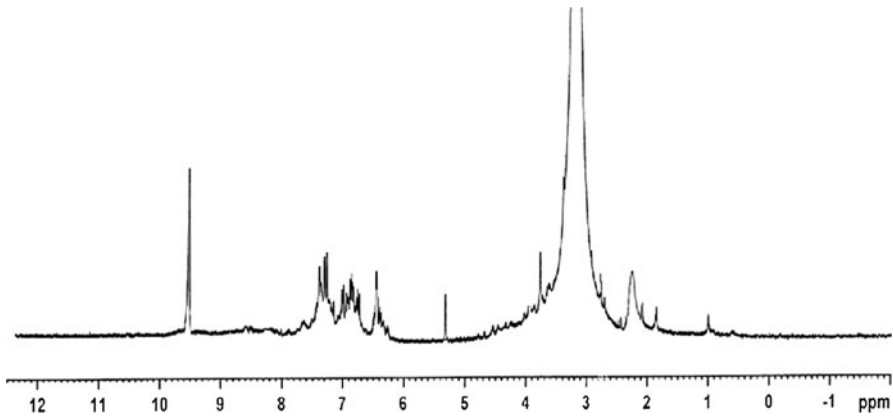
**Fig. 1** FTIR of AUF-I terpolymer

**Table 1** FTIR spectral data of AUF-I terpolymer resin

Vibrational mode	Frequency (cm <sup>-1</sup> )	
	Reported	Observed
-OH of -COOH group	3500–3200	3442.5
Aromatic ring stretching (C-H)	2700–3000	2884.7
Methylene(-CH <sub>2</sub> ) stretching	3000–2830	2837.6
>C=O stretching (carboxylic ketone and amide moiety)	1690–1620	1622.7
1,2,3,5-substituted benzene ring	1200–800	1121.5 and 990.4
(C-N) stretching of Ar-NH <sub>2</sub>	1200–1300	1293.1
-NH bridge	3500–3200	3442.5

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of AUF-I terpolymer resin is depicted in Fig. 2, and the spectral data are presented in Table 2. The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of the literature [7, 10, 23]. The medium singlet at 2.2 ( $\delta$ ) ppm may be due to methylene proton of Ar-CH<sub>2</sub> bridge. A singlet observed in the region 3.62 ( $\delta$ ) ppm is due to methylene proton of Ar-CH<sub>2</sub>-N moiety. A singlet observed in the region 5.31 ( $\delta$ ) ppm may be attributed to the protons in -NH linkage. The signal at 9.71 ( $\delta$ ) ppm is assigned to the -OH of Ar-COOH indicates the intramolecular hydrogen bonding between -OH of Ar-COOH and -NH<sub>2</sub> of Ar-NH<sub>2</sub> groups in the terpolymer resin. The signals in the region at 6.5–8.3 ( $\delta$ ) ppm may be assigned to the protons in the aromatic ring.



