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Synthesis, characterization polymerization and antibacterial properties of novel thiophene substituted acrylamide

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ABSTRACT

Ethyl 2-acrylamido-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate (ETTCA) has been synthesized and its structure has been elucidated by elemental analysis and spectral tools. Free radical polymerization of (ETTCA) has been conducted in several solvents using azobisisobutyronitrile (AIBN) as an initiator. The kinetic parameters of polymerization of the ETTCA were investigated, and it was found that the polymerization reaction follows the conventional free radical scheme. The overall activation energy of polymerization ΔE was determined ($\Delta E = 45.11$ kJ mol^{-1}). The copolymerization of ETTCA with three conventional monomers was carried out in dioxane at 65 °C. The monomer reactivity ratios for the copolymerization of ETTCA with methyl methacrylate (MMA), vinyl acetate (VA) and vinyl ether (VE) were calculated. Thermal stability of the ETTCA polymer and its copolymers were investigated by thermogravimetric analysis. It has been found that the prepared polymer (PETTCA) and its copolymers with VA have moderate biological activity and highly dependent on the copolymer composition.

1. Introduction

The synthesis of polymers with well-defined compositions, architectures, and functionalities has become an important topic of contemporary polymer science. N-substituted acrylates are very interesting monomers because they have acquired prime importance in various avenues of application. Recently acrylamide derivatives were found to have antiviral activity as inhibitors of hepatitis B virus replication [1]. Moreover, the N-substituted acrylamides are used to prepare thermosensitive materials. These thermoplastic polymers present also great potential in application as drug delivery system [2], as glycogen phosphorylase inhibitors [3] human gene vectors [4] and biocatalysts [5]. It is possible to obtain N-acryloyl and N-methacryloyl derivatives of human serum albumin (HSA), in which acryloyl fragments are bound to asparagines and lyzin fragments [6]. The development of antimicrobial macromolecules holds a good promise for novel therapeutics and new materials to prevent the spread of infectious disease [7].

The reaction of acryloyl chloride or methylacryloyl chloride with the corresponding amines to prepare new functional monomers has been reported [8–10]. Many investigations have focused on the synthesis and characterization of functional copolymers with physical, chemical, and electrical stimuli properties which can respond to different environmental conditions. The present work deals with the preparation of a novel acrylamide derivatives which contains a thiophene moiety which could have a biological activity. The new monomer has been characterized and copolymerized with different conventional monomers, the antifungal and antibacterial behavior of one copolymer with vinyl acetate has been investigated against several fungi and bacteria.

2. Experimental

2.1. Materials

Cyclohexanone, ethyl cyanoacetate, elemental sulfur, triethylamine and acryloyl chloride were used as received. Methyl methacrylate (MMA) was purified by washing with 50 ml of 5% NaOH several times followed by distilled water. Finally, the washed methyl methacrylate was dried with anhydrous sodium sulfate (Na_2SO_4), filtered and distilled before use. Vinyl ether (VE) and vinyl acetate (VA) (Aldrich) were distilled before use. All the reagents and solvents were purified by conventional methods. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol and then dried in the dark.

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2.2. Monomer synthesis

2.2.1. Preparation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate

A mixture of 39.2 g (0.4 mol) of cyclohexanone, 45.2 g (0.4 mol) ethylcyano acetate, 12.8 g (0.4 mol) elemental sulfur and 40.4 g (0.4 mol) triethylamine was refluxed in absolute ethanol for two hours. The reaction mixture was poured into cold water. The solid product was filtrated and recrystallized from ethanol. The yield was 80%, and the golden crystals with melting point 112 °C were collected (Scheme 1).

Elemental analyses (%) were: found (theoretical), *C* = 58.66 (58.64)%, *H* = 6.97 (6.71)%, *N* = 6.17 (6.22)% and *S* = 14.15 (14.23)%.

2.2.2. Preparation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate acrylamide (ETTCA)

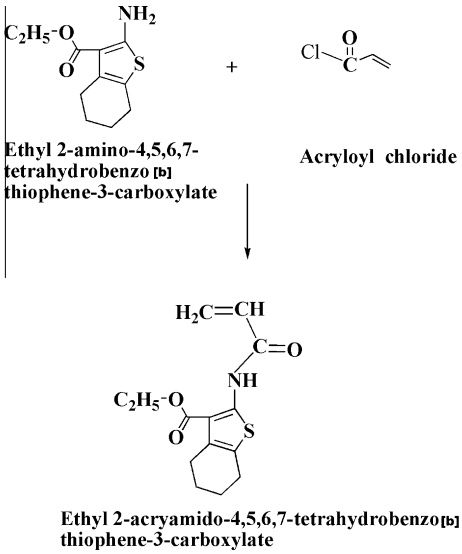
24.7 g (0.1 mol) ethyl 2-amino-4,5,6,7 tetrahydrobenzo thiophene-3-carboxylate was dissolved in diethyl ether, and in the same solvent acryloyl chloride 9.05 g (0.1 mol) was added drop wise. The mixture was maintained at low temperature 4 °C using an ice bath and stirred for 5–7 h. The resulting product was poured into water, stirred and washed with diethyl ether, then dried at room temperature. The yield was 70%, and the pale brown crystals melting point was 115 °C. Scheme 2 describes the synthesis of ETTCA monomer.

