
SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF THIOUREA CONTAINING POLYMERS

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Abstract

N-acryloyl-N-phenylthiourea (APTU) is synthesized by reacting acryloyl chloride with phenylthiourea in the presence of triethylamine (TEA) as a base and characterized by FT-IR, ¹H-NMR and mass spectra. The acrylic polymers from different feed ratios of ethylacrylate (EA), methylmethacrylate (MMA), styrene (St) and APTU have been prepared by emulsion polymerization in water containing sodium lauryl sulfate as a surfactant and ammonium persulfate as a water-soluble radical initiator. The polymers are characterized by FT-IR spectroscopy. The solubility is tested in various polar and non-polar solvents. The molecular weight and polydispersity are determined using gel permeation chromatography (GPC). Thermal behavior of the prepared polymers is also investigated by thermogravimetric analysis (TGA). The polymers are tested for their antimicrobial activities against selected microorganisms.

Keywords: Thiourea; acrylic polymers; Thermal properties; activation energy; Antimicrobial activity

1. Introduction

In recent years some comprehensive work has been published on functional monomers and their polymers [1–3]. Pazhanisamy and coworkers synthesized copolymers of N-cyclohexylacrylamide/ n-butyl acrylate [4]. M. G. Patel et al synthesized 2,4-Dichlorophenyl-acrylate monomer from 2,4-Dichlorophenol and acryloyl chloride. Homo- and copolymers with 2-Hydroxyethylmethacrylate were synthesized by free radical solution polymerization [5]. H. J. Patel et al synthesized the acrylate monomer, 7-acryloyloxy-4-methyl coumarin and its homo- and copolymers with vinyl acetate [6]. Considerable efforts have been made to study the thermal characteristics of polymers using thermogravimetric analysis (TGA), because it analyzes the degradation response and determines the upper temperature limit of use and durability [5, 7, 8].

The antimicrobial property of the polymers plays an important role for many of its applications. Contamination by microorganisms is of great concern in many fields, particularly in medical devices, drugs, hospital surfaces/furniture, dental restoration and surgery equipment, health care products and hygienic applications, water purification systems, textiles, food packaging and storage, major or domestic appliances, aeronautic, etc. Infectious diseases kill worldwide more people than any other single cause. Mainly, the infections are produced by touching, eating, drinking or breathing something that contains a germ. Generally, these infections are

combated with specific antimicrobial systems. Therefore, the use of polymeric materials with antimicrobial properties gains an increasing interest from both academic and industrial point of view [9, 10].

In the present investigation we report the synthesis and characterization of monomer N-acryloyl-N-phenylthiourea as well as synthesis of acrylic polymers using different feed ratios with styrene (St), metylmethacrylate (MMA) and ethyl acrylate (EA). The molecular weight, weight distribution and thermal properties of resulting polymers have been investigated. The prepared polymers are also tested for their antimicrobial activity against microorganisms such as gram-positive bacteria (*Bacillus subtilis* and *Micrococcus luteus*), gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*), fungi (*Aspergillus niger*) and yeast (*Candida albicans*).

2. Experimental part

2.1. Materials

Acryloyl chloride, aniline, ammoniumthiocyanate and polyvinylalcohol (PVA) are purchased from Sigma-Aldrich Company Ltd, England. Ethylacrylate (EA), methylmethacrylate (MMA) and styrene (St) are obtained from EIF chem. (ATO) company, France. Sodiumlaurylsulfate (SLS), ammonium persulfate and other chemicals are obtained from El-Naser pharmaceutical chemical company, Egypt. Deionised water is used throughout the work. All chemicals are used as received without further purification.

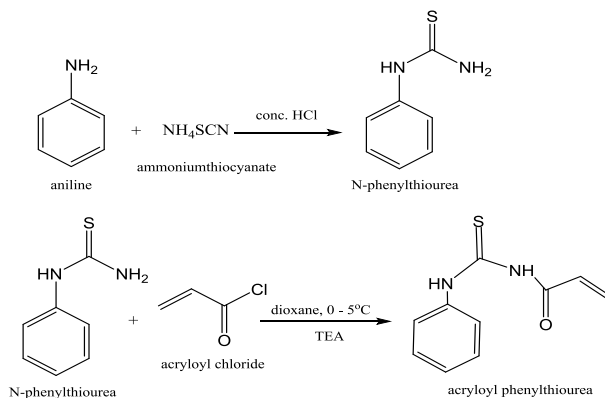
2.2. Synthesis of phenyl Thiourea (PTU): [11]

A solution of aniline (0.25 mol, 23.25 g) in 25 ml. of conc. HCl acid placed in a round-bottom flask containing a magnetic stirrer is warmed. To this solution, a saturated solution of ammonium thiocyanate (0.25 mol, 19 g) in 50 ml warm water is added slowly with constant stirring. The reaction mixture is refluxed in a water bath until the solution gets turbid. It is allowed to cool and poured in cooled water. The obtained white crystals are filtered, washed with water and recrystallised from aqueous ethanol. The product is examined by IR, ¹H-NMR and Mass spectra.