**Fig. 2**  $^1\text{H}$  NMR of AUF-I terpolymer

**Table 2**  $^1\text{H}$  NMR spectral data of AUF-I terpolymer resin

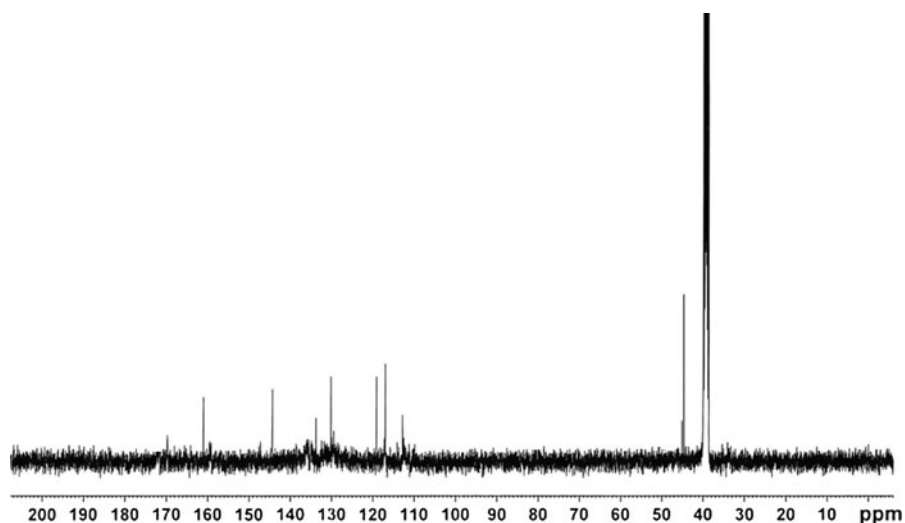
Nature of the proton assigned in the spectrum	Expected chemical shift ( $\delta$ ) ppm	Observed chemical shift ( $\delta$ ) ppm
Aromatic protons (Ar-H)	6.5–8.5	6.5–8.3
Proton of –OH of –COOH group involved intramolecular hydrogen bonding with proton of –NH <sub>2</sub> in Ar–NH <sub>2</sub>	8.00–12.00	9.7
Methylenic proton of Ar–CH <sub>2</sub> –N moiety	3.00–3.7	3.6
Proton of –NH bridge	5.00–8.00	5.1
Ar–CH <sub>2</sub> moiety	2.00–3.00	2.2

### $^{13}\text{C}$ NMR spectra

The  $^{13}\text{C}$  NMR spectrum of AUF-I resin is shown in Fig. 3, and the peak positions are assigned according to the literature [26]. The  $^{13}\text{C}$  NMR spectrum shows the corresponding peaks at 110.1, 145.3, 128.4, 130.5, 128.1, and 133.8 ppm with respect to C<sub>1</sub> to C<sub>6</sub> of the aromatic ring. Peak at 169.6 ppm may be due to the –C=O of carboxylic acid and amide moiety. The peak appeared at 43.4 ppm is assigned to the –CH<sub>2</sub> bridge in the terpolymer. From the spectral analyses, (FTIR and NMR) the structure of the AUF-I is proposed.

### GPC and SEM analyses

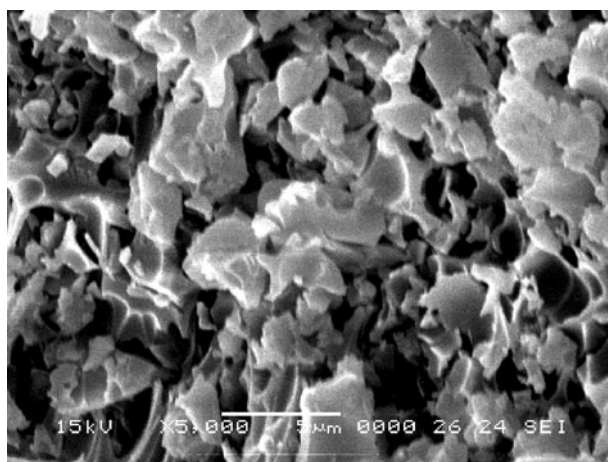
The average molecular weights of the AUF terpolymers I, II, and III were found to be around 2900. The GPC data are presented in Table 3. The SEM image of the AUF-I at 5000 $\times$  magnification is shown in Fig. 4. The image is a bulbous and honey-bee cluster. The resin is less close packed with high porosity on the surface. Further, the surface of the resin has deep pits with an amorphous character.



**Fig. 3**  $^{13}\text{C}$  NMR of AUF-I terpolymer

**Table 3** Average molecular weights of AUF terpolymer resin

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	Polydispersity ( $\overline{M}_w/\overline{M}_n$ )
AUF-I	2801	2845	2830	1.015
AUF-II	2925	2965	2910	1.013
AUF-III	2950	2980	2955	1.010