Elemental analysis: found (theoretical) *C* = 59.34 (60.19)%, *H* = 6.44 (6.13)% *N* = 5.06 (5.01)% and *S* = 11.09 (11.48)%.

2.3. Homopolymerization and copolymerization

Radical solution polymerization of ETTCA was carried out in sealed glass tubes with the proper solvent (tetrahydrofurane THF or 1,4-dioxane) and initiator AIBN at 65 °C. The polymerizations were homogeneous in all cases.

Copolymerization of ETTCA with MMA, VA and VE was carried out following the above procedure. The composition of the copolymers was determined by elemental analysis.



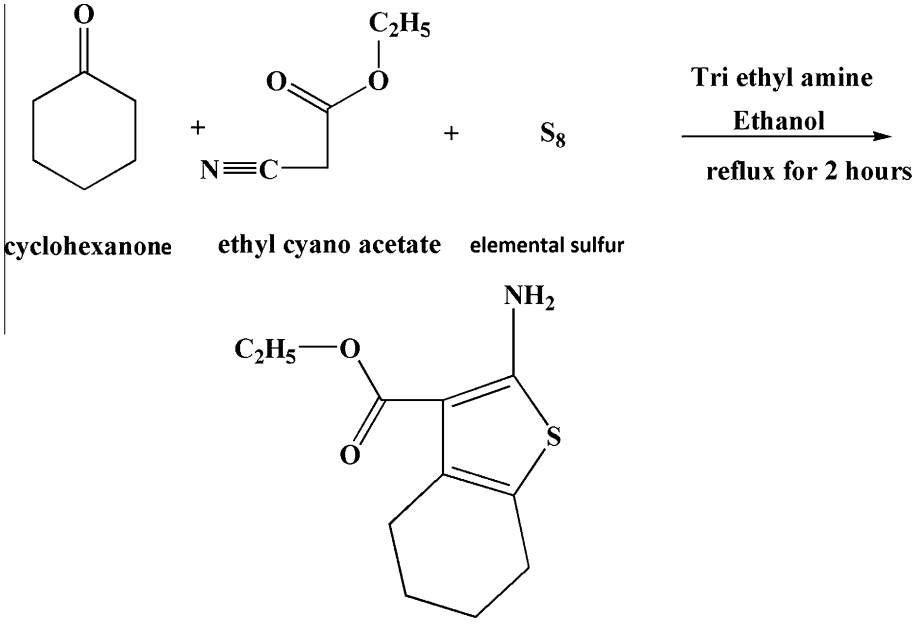
Scheme 2. Preparation of Ethyl 2-acrylamido-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate (ETTCA).

2.4. Thermal analysis, NMR, FTIR

Thermogravimetric analysis TGA studies were performed on a Shimadzu TGA-50H instrument. Typically 7–10 mg samples were heated at a rate of 10.0 °C/min in nitrogen atmosphere. FTIR infrared measurement was obtained using a Perkin–Elmer 398 FTIR spectrophotometer between 400 and 4000 cm^{-1}. ^1H NMR spectra of the samples were obtained on a Bruker AC-400 at 20 °C in $CDCl_3$ solution.

2.5. Molecular weight determination

The viscosity measurements were carried out using an Ubbelohde viscometer suspended level dilution viscometer. Dioxane



Scheme 1. Preparation of ethyl 2-amino-4,5,6,7-tetrahydrobenzo [b] thiophene-3-carboxylate (EATTC).