2.3. Synthesis of N-acryloyl-N-phenylthiourea:(APTU)

To a mixture of PTU (0.1 mol, 15.2 g) and triethylamine (few drops) in 120 mL of Dioxan acryloyl chloride (0.1mol, 8.5 ml (excess)) dissolved in 10 mL Dioxan is added dropwise under nitrogen atmosphere in an ice bath. After the mixture is allowed to warm to room temperature, it is stirred for 24 h. Dioxan and remaining acryloyl chloride are then evaporated under vacuum. Water is added to the residue, followed by two extractions with chloroform. The combined organic phases are

washed with HCl (5 wt %) to remove the remaining triethylamine followed by washing three times with water. After drying on magnesium sulfate, filtration and removal of the solvent, the target compound as semi-oil powder is dried under vacuum, to remove the traces of acrylic acid. The product is examined by IR (fig.1), $^1\text{H-NMR}$ (fig.2) and Mass (fig.3) spectroscopic techniques. The reaction scheme for the synthesis of APTU is shown in Scheme 1.



Scheme 1: Synthesis of acryloyl phenylthiourea (APTU)

2.4. Polymer synthesis

The acrylic emulsion polymerization is run using the semi-continuous process. A typical recipe for the preparation is given in Table 1. EA (24 g), MMA (1 g), St (variable), APTU (variable) and emulsifier (SLS, 0.8 g) are dispersed in 30 g of 1% PVA solution (0.3 g PVA in 29.7 g deionized water) to get pre-emulsion by fast agitation. To a 500 mL five-necked round-bottom flask equipped with a reflux condenser, a thermometer, a magnetic stirring bar and two separate feed streams 15 g of 1% PVA solution (0.15 g PVA in 14.85 g deionized water), 0.5 g ammonium hydroxide (25%), 20% of the ammonium persulfate initiator weight (0.096 g) and 10% of the pre-emulsion are charged and the agitation is maintained at 200 rpm. Initially the reaction flask purged with nitrogen for 15 min and immersed in a water bath. When the temperature is raised to 80°C , the remaining pre-emulsion and the solution of the remaining initiator (0.384 g in 5.22 g deionized water) are dropped into the flask in 3 h. when the addition is complete, The reaction is kept at 80°C for a further 2 h to ensure complete monomer conversion and then cooled. Part of the emulsion is diluted with water and the polymers are precipitated into excess acetone and extracted with ethanol for 12 h to remove all traces of water, surfactant, and residual monomers before dried under reduced pressure at room temperature for 24h. The generalized structure of the produced polymer is represented in Fig. 4. The produced polymers are characterized by IR (Fig. 5.) as well as the thermal properties.

2.5. Solid content and monomer conversion (%)

Total solid content (TSC) and monomer conversion (MC) are determined by gravimetric analysis method from equations 1 and 2, respectively. The results are given in table 6.

$$\text{TSC (\%)} = \frac{\text{weight of dry latex}}{\text{weight of latex}} \times 100 \quad (1)$$

$$\text{MC (\%)} = \frac{\text{weight of dry latex}}{\text{total weight of monomers}} \times 100 \quad (2)$$