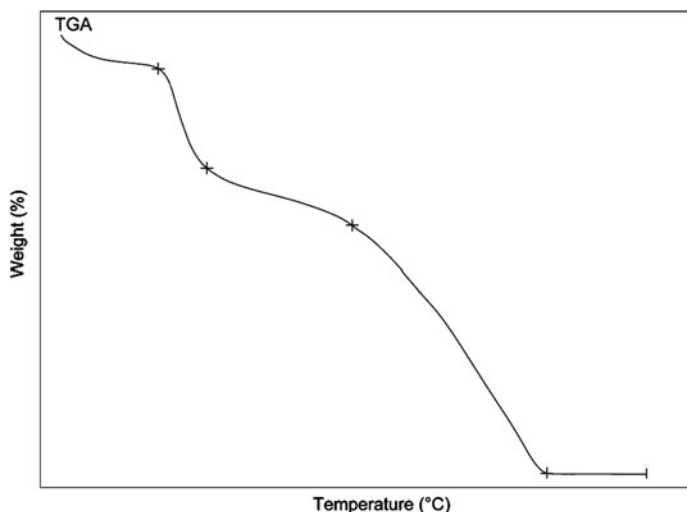


**Fig. 4** SEM image of AUF-I terpolymer

## TGA

Thermogravimetric technique is found to be a valuable method to evaluate the thermal decomposition pattern of the polymer. Thermogram of the AUF-I





**Fig. 5** TGA of AUF-I terpolymer

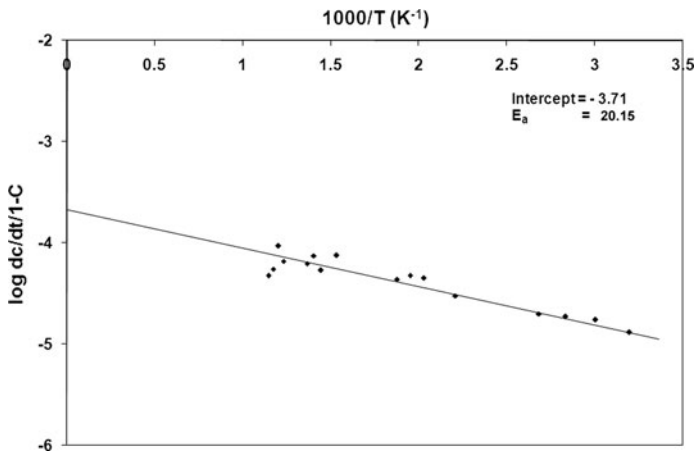
terpolymer is depicted in Fig. 5, and the data are presented in Table 4. The AUF-I resin exhibits the decomposition involving three stages. The first stage decomposition begins at 160 °C with a weight loss of 22.25% (calc. 21.44%) of the resin and ends at 270 °C which may be due to the removal of carboxylic group present in the terpolymer. In the second stage, the decomposition starts at 270 °C with 14.73% of weight loss (calc. 14.56%) and ends up at 510 °C, and this loss may be due to the elimination of  $-\text{NH}_2$  and  $-\text{CH}_2$  groups attached to the aromatic nucleus. The final stage of the decomposition starts at 510 °C, and the complete decomposition of the terpolymer takes place at 775 °C involving 58.01% (calc. 59.32%) of weight loss of the remaining terpolymer resin.

- (i)  $[\text{AUF}]_n \xrightarrow{160^\circ\text{C}} [\text{AUF}]_n + n\text{H}_2\text{O}$
- (ii)  $[\text{AUF}]_n \xrightarrow{160-270^\circ\text{C}} [\text{AUF}]_n + \text{loss of COOH as CO}_2$
- (iii)  $[\text{AUF}]_n \xrightarrow{270-510^\circ\text{C}} [\text{AU}]_n + \text{loss of } -\text{NH}_2 \text{ and } -\text{CH}_2$
- (iv)  $[\text{AU}]_n \xrightarrow{510-775^\circ\text{C}} \text{Complete degradation}$

**Table 4** Thermal behavior data of AUF-I terpolymer resin

Sample	Percentage of weight loss at various temperature (°C)					Decomposition temperature range (°C)	$T_{\text{max}}^{\text{a}}$ (°C)	$T_{50}^{\text{b}}$ (°C)
	350	450	550	650	750			
AUF-I terpolymer	34.5	39.5	51.8	70.2	92.0	169–780	775.3	530.2

<sup>a</sup> Maximum decomposition temperature; <sup>b</sup> Temperature at 50% weight loss



**Fig. 6** SW plot of AUF-I terpolymer

From the TG data, the following methods have been used to calculate the various kinetic and thermodynamic parameters and to propose the thermal degradation model.