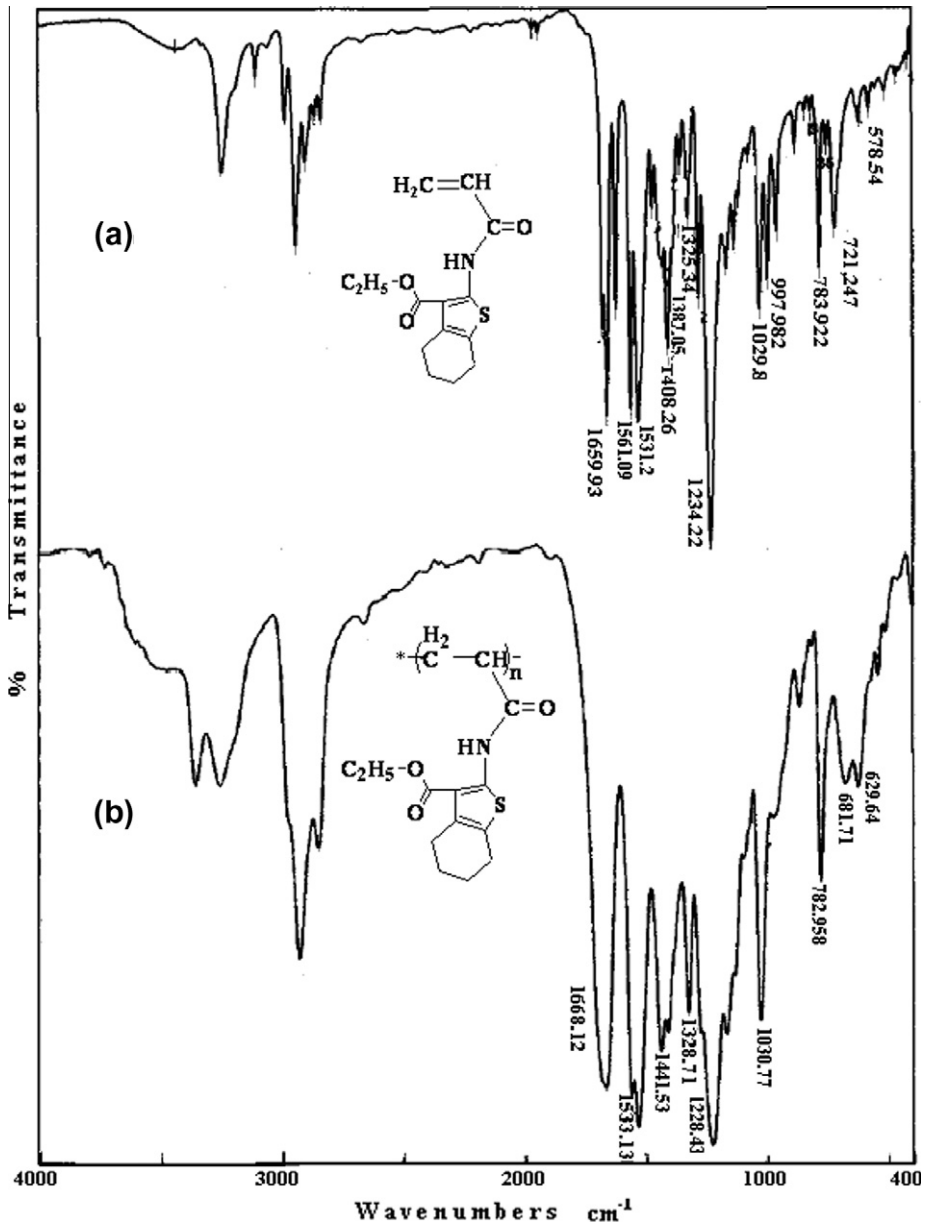


Fig. 1. FTIR spectra for the monomer ETTCA and of its polymer.

was used as solvent with a flow time of 121 s at 25 °C. Gel permeation chromatography (GPC) of the samples was performed using 1100 Aligant instrument equipped with organic GPC–SEC start up kits with a flow rate of 1 ml/min, THF as mobile phase, maximum pressure 150 bar, minimum pressure 5 bar, injection volume 20 μl and column temperature thermostat 25 °C. The eluent was monitored with a refractive index detector of optical unit temperature 25 °C and peak width 0.1 min. Polymer concentration was 0.1 wt.%.

2.6. Antimicrobial activity

2.6.1. Sources and cultures of microorganisms

Different microorganisms including Gram positive and Gram negative bacteria, yeasts and fungi were kindly provided by the Microbial center, Ain-Shams University, Faculty of Agricultural, Egypt (CAIM, Cairo Mircen) and from the Bacteriological Department Laboratory of National Organization for Drug Control and Research (NODCAR), Egypt. These involved *Bacillus subtilis* (CAIM-1007) BS, *Staphylococcus aureus* (CAIM-1352) SA, and *Micrococcus luteus* (CAIM-1246) ML, from Gram positive bacteria; *Escherichia coli* (CAIM-1357) EC, *Pseudomonas aeruginosae*, *Shigella* spp. (NMRO), *Salmonella typhimurium* (CAIM-1350) ST, and *Klebsiella pneumoniae* KP from Gram negative bacteria; *Saccharomyces cerevisiae* (CAIM-14) SC, *Candida albicans* (CAIM-22) CA, *Candida tropicalis* CT, *Candida parapsilosis* CP and *Candida nonalbicans* CN from Yeasts, *Fusarium oxysporum* (CAIM-123) FO, *Aspergillus niger* (CAIM-147) AN, and *Aspergillus flavus* (CAIM-127) AF, from filamentous fungi.

The cultures were maintained on slants of appropriate medium, where the bacteria was kept on slants of nutrient agar medium, yeast was kept on slants of Sabouraud's dextrose medium and fungi was kept on slants of Czapek-dox agar medium.

2.6.2. Antimicrobial assays

In preliminary tests, the antibacterial and antifungal activities of the compounds were assayed by the paper disc diffusion technique, Betina and Micekov [11].