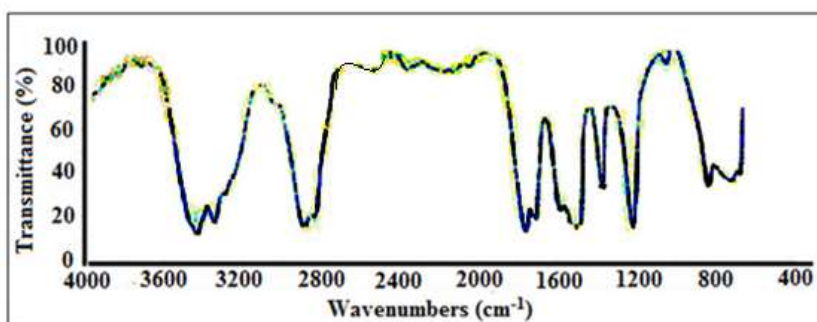


Fig.1: IR spectra of APTU

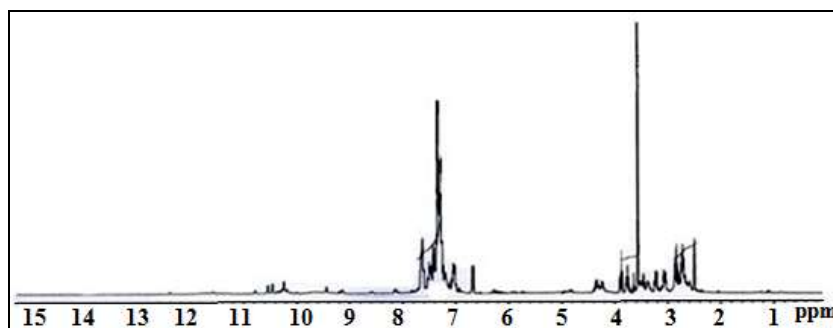


Fig.2: ¹H NMR spectra of APTU

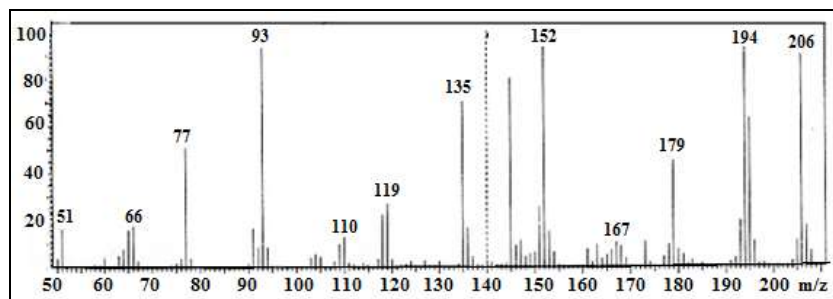


Fig.3: Mass spectra of APTU

2.6. Solubility studies [12]

Solubility of the synthesised monomer and the produced polymers is tested in various polar and non-polar solvents. About 5–10 mg of the sample is added to about 2 ml of the solvent in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers is noted after 24 h.

Table (1): Polymerization recipe at 80 °C

	P ₀	P ₁	P ₂	P ₃	P ₄
Reaction vessel charge					
Deionized water (g)	14.85	14.85	14.85	14.85	14.85
Protective colloid (PVA) (g)	0.15	0.15	0.15	0.15	0.15
Ammonium persulfate(g)	0.096	0.096	0.096	0.096	0.096
ammonium hydroxide(25%)(g)	0.5	0.5	0.5	0.5	0.5
Pre-emulsion					
EA(g)	24	24	24	24	24
St (g)	23	22.52	22.04	21.56	21.08
APTU (g)	0	0.48	0.96	1.44	1.92
MMA (g)	1	1	1	1	1
SLS (g)	0.8	0.8	0.8	0.8	0.8
Deionized water (g)	29.7	29.7	29.7	29.7	29.7
Protective colloid (PVA) (g)	0.3	0.3	0.3	0.3	0.3
Initiator solution					
Deionized water (g)	5.22	5.22	5.22	5.22	5.22
Ammonium persulfate(g)	0.384	0.384	0.384	0.384	0.384

The amount of APTU used in emulsion P₀ – P₄ is 0, 1, 2, 3, 4 wt%, respectively based on monomers.

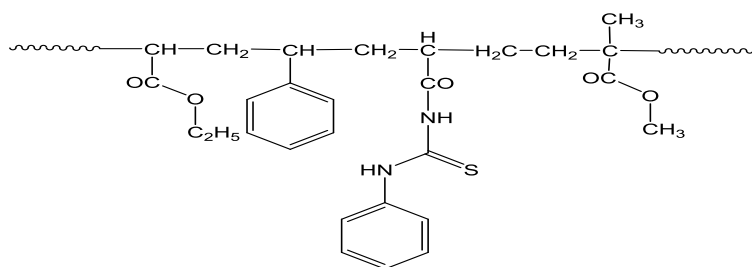


Fig.4: Molecular structure of acrylic copolymers containing thiourea moiety

2.7. Measurements

IR spectra (4000–400 cm⁻¹) of the monomer and polymers are recorded on Nicolet 400D FT-IR spectrometer using KBr pellets. The ¹H-NMR spectra are recorded in DMSO-d₆ at (300) MHz on a Varian Mercury VX-300 NMR (Tokyo, japan) spectrometer (δ, ppm). Mass spectrum is recorded the aid of a Shimadzu QP-2010 (Tokyo, Japan) GC-Mass instrument. The number average and weight average molecular weight of the polymers are determined by WATERS 410- gel permeation chromatography using polystyrene as standard and THF is used as eluent. Thermal

properties were examined using simultaneous DSC-TGA (USA), Q600-SDT System in the temperature range 25–600°C at a scanning rate of 10 °C min⁻¹ under nitrogen atmosphere. Elemental analyses are carried out by the micro-analytical unit at the national Research center, Giza, Egypt.

2.8. Antimicrobial activity

The obtained polymers are evaluated for their antimicrobial activity using the agar diffusion technique. The tested organisms are Gram negative bacteria (*Pseudomonas aeruginosa* ATCC 10145 and *Escherichia coli* ATCC 23282), Gram positive bacteria (*Bacillus subtilis* ATCC 6633 and *Micrococcus luteus* ATCC 25922), Yeast (*Candida albicans* IMRU 3669) and Filamentous Fungus (*Aspergillus niger* ATCC 16404). The bacteria and yeast strains are grown on nutrient agar while the fungal strains are grown on Czapek's Dox agar medium.

In the agar diffusion method [13, 14], the solid polymers dissolved in dimethylformamide (DMF) at a concentration of 1 mg/ml solution are used. Agar media seeded with the tested microorganism are poured in petri dishes and allowed to solidify, and then holes of about 7 mm were punched in the agar using a sterile cork porrer. A 50 µl volume of the dissolved polymer are added to the pores and polymer free DMF is included as solvent control. Plates are allowed to stand in a refrigerator for two hours before incubation to allow the tested polymer to diffuse through the agar. The plates containing bacterial cultures are incubated at 37 °C for 24h and those containing yeasts and fungus are incubated at 30 °C for 48h. After incubation, the diameter of inhibition zone (mm) is measured. All examinations are done in duplicates and the data are the average of the obtained results.