#### FC method

The activation energy ( $E_a$ ) and the order of reaction ( $n$ ) for the terpolymer decomposition were calculated using the following expression proposed by FC.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \frac{-E_a}{2.303R} \left\langle \frac{\Delta(1/T)}{\Delta \log W_r} \right\rangle + n$$

where,  $dw/dt$  is the rate of change of weight with time;  $W_r = W_c - W$ , where  $W_c$  is the weight loss at the completion of reaction or at definite time and  $W$  is the total weight loss up to time  $t$ ;  $n$  is the order of the reaction,  $T$  and  $R$  are the temperature and the gas constant, respectively.

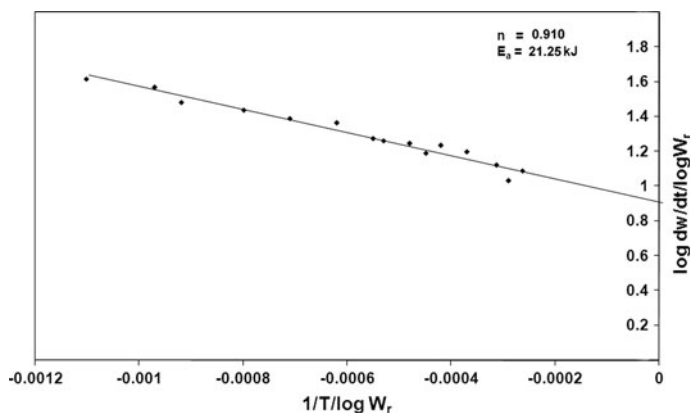
Hence, a plot of  $\Delta \log(dw/dt)/\Delta \log W_r$  versus  $\Delta(1/T)/\Delta \log W_r$  gives a slope of  $-E_a/2.303R$  with an intercept equals to  $n$  on the  $y$ -axis where  $x = 0$ .

#### SW method

The following expression given by SW was used to determine the activation energy ( $E_a$ ), entropy change ( $\Delta S$ ), and free energy change ( $\Delta F$ ).

$$\frac{\log(dc/dt)}{(1-C)} = \frac{\log \alpha'}{\beta} = \frac{E_a}{2.303RT}$$

where  $\beta$  is the linear heating rate. The graph of  $\log dc/dt/(1-C)$  versus  $1000/T$  gives a slope of  $-E_a/2.303R$  with an intercept on the  $y$ -axis where  $x = 0$ .



**Fig. 7** FC plot of AUF-I terpolymer

A representative thermal activation energy plot of SW and FC method for the AUF-I terpolymer resin is shown in Figs. 6 and 7, respectively. The expressions shown in Table 5 are used to calculate the entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), and frequency factor ( $Z$ ).

Using the FC and SW methods, the kinetic and thermodynamic parameters were calculated and presented in the Table 6. The values obtained for all the terpolymer resins suggest that the decomposition takes place in the same mode for AUF-I, II, and III. From the results, it is obvious that the activation energy calculated from FC and SW methods is in good agreement with each other for all the terpolymers. The thermal stabilities of the terpolymer resins were predicted to be high due to the low activation energies. The linear structure and the presence of intramolecular hydrogen bonding in the aromatic ring further confirm the higher thermal stability of the resin. The low frequency factor value obtained predicts that the decomposition reaction is slow [7, 27]. This is further supported by the negative entropy change. However, a few points do not fall on the straight line in the graphs which shows that the reaction does not obey the exact first-order kinetics.

#### PD method

PD method is a mathematical tool to propose the mechanistic model for a solid-state reaction from thermo-analytical curves obtained isothermally or non-isothermally. In general, the correlation coefficient of the plot for different mechanism functions was regarded as a standard procedure for determining the reaction mechanism [28].

$g'(\alpha) = -E_a/RT$  is one of the expressions used to propose the model for the thermal decomposition. Where  $g'(\alpha)$  is the integral function of conversion  $\alpha$ . The functions of  $g'(\alpha)$  frequently used are listed in Table 7.