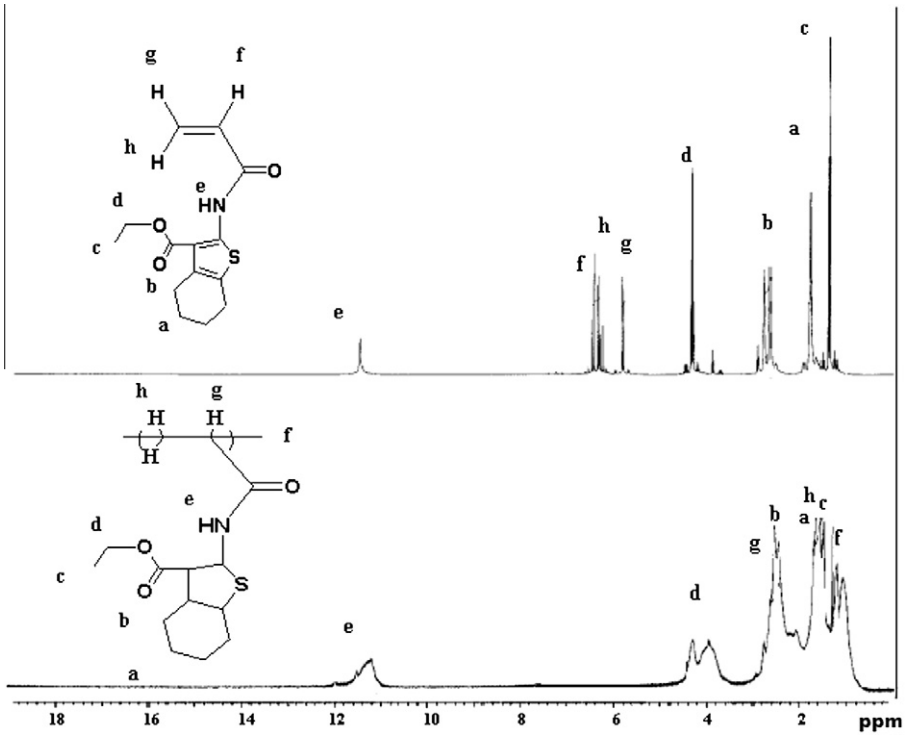


Fig. 2. ^{1}H NMR spectra for the monomer ETTCA and of its polymer.

2.6.3. Minimum inhibition concentration (MICS)

The minimum inhibition concentrations (MICS) of the samples upon the tested fungal and bacterial species were determined by the dilution method described by Nair et al. [12]. The detailed description of the antibacterial assays can be found in Ref. [13].

2.6.4. Statistics

The experiments were conducted in three to five replicates and the results obtained were treated statistically with an analysis of variance and the significance was expressed at L.S.D. 5% and 1%.

3. Results and discussion

3.1. Monomer synthesis

A novel acrylamide monomer ETTCA has been synthesized, the structure of the new monomer was confirmed by elemental and spectral analyses. Figs. 1 and 2 show the FTIR and ^{1}H NMR spectra of the monomer and its polymer respectively.

3.2. Homopolymerization

ETTCA was polymerized in 1,4-dioxane and THF. The FTIR spectra of the prepared polymer shows the disappearance of bands at 1531–1561 cm^{-1} which are due to the (C=C stretching), which confirms the polymerization of ETTCA. The FTIR spectra of both the monomer and polymer (Fig. 1) show sharp peaks at 1660 and 1680 cm^{-1}, due to the presence of many C=O groups (the acrylamide and the ester carbonyl groups). N—H stretching appears at around 3400 cm^{-1} in monomer and polymer spectra (O—H stretching vibration from traces of water could also contribute to this wide band). A similar observation can be found in the ^{1}H NMR spectrum of the monomer and its homopolymer, since the band due to the ethylenic double bond at around 6.8 ppm has disappeared in the polymer spectrum (Fig. 2).

3.3. Kinetics of polymerization of ETTCA

3.3.1. Effect of monomer and initiator concentration on the rate of polymerization of ETTCA

The polymerization rate was determined using calibrated dilatometers with a bulb of (3–5 ml in capacity) and calibrated capillary tube ended with ground joint stoppers. The dilatometer contains the required amount of monomer and initiator dissolving in the appropriate amount of solvent was placed in ultrathermostat. The decrease in the meniscus of the capillary (Δh) was monitored every 5 min and plotted against time. The rate was usually followed in the early stages of polymerization and the rate was always a straight line. The temperature was regulated to (±0.1 °C). The extent of polymerization is proportional to the decrease in volume of the polymerization medium with time. The conversion–time curves for the polymerization of ETTCA in THF at 65 °C for different monomer concentration were measured at constant initiator concentration [AIBN] of 8.1×10^{-4} M. From the slopes of conversion–time curves the rate of polymerization log R_p was calculated and its logarithm was plotted versus the logarithm of the monomer concentration log [M]. A straight line is obtained with a slope equals to the order of reaction regarding the monomer concentration and equals 0.86. In a similar way at constant monomer concentration, the order of initiator concentration was obtained 0.67. Consequently, the polymerization rate equation is $R_p = k[M]^{0.86}[I]^{0.67}$. These values indicate that the polymerization followed the conventional free radical mechanism with bimolecular termination [14].