The negative control is DMF showed no antimicrobial activity against the tested microorganisms, and the positive control is Erythromycin for bacteria and Metronidazole for yeast and fungus.

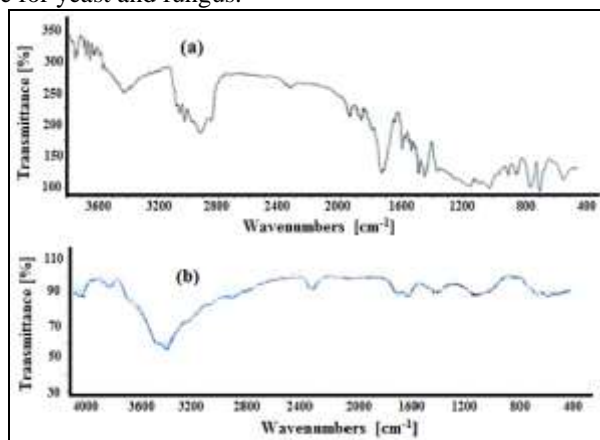


Fig.5: IR spectra of (a) P₀ and (b) APTU acrylic copolymer

3. Results and discussion

3.1 Synthesis and characterization of N-acryloyl-N-phenylthiourea:(APTU)

N-acryloyl-N-phenylthiourea (APTU) is prepared from the aromatic amine (aniline) which in the presence of ammonium thiocyanate forms 1-phenylthiourea in acidic medium. This phenylthiourea is reacted with acryloyl chloride to give target compound as semi-oil powder (scheme 1). The details of preparation are described in experimental part. The synthesized compounds are characterized by elemental analysis, IR, $^1\text{H-NMR}$ and Mass spectral studies as shown below. All the physical and analytical data are given in table 2.

Table (2): Physicochemical Parameters

Compound	Yield %	Molecular Formula	m.p (°C)	Elemental analysis					
				% C		% H		% N	
				Calcd.	found	Calcd.	found	Calcd.	found
phenylthiourea	87	$\text{C}_7\text{H}_8\text{N}_2\text{S}$	152	55.24	55.32	5.30	5.32	18.40	18.40
APTU	50.4	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}$	oily	58.23	57.9	4.89	4.4	13.58	13.23

Spectral data of synthesized thioureas:

Phenyl thioure: IR (KBr, cm^{-1}): 3430, 3320 (NH), 3016 (C-H, Aromatic), 1538 (C=C), 1260 (N-CS-N); **$^1\text{H-NMR}$ (DMSO, δ ppm):** 9.76 (s, 1H, NH), 6.5 (bs, 2H, CSNH_2), 6.97-7.5(m, 4H, ArH); **mass (m/z):** calculated for $\text{C}_7\text{H}_8\text{N}_2\text{S}$: 152.04; found: 152.

N-acryloyl-N-phenylthiourea: IR (KBr, cm^{-1}): 3538, 3434 (NH), 2932 (C-H, Aliphatic), 1694 (CONH), 1636 ($\text{CH}_2=\text{CH}-$), 1254 (N-CS-N); **$^1\text{H-NMR}$ (DMSO, δ ppm) :** 12.4 (s, 1H, ArNHCS), 10.2(s, 1H, CNHCS), 7.01-7.46(m, 4H, ArH), 6.65-6.69 (m, 3H, $\text{CH}_2=\text{CH}$); **mass (m/z):** calculated for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}$: 206.05; found: 205.95. Figs. 1, 2 and 3 represent the spectral analysis of APTU.

3.2. Solubility of APTU monomer

The APTU monomer is easily soluble in acetone, dioxane, tetrahydrofuran (THF), Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), ethyl acetate, methylene chloride, chloroform, diethylether and hydroxyl group containing solvents such as methanol, ethanol, and isopropanol but insoluble in distilled water, petroleum ether, and hydrocarbons (e.g., n- hexane, benzene, toluene and xylene). The solubility test of APTU monomer clearly shows that there is wide possibility for using different solvents for the synthesized monomer to be polymerized in solution.

3.3. Synthesis and characterization of polymers

The acrylic polymers from different feed ratios of ethylacrylate (EA), methylmethacrylate (MMA), styrene (St) and APTU have been prepared by

emulsion polymerization in water using ammonium persulfate as a water-soluble radical initiator and sodium lauryl sulfate as a surfactant.