The activation energies calculated for AUF terpolymers according to PD method are presented in Table 8. It is identified that the activation energy values of AUF terpolymers calculated by the above expression coincide with the reaction

**Table 5** Formulae for calculating kinetic parameters

	(i) Entropy change ( $\Delta S$ )	
	Intercept = $\log \frac{KR}{h\Phi E} + \frac{\Delta S}{2.303R}$	(1)
	where $K = 1.3806 \times 10^{-16}$ erg/deg/mol,	
	$R = 1.987$ cal/deg/mol (8.314 J/K/Mol),	
	$h = 6.625 \times 10^{-27}$ erg s,	
	$\Phi = 0.166$ ,	
	$\Delta S$ = change in entropy,	
	$E$ = activation energy from graph,	
	(ii) Free energy change ( $\Delta F$ )	
	$\Delta F = \Delta H - T\Delta S$	(2)
	where $\Delta H$ = enthalpy change = activation energy,	
	$T$ = temperature in K,	
	$\Delta S$ = from Eq. 1	
	(iii) Frequency factor ( $Z$ )	
	$B_{2/3} = \frac{\log Z E_a}{R\Phi}$	(3)
	$B_{2/3} = \log 3 + \log[1 - 3\sqrt{1 - \alpha}] - \log p(x)$	(4)
	where $Z$ = frequency factor,	
	$B$ = calculated from Eq. 4,	
	$\log p(x)$ = calculated from Doyle's table corresponding to activation energy	
	$\alpha$ = degree of transformation ( $\alpha = W/W_c$ )	
	(iv) Apparent entropy ( $S^*$ )	
	$S^* = 2.303R \log \frac{Zh}{RT^*}$	(5)
	$Z$ = from Eq. 3	
	$T^*$ = half decomposition temperature	

**Table 6** Thermal and kinetic parameters of AUF terpolymer resins

Samples	Half decomposition temperature, $T_h/K$	Activation energy, $E_a/kJ/mol$		Entropy change, $\Delta S/J$	Free energy, $\Delta F/kJ$	Frequency factor, $Z/s^{-1}$	Apparent entropy, $S^*/J$	Order of reaction, $n$
		SW	FC					
AUF-I	530.2	20.15	21.25	-3.61	21.09	560.03	-20.18	0.910
AUF-II	535.3	20.01	21.32	-3.55	20.01	550.38	-19.86	0.921
AUF-III	540.5	18.92	20.15	-3.48	25.36	546.29	-21.02	0.989

mechanism number 4 proposed by PD [18]. This is comparable to  $E_a$  calculated by FC and SW methods. Hence, the AUF terpolymers decomposition kinetic model follows a phase boundary (contracting cylinder) mechanism.

### Antimicrobial screening

The results of antimicrobial screening of the AUF-I, II, and III terpolymer resins are presented in Table 9 for antibacterial and Table 10 for antifungal studies.

**Table 7** PD expressions for solid-state reaction mechanism

Mechanism	$g'(\alpha)$	Reaction mechanism model
1	$\ln\alpha$	Power law
2	$2\ln\alpha$	Power law
3	$\ln[1 - (1 - \alpha)^{1/3}]$	Phase boundary (contracting sphere)
4	$\ln[1 - (1 - \alpha)^{1/2}]$	Phase boundary (contracting cylinder)
5	$1/2\ln[-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami–Erofeev nuclei growth)
6	$1/3\ln[-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami–Erofeev nuclei growth)
7	$1/4\ln[-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami–Erofeev nuclei growth)
8	$\ln[(1 - \alpha)\ln(1 - \alpha) + \alpha]$	Valensi, 2-dimensional diffusion
9	$2\ln[1 - (1 - \alpha)^{1/3}]$	Jander, 3-dimensional diffusion
10	$\ln[1 - 2/3\alpha - (1 - \alpha)^{2/3}]$	Brounshtein–Ginstling, 3-dimensional diffusion