3.3.2. Effect of temperature on the polymerization of ETTCA

The effect of temperature on the polymerization process usually entails the determination of activation energy of polymerization ΔE. The activation energy is determined by the well known Arrhenius equation:

$$k = Ae^{\left(\frac{-\Delta E}{RT}\right)} \quad (1)$$

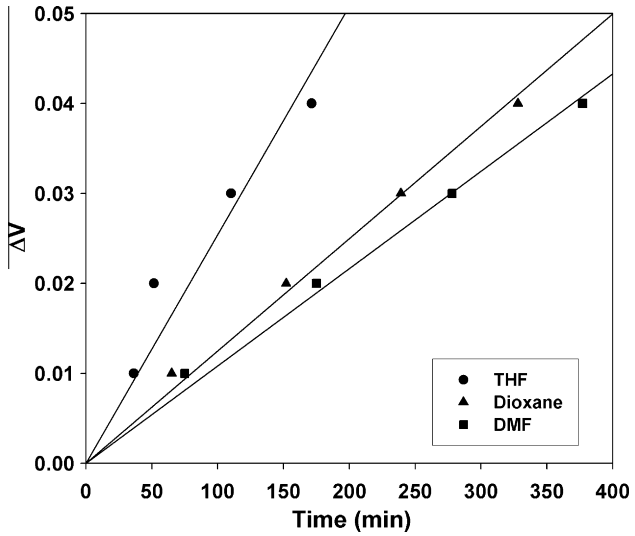


Fig. 3. The relation between the volume contraction ΔV of ETTCA polymerization and time in different solvents [ETTCA] = 0.2 M [AIBN] = 8.1×10^{-4} M and at 65 °C.

where k is the rate constant of a chemical reaction, A is the collision frequency factor, ΔE is the activation energy of the particular process, and T is the absolute temperature. Here ΔE of polymerization is composed of the following terms [15]:

$$\Delta E = E_p - \frac{1}{2}(E_d - E_t) \quad (2)$$

Polymerization was performed in THF with constant monomer and initiator concentration [ETTCA] = 0.4 M and [AIBN] = 8.14×10^{-4} M at 65 °C, 60 °C, 55 °C and 50 °C.

By plotting log R_p (which is proportional to k, the rate constant in this particular case) versus the reciprocal of the absolute temperature, a straight line is obtained with a slope equals to $\frac{-\Delta E}{2.03R}$, where R is the universal gas constant. From the slopes of the lines obtained from the relation between the volume contraction ΔV and time for different temperatures of ETTCA, polymerization R_p was determined. The overall activation energy (ΔE) of the polymerization was calculated from the relation between log R_p and $1/T$ and was found to be equal to 45.11 kJ mol^{-1}. This value was found in the range in most cases of free radical polymerization [16].

3.3.3. Effect of solvent on the polymerization of ETTCA

The polymerization behavior in different solvents has been investigated with this new monomer as well, and Fig. 3 shows the conversion–time curves for the polymerization of ETTCA in different solvents, THF, dioxane and DMF, at 65 °C at constant monomer concentration equals to 0.2 mol $L^{-1}$and at constant initiator concentration [AIBN] of 8.1×10^{-4} M. From the slope of the lines in Fig. 3, it has been found that the rate of polymerization follows the order THF ($R_p = 2.54 \times 10^{-4}$ mol L^{-1} s^{-1}) > Dioxane ($R_p = 1.25 \times 10^{-4}$ mol L^{-1} s^{-1}) > DMF ($R_p = 1.08 \times 10^{-4}$ mol L^{-1} s^{-1}). The high R_p value in THF could be due to favorable physical interaction with THF.

3.4. Copolymerization

The measured intrinsic viscosity for PETTCA was [η] = 2.8 dl/g. This tendency was similar to those for polymaleimides reported previously to have relatively low molecular weights [17–19]. The presence of bulky side group is probably behind the lowering of molecular weight of this homopolymer. Therefore, the introduction of a new monomer in the polymer chain may reduce the high chain transfer to the thiophene moiety and consequently copolymerization may lead to higher molecular weight compounds. From this point of view, the copolymerization of ETTCA with three conventional vinyl monomers was investigated.

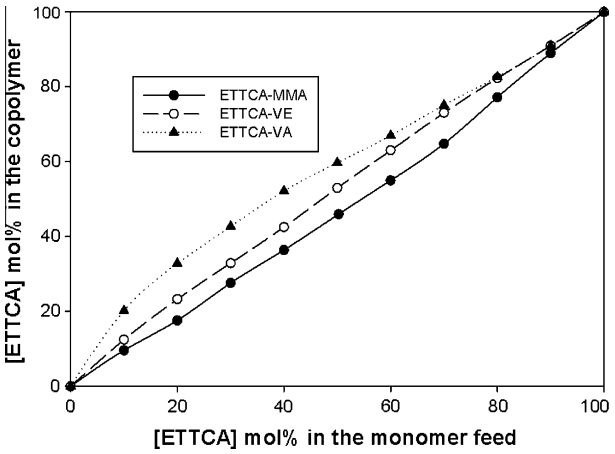


Fig. 4. Copolymer composition curves for the three systems ETTCA with VA, MMA and VE.

Table 1
Reactivity ratio of ETTCA with the three monomers (VA, MMA and VE) using free radical solution polymerization by AIBN at 65 °C.