3.3.1. Solubility and FTIR analysis of polymers

The emulsion copolymers basically have low solubility or do not have any solubility in organic solvents at all. The acrylic polymers, which have been synthesized from St, EA and MMA with or without APTU are sparingly soluble by heating in DMF, THF and toluene but insoluble in acetone, Dioxane, DMSO, chloroform, n-hexane, and hydroxyl group containing solvents such as methanol and ethanol. The characterization of these polymers is very difficult due to their solubility. For example, NMR study of these copolymers is nearly impossible to perform, but FT-IR spectra in the region from 4000 to 400 cm^{-1} are recorded using KBr pellets. The conversions determined gravimetrically and other characteristics of the resulting copolymers are given in Table 3. The FT-IR spectrum of EA/St/MMA polymer system (P_0), depicted in fig. 5a, showed specific bands at 1708 cm^{-1} and 1715 cm^{-1} attributed to C=O Stretching vibration of the ester groups. The bands at 2925 cm^{-1} and 2977 cm^{-1} are assigned to aliphatic C-H stretching vibration of methyl and methylene groups. The C-H stretching vibration of the aromatic ring is indicated by a band around 3025 cm^{-1} . The bands at 1450 cm^{-1} and 1495 cm^{-1} are assigned to aromatic ring. The absorption around 1377 cm^{-1} may be traced to the in plane bending vibrations of methyl or methylene groups. The band at 1150 cm^{-1} may be attributed to the C–O stretching vibration of ester group. Fig. 5b showed a characteristic band around 3418 cm^{-1} which is attributed to N–H Stretching vibration. This absorption band indicates that the APTU monomer has involved in the polymerization process. This is supported by appearance of absorption band at 1642 cm^{-1} which is attributed to C=O stretching vibration of the amide group. The main evidence of the polymer formation is certainly the disappearance of characteristic band of vinyl groups at 1680 cm^{-1} .

3.3.2. Molecular weights

The number average, weight average molecular weights (M_n , M_w) and the polydispersity index of copolymer samples (P_0 - P_4) are obtained from gel permeation chromatography (GPC) (Table 3). The values of number average and weight average molecular weights range from 28753 to 98505 and 69817 to 156648, respectively. M_w is sensitive to the presence of high molecular weight species where as M_n is influenced by species at the lower end of the molecular weight distribution. The copolymers are not monodisperse and found to be polydisperse because M_w/M_n ratio more than the unity. The polydispersity index of APTU free polymer sample (P_0) is 1.59, whereas the polydispersity indices of polymer samples containing APTU monomer (P_1 - P_4) varied in the range of 2.45 to 3.0. The theoretical value of

polydispersity indices for polymers produced by radical combination and disproportionation are 1.5 and 2.0, respectively [15]. The values of M_w/M_n suggest that in polymerization of APTU monomer with St, MMA and EA the chain termination takes place predominantly by disproportionation than coupling. The data clearly indicates that as APTU content in the copolymer increases the number average molecular weight decreases.

Table (3): Average molecular weights by data for the copolymers

Polymer code no.	M_n	M_w	M_z	Polydispersity (M_w/M_n)	Conversion (%)	Solid content (%)
P₀	98505	156648	229517	1.590	78.33	37.6
P₁	29182	75481	134056	2.587	19.6	9.42
P₂	35839	87954	153267	2.454	9.37	4.5
P₃	28753	77423	137655	2.693	7.3	3.5
P₄	23208	69718	127984	3.004	19.53	9.37

3.3.3. Thermal analysis

Thermogravimetric analysis (TGA) is carried out to study the thermal stability and degradation behavior of the polymeric systems. The knowledge of degradation and mode of decomposition under the influence of heat is highly recommended for the optimization of process parameters. The study of the kinetics of the different decomposition processes may help in the identification of the degradation mechanism. Usually, the analysis of TGA data is not straightforward. The rough results cannot be directly converted into absolute features of the studied material. In fact, they may depend of factors such as sample mass, heating rate or gas environment. The results reported in this work are specific to the experimental conditions used.

Table (4): TGA data of the synthesized polymers.

Polymer code no.	% Weight loss at various temperature (°C)					Decomposition temperature range (°C)	T_{15} (°C)	T_{50} (°C)	T_{90} (°C)	T_{Max} (°C)	
	200	300	400	500	600					Stage I (S1)	Stage II (S2)
P₀	2.58	5.68	37.15	93.806	94.337	345-435	383	405	423	409	-
P₁	2.05	8.67	52.98	96.54	97.77	330 -435	346.7	398.6	418.7	406	-
P₂	3.34	18.07	65.96	89.55	90.85	190-330 331 -425	289.8	382.1	532	317	403
P₃	2.85	14.74	70.01	90.91	91.88	190-344 345 -430	301.04	378.97	450.83	339	399
P₄	2.24	11.2	61.83	95.1	95.75	215-357 358 -428	324.85	392.5	419.7	351	404

The TGA thermograms of the polymer samples (P₀-P₄) are shown in Figures 6a-6e, respectively along with derivative thermograms (DTG). TGA thermograms of all polymer samples are shown in Figure 7. Table 4 corroborated with the results presented in Figures 6 and 7. TGA thermograms of P₀ (0% APTU) and P₁ (1% APTU) indicate one stage thermal degradation process whereas the samples (P₂-P₄) show two distinct stages of thermal decomposition. The thermal degradation of P₀ occurred in the temperature range 345-435 °C with one DTG peak at 409 °C. The thermal degradation of APTU contained polymers occurred in the temperature range 250-440 °C.