**Table 8** Activation energies of AUF resins based on PD method

Reaction mechanism	$E_a$ (kJ/mol)		
	AUF-I	AUF-II	AUF-III
1	60.1	62.8	59.3
2	82.2	88.9	78.5
3	110.3	94.3	101.4
4	<b>21.1</b>	<b>20.9</b>	<b>21.8</b>
5	195.6	188.3	196.2
6	52.2	49.6	48.8
7	178.2	181.0	175.9
8	36.5	30.7	32.3
9	189.3	188.5	190.1
10	80.2	78.4	81.1

The values indicated in bold is closest to the  $E_a$  value calculated by FC and SW methods

**Table 9** Antibacterial activity of the AUF terpolymer resins

Compound	Zone of inhibition (mm)			
	<i>E. coli</i>	<i>Klebseilla</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>
AUF-I	11	15	11	08
AUF-II	11	12	10	07
AUF-III	12	13	12	07
Standard (Ciprofloxacin)	15	20	15	12
Control (DMSO)	–	–	–	–

**Table 10** Antifungal activity of the AUF terpolymer resins

Compound	Zone of inhibition (mm)					
	<i>A. flavus</i>	<i>A. niger</i>	<i>Penicillium species</i>	<i>C. albicans</i>	<i>C. neoformans</i>	<i>Mucor species</i>
AUF-I	13	12	13	24	16	23
AUF-II	14	13	08	24	14	20
AUF-III	15	15	10	22	16	20
Standard (Fluconazole)	20	21	19	21	18	22
Control (DMSO)	–	–	–	–	–	–

### Antibacterial activity

A commendable activity was obtained for the AUF terpolymers against *E. coli* bacterium. *E. coli*, a gram-negative rod-shaped bacterium which affects the urinary track in humans. *Klebsiella* is a genus of non-motile, gram-negative bacterium causes a wide range of diseases, notably pneumonia, septicemia, and soft tissue infections. The results showed a moderate inhibition against *Klebsiella*. *S. aureus*, a gram-positive and spherical bacterium leads to life-threatening diseases like pneumonia, osteomyelitis, endocarditis, and toxic shock syndrome. From the experimental results, the resins were found to have good action against *S. aureus* species. The AUF resins showed a moderate activity against *P. aeruginosa*, a common bacterium which causes diseases like pulmonary tract and urinary tract burns and wounds in animals and human beings.

### Antifungal activity

The antifungal activities of the AUF terpolymer resins also provide remarkable soaring results against the chosen fungal strains. *C. albicans* is a diploid fungus and a causal agent of opportunistic oral and genital infections in humans and also emerged as an important cause of morbidity and mortality in immuno-compromised patients. The AUF resins performed a very good inhibition against *C. albicans* over the standard. The resins showed good inhibition against *Mucor species*, a filamentous fungus which causes septic arthritis, renal infections, and pulmonary infections. The resin obtained a moderate activity against *A. flavus*, a mold type fungal strain which may invade arteries of the lung or brain to cause infections and also produces a toxin. *A. niger* is one of the most common causes for otomycosis. The resins found to have moderate inhibition for *A. niger*. *Penicillium species* causes infection in humans, and the resulting disease is known generically as penicilliosis. The resins had moderate activity against *Penicillium species*. *C. neoformans* is an encapsulated yeast-like fungus that can live in both plants and animals cause lung infection. The resins had noticeable inhibition effect against this fungal strain. These noteworthy results can be effectively defended due to the presence of  $-\text{NH}_2$ ,  $-\text{OH}$  groups, and amide moiety in the terpolymer. It is proposed

that the factors such as solubility, conductivity, dipole moment, and cell permeability may also contribute for the increased antimicrobial activity [29].

## Conclusion

Terpolymers AUF-I, II, and III were synthesized from anthranilic acid and urea with formaldehyde using solution polymerization technique. The structure of the resin was proposed by spectral analyses. AUF terpolymer resins were thermally stable even at high temperature. The order of the reaction for thermal decomposition was nearly one, and the activation energy was found to be less for the decomposition. Further, the thermal decomposition rate was slow. The AUF terpolymers establish a phase boundary (contracting cylinder) decomposition model. However, the synthesized terpolymer resins were found to be a potent antimicrobial agent for the chosen microbes.

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