Method	Co monomer		
	VA	MMA	VE
r1			
K–T	1.006	0.699	1.093
NLLS	1.07	0.706	1.08
r2			
K–T	0.399	1.042	0.875
NLLS	0.400	1.03	0.835

The ETTCA monomer was copolymerized with three of commercial importance, methyl methacrylate (MMA), vinyl ether (VE) and vinyl acetate (VA). The copolymerization of ETTCA with VA, VE and MMA was confirmed by ^{1}H NMR spectra. The appearance of the peak of acetoxy proton [20] at 2.1–2.3 ppm, gives an indication of the participation of VA in the copolymer. ETTCA copolymerization with VE indicated the appearance of a band at 3.82 ppm corresponding to ($O{=}CH_2$). ETTCA and MMA copolymers are characterized by sharp peak at 3.76 ppm corresponding to the (CH_3) proton in MMA. Fig. 4 illustrates the composition curves for all the copolymer systems.

3.5. Calculation of the reactivity ratios of the monomers

The reactivity ratios of the ETTCA have been calculated using Kelen–Tüdos (K–T) [21] and non-linear least square methods. The Fineman–Ross [22] method is used for preliminary estimation of the reactivity ratios. A non-linear least square method was used to calculate the reactivity ratios starting from the values obtained from the Fineman–Ross method (the commercial sigma-plot program was used for this purpose). The values of the reactivity ratios of the investigated systems are depicted in Table 1. These values of r_1 and r_2 were used to construct theoretical curves in the copolymer composition diagram in Fig. 4. The data shows that the values of the reactivity ratios obtained by linear K–T method are in agreement with those calculated with non-linear least square method. As evidenced from the values, random copolymerization is realized in ETTCA with the three monomers.

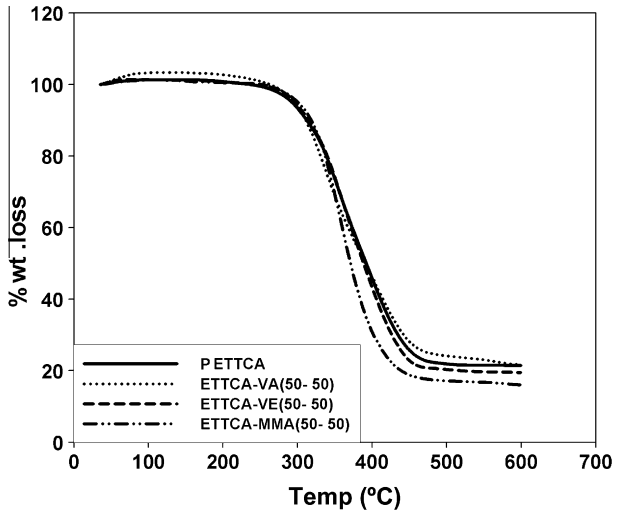


Fig. 5. Thermogravimetric analysis of ETTCA–VA, ETTCA–VE and ETTCA–MMA copolymers.

3.6. Characterization of the polymers and the copolymers

3.6.1. Thermal stability

Thermogravimetric analysis TGA data of PETTCA and its copolymers with VE and MMA are presented in Figs. 5 and 6. The TGA thermograms show that the decomposition of PETTCA takes place around 310 °C. The weight loss is 11.2 and 80.41–80.16% at 310 °C and 600 °C, respectively. It was therefore, important to investigate the effect of introducing some units of VA, VE and MMA. The investigation here is not very intensive, but it shows that the ETTCA–MMA copolymer decomposition starts at 325 °C and the contribution of MMA in the copolymer increases thermal stability to get T_{max} = 357.4 °C. The PETTCA is higher than the thermal stability of the ETTCA–VA copolymer because thermal stability of PVA tends to be low. The activation energy (ΔE, kJ mol^{-1}) for the major degradation step was computed using the Dharwadkar and Kharkhanavala equation: [23]

$$\ln[-\ln(1-\alpha)] = \left(\frac{\Delta E}{RT_i^2}\right)\left(\frac{100}{T_f - T_i}\right)\theta + C \quad (3)$$

where α is the fraction of the polymer degraded at temperature T under consideration

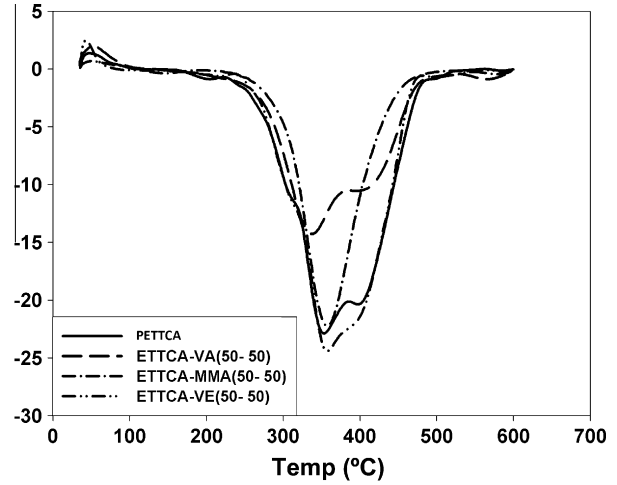


Fig. 6. Differential thermogravimetric analysis (DTGA) of ETTCA–VA, ETTCA–VE and ETTCA–MMA copolymers.