Some characteristics TGA data related to the temperature corresponding to weight loss such as T₁₅ (temperature for 15% weight loss), T₅₀ (temperature for 50% weight loss), T₉₀ (temperature for 90% weight loss) and T_{max} (temperature for maximum weight loss) are main criteria to indicate their thermal stability of the polymeric systems. The relative thermal stability of the synthesized polymers has been evaluated by comparing the decomposition temperatures at different percentage weight loss (table 4). Higher the values of T₁₅, T₅₀, T₉₀ and T_{max} higher will be the thermal stability of the polymeric systems [16].

Kinetic analysis of thermal degradation:

Thermal degradation kinetic parameters are determined for polymer samples From TGA curves using Broido's (17), Coats-Redfern (18) and Horowitz-Mitzger (19) methods which provide overall kinetic data. Mathematical expression of Broido's (BR) method is as follows;

$$\log [-\log (1-\alpha)] = - \frac{E^*}{2.303 RT} \dots \dots \dots (3)$$

Where, (1- α) is the fraction of number of initial molecules not yet decomposed), α is the fraction decomposed at time, t and is given by $\alpha = \frac{w_i - w_t}{w_i - w_f}$ (w_i is the mass at the beginning of the decomposition step, w_t is the mass at time t. w_f is the mass at the end of the decomposition step), T is temperature in kelvin, E^* is the activation energy in J mol⁻¹, R is the gas constant. In this method a straight line should be observed between Log {-log (1- α)} and 1/T with a slope of - ($E^*/2.303R$).

Coats-Redfern (C-R) relation used to evaluate the degradation kinetic is;

$$\log \left[\frac{-\log (1-\alpha)}{T^2} \right] = \log \left[\frac{AR}{\phi E^*} \right] - \frac{E^*}{2.303 RT} \dots \dots (4)$$

Where, ϕ is the heating rate and A is the frequency factor. A Plot of log {-log (1- α) / T²} versus 1/ T give the slope for evaluation of the activation energy most appropriately.