Table 2
Energy of activation and degradation temperature range for the major degradation of PETTCA, copolymers and molecular weights of PETTCA and copolymers.

Sample	Major degradation temp (°C)	ΔEa (kJ mol^{-1})	M_n, $M_w \times 10^3$	D.I.
PETTCA	310–440	28.47	3.64 8.00	2.2
ETTCA/VE	310–430	23.46	2.15 5.55	2.6
ETTCA/MMA	325–410	51.15	5.38 36.2	6.7
ETTCA/VA	300–450	27.47	3.57 8.86	2.4

D.I. polydispersity index.

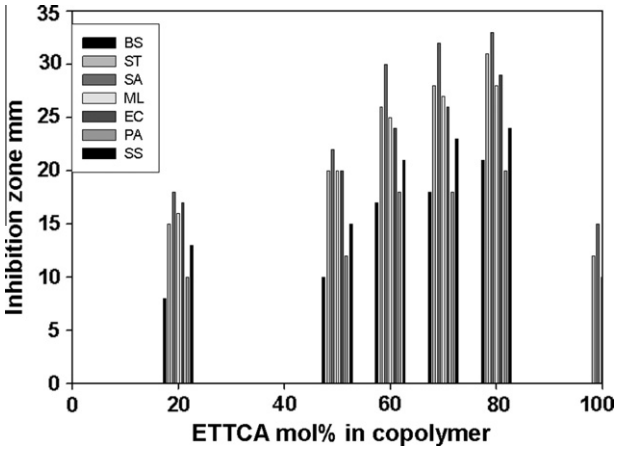


Fig. 7. Inhibition zone values versus copolymers composition of ETTCA–VA for 3 G+ve and 5 G−ve bacteria (antibacterial behavior): *Bacillus subtilis* BS, *Staphylococcus aureus* SA, and *Micrococcus luteus* ML, from Gram positive bacteria; *Escherichia coli* EC, *Pseudomonas aeruginosae* PA, *Shigella* spp. SS, *Salmonella typhimurium* ST, and *Klebsiella pneumoniae* KP from Gram negative bacteria.

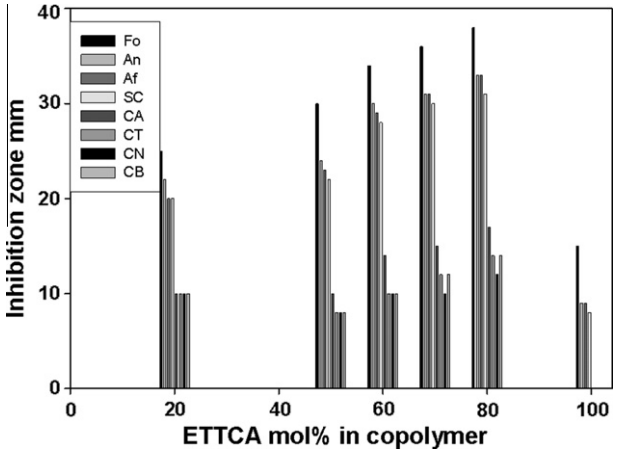


Fig. 8. Inhibition zone values versus copolymers composition of ETTCA–VA for eight fungi (antifungal behavior) FO = *Fusariam oxysporum,* AN = *Aspergillus niger,* AF = *Aspergillus flavus,* SC = *Sacchromyces cerivisiae,* CA = *Candida albicans,* CT = *Candida tropicalis,* CN = *Candida non-albicans,* CP = *Candida parapsilosis.*

$$\alpha = \frac{m_s - m}{m_s - m_f} \quad (4)$$

where m_s, m, m_f are the initial, actual and final mass of the sample, respectively; E is the energy of activation; R is the gas constant; T_i is the temperature of inception of the reaction; T_f is the temperature of completion of the reaction;

$$\theta = T - T_s \quad (5)$$

Table 3
Minimum inhibitory concentration of PETTCA and (ETTCA–VA) copolymers for different fungi.

Compound	% of ETTCA	Tested organisms used							
		Fusarium oxysporum	*Aspergillus niger*	*Aspergillus flavus*	*Saccharomyces cerevisiae*	*Candida albicans*	*Candida tropicalis*	*Candida non-albicans*	*Candida parapsilosis*
PETTCA	100	100	100	100	100	250	250	250	250
ETTCA/VA	80(82.4)	0.75	0.75	0.75	0.75	5.0	5.0	5.0	5.0
ETTCA/VA	70(75.6)	1	1	1	1	10	10	10	10
ETTCA/VA	60(69.7)	25	25	25	25	75	75	75	75
ETTCA/VA	50(64.3)	10	10	10	10	100	100	100	100
ETTCA/VA	20(48.3)	75	75	75	75	50	50	50	50
LSD									
5%		3.41	3.91	3.93	4.42	4.91	5.61	5.81	5.91
1%		7.60	8.42	9.52	10.56	11.80	12.43	14.10	15.20

The data between brackets are the actual molar ratios of ETTCA in the copolymer composition.
Each measurement is an average of three experiments.