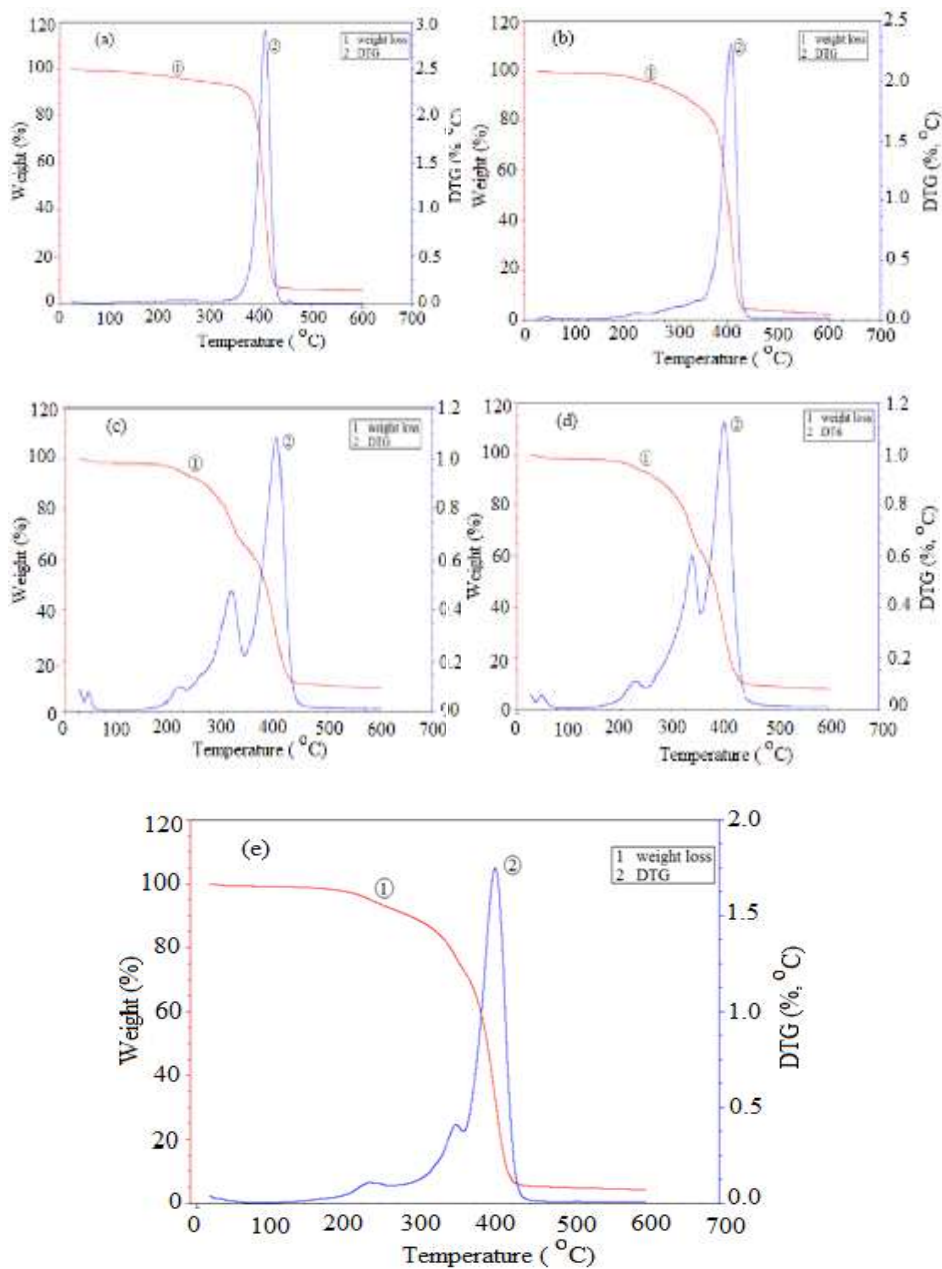


Fig.6: TGA and derivative thermograms of (a) P₀, (b) P₁, (c) P₂, (d) P₃, (e) P₄ APTU acrylic copolymer

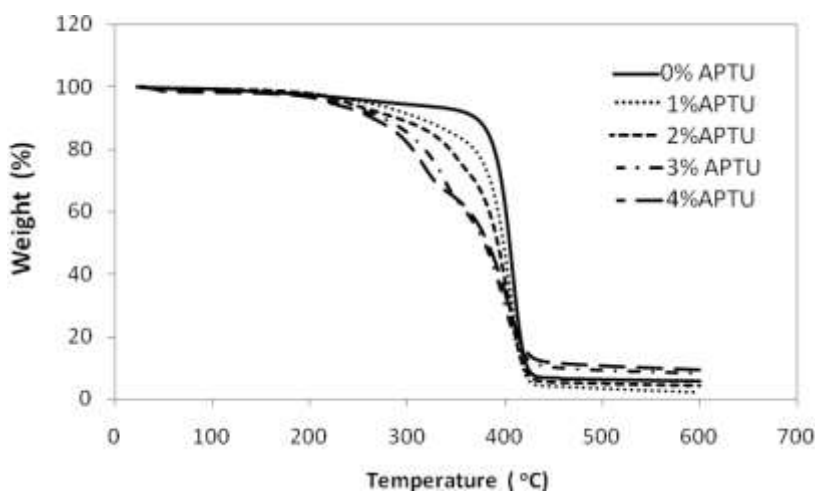


Fig.7: TGA thermograms of acrylic polymers with and without APTU

Horowitz–Metzger (H-M) relation used to evaluate the degradation kinetic is;

$$\log[-\log(1-\alpha)] = \frac{\theta E^*}{2.303 RT_s^2} \dots \dots \dots (5)$$

Where, $\theta = T - T_s$, T is the temperature corresponding to weight loss; w_t , T_s is the temperature at maximum degradation rate. Plot of $\log\{-\log(1-\alpha)\}$ versus θ should give a straight line whose slope is $E^*/2.303RT_s^2$.

The plots of $\text{Log}\{-\log(1-\alpha)\}$ versus $1/T$ (BR), $\text{Log}\{-\log(1-\alpha)/T^2\}$ versus $1/T$ (C-R) and $\text{Log}\{-\log(1-\alpha)\}$ versus θ (H-M) for polymers are shown in Figures 8-10, respectively. The regression analysis gives the slopes, constants and R^2 for degradation process. The linear plot with concurrency value (R^2) closer to one is chosen for both methods. The R^2 values and calculated activation energy (E^*) for thermal degradation process and for each method are tabulated in Table 5. It is observed that the differences in the values of the activation energies due to the three calculation methods are relatively small. Table 5 seems to indicate a tendency for higher activation energies when calculated with the H-M method. The activation energy of the low degradation process does not depend on the polymeric material, giving the values around 77.9 – 87.1 KJ/mol (BR values). The activation energy values lies in the range 110.9- 354.3 kJ/mol for Broido's method, 100.7-343.3 kJ/mol for Coats–Redfern method and 136.2-377.6 kJ/mol for Horowitz-Mitzger method. The results indicate that the E^* values increases as the percent of APTU monomer increases in the polymers.

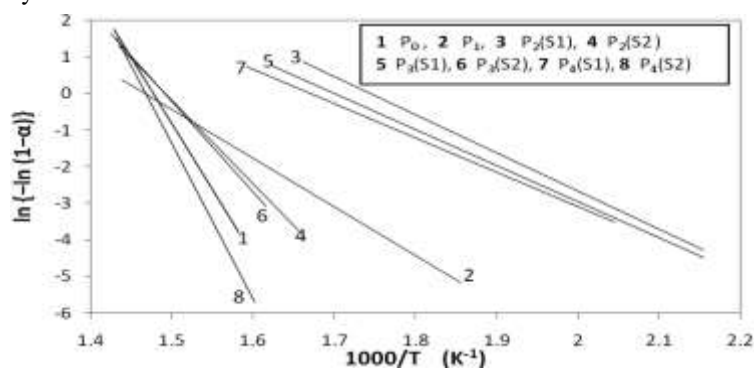
Table (5): Activation energies calculated by Broido's (BR), Coats-Redfern (C-R) and Horowitz-Mitzger (H-M) methods with the respective concurrency value (R^2) for the polymers

Polymer code no.	Activation energy (E^*) (kJ/mol) $\pm 4\%$											
	BR				C-R				H-M			
	Step I	R^2	Step II	R^2	Step I	R^2	Step II	R^2	Step I	R^2	Step II	R^2
P₀	354.3	0.99	-	-	343.3	0.99	-	-	377.6	0.99	-	-
P₁	110.9	0.93	-	-	100.7	0.94	-	-	136.2	0.96	-	-
P₂	87.1	0.94	190.1	0.98	78.3	0.96	179.3	0.99	107.2	0.96	205.7	0.99
P₃	82	0.93	205.6	0.99	73	0.95	194	0.99	105.5	0.94	213.2	0.99
P₄	77.9	0.91	299.6	0.98	68.7	0.96	288.5	0.99	97.3	0.93	309.3	0.99

3.4. Antimicrobial activity

The synthesized target polymers are evaluated for their in vitro antibacterial activity using the agar diffusion technique against the tested microorganisms. The results are observed for each tested polymer sample as the average diameter of inhibition zones of tested microorganism growth around the disks in mm.

The results revealed that the tested polymers displayed moderate activity against fungal strains and yeast strains. The APTU free polymer showed 66.7% of the activity of Metronidazole against *Candida albicans* and 68% against *Aspergillus niger*. The APTU contained polymers showed 55.6% -66.7% of the activity of Metronidazole against *Candida albicans* and 68%- 84% against *Aspergillus niger*. On the other hand, the tested polymers showed totally no activity toward *Bacillus subtilis* (gram +ve bacteria) and *Pseudomonas aeruginosa* (gram -ve bacteria). The APTU free polymer showed 43.7 % of the activity of Erythromycin against *Micrococcus luteus* whereas P₂ and P₄ samples showed 56.25 % and 59.38 %, respectively. The APTU free polymer sample does not exhibit growth inhibitory activity against *Escherichia coli* whereas P₄ sample exhibit 41% of the activity of Erythromycin.

**Fig.8: plots of $\ln\{-\ln(1-\alpha)\}$ versus $1/T$ using Broido method**

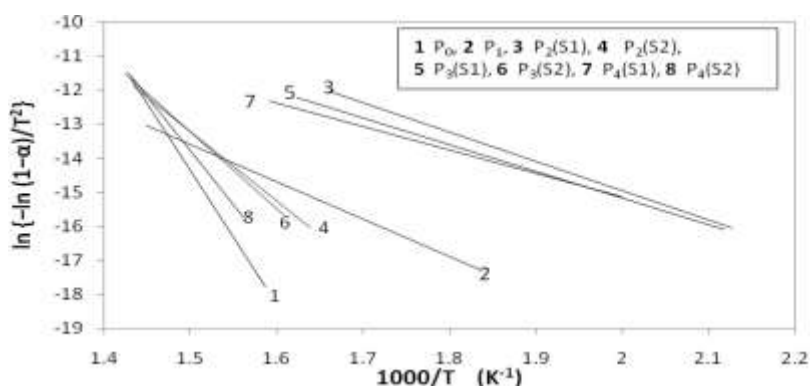


Fig.9: plots of $\ln\{-\ln(1-\alpha)/T^2\}$ versus $1/T$ using Coats-Redfern method

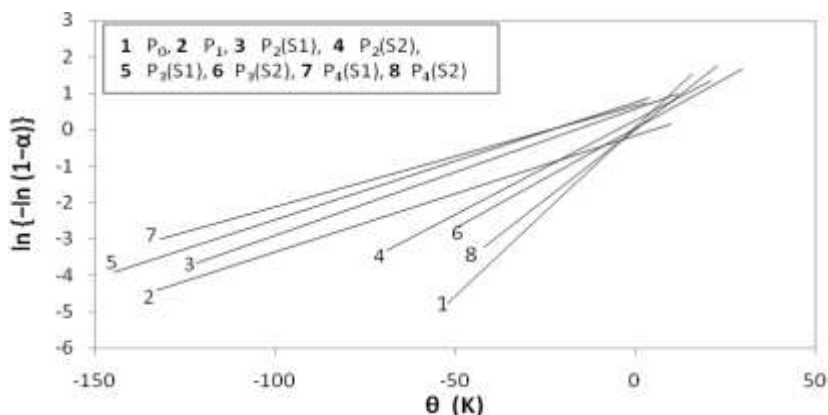


Fig.10: plots of $\ln\{-\ln(1-\alpha)\}$ versus θ using Horowitz-Metzger method

4. Conclusion

Synthesis and characterization of N-acryloyl-N-phenylthiourea (APTU) is reported. Several copolymers of APTU monomer with MMA, St and EA were synthesized by emulsion free radical copolymerization using ammonium persulfate as initiator and SLS as surfactant. The monomer and copolymers are characterized by spectroscopic methods. Thermal stability of the polymers is reported. Kinetic parameters are evaluated from the TGA curves using the plots of Broido (BR), Coats-Redfern (C-R) and Horowitz - Metzger (H-M) methods. All the synthesized polymers are tested for their antimicrobial properties against microorganisms. The results revealed that the tested polymers displayed moderate activity against fungal and yeast strains.

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