Table 4
Minimum inhibitory concentration of PETTCA and (ETTCA/VA) copolymers for several bacteria.

Compound	% of ETTCA	Tested organisms used							
		Bacillus subtilis (Gm+ve)	*Salmonella typhimurium* (Gm−ve)	*Staphylococcus aureus* (Gm+ve)	*Micrococcus luteus* (Gm+ve)	*Escherichia coli* (Gm−ve)	*Pseudomonas aeruginosae* (Gm−ve)	*Shigella* spp. (Gm−ve)	*Klebsiella pneumoniae* (Gm−ve)
PETTCA	100	450	225	225	225	225	450	225	225
ETTCA/VA	80(82.4)	7.5	7.5	5	5	5	7.5	7.5	7.5
ETTCA/VA	70(75.6)	10	10	10	10	1	10	1	1
ETTCA/VA	60(70)	12.5	15	15	12.5	12.5	15	15	12.5
ETTCA/VA	50(65)	225	100	100	100	10	10	10	100
ETTCA/VA	20(48)	250	150	150	150	100	100	100	200
LSD									
5%		4.80	5.21	5.91	6.91	6.92	7.93	8.6	8.4
1%		10.10	10.6	12.81	14.4	17.8	18.9	18.4	15.9

The data between brackets are the actual molar ratios of ETTCA in the copolymer composition.
Each measurement is an average of three experiments.

where T_s is the temperature at the point of inflection in the TGA curve; C, constant. By plotting ln $[-/\ln(1-/\alpha)]$ versus θ a straight line results, from the slope, $(\frac{\Delta E}{RT_i^2})(\frac{100}{T_f - T_i})$, E can be calculated. Table 2 contains the activation energy values for degradation of PETTCA and its copolymers with VA, VE and MMA, it also contains values of M_n, M_w and D.I. (polydispersity index of the homo and copolymers). The degradation of PETTCA needs high activation energy of 28.47 kJ mol^{-1}, which is slightly greater than the activation energy for degradation of ETTCA–VA and ETTCA–VE copolymers. However, the activation energy of degradation of ETTCA–MMA copolymer is greater than PETTCA. The molecular weight of the latter copolymer ETTCA/MMA as shown in Table 2 is slightly higher than the other copolymers. However, the differences in molecular weight are quite small and could not reflect much on the thermal behavior of these polymers. The contribution of both ETTCA and MMA increase the thermal stability as has been shown before.

3.7. 7 Biological activity of the PETTCA and some of its copolymers

The presence of sulfur in a molecule is usually accompanied by increased antibacterial activity, as an example the introduction of a thiourea into chitosan increased its antibacterial activity by 60 times [24]. The thiophene moiety in the prepared monomer could offer a reasonable base to expect a biological activity for the prepared polymer or its copolymer. Several Gram positive and Gram negative bacteria have been selected to test the biological activity of the vinyl acetate/ETTCA copolymers. Vinyl acetate is suitable monomer since its polymer can be converted easily to the biocompatible polyvinyl alcohol. Although, polyvinyl acetate, as such is not known to have any antibacterial properties however its copolymer were found to biologically active. Systematic studies of the homopolymer together with some selected copolymers were done. The inhibition zones reflecting the antibacterial and antifungal activity for each species are shown in Figs. 7 and 8, respectively. Tables 3 and 4 contain the data of the minimum inhibitory concentration MIC (mg/l) of the homopolymer as well as its copolymers with VA on the tested bacteria and fungi respectively. These data contain common features. It seems that the ETTCA homopolymer has low antibacterial properties however this activity increases in the copolymers with VA reaching a maximum at an average content of ETTCA around 70–85% then it declines to a minimum for the homopolymer poly ETTCA. The minimum inhibitory concentration of PETTCA is about 450 μg against *B. subtilis* declines to just 7.5 μg for copolymer with ca 82 mol% ETTCA. In the same manner the MIC for poly ETTCA is about 100 μg against *F. oxysporum* but reaches only 0.75 μg for the copolymer with 82.4% ETTCA. The same behavior can be seen for *E. coli* and the rest of tested bacteria and fungi in (Tables 3 and 4). Figs. 7 and 8 show similar results where the maximum inhibition zone for both bacteria and fungi is valued around the 80% ETTCA value in the copolymers. This is a remarkable behavior for the copolymers and could be due to the sequence distribution of the thiophene side groups along the copolymer backbone. At present no plausible explanation is evident.

4. Conclusion

New acrylamide monomer containing a thiophene side group has been synthesized and its structure was confirmed by elemental analysis and FTIR and NMR spectroscopy. The rate equation for the polymerization of this monomer indicated a conventional free

radical mechanism. The presences of the bulky side group with sulfur atom lead to low molecular weight of the polymer as evident from viscosity measurements. The new monomer has been copolymerized with three conventional monomers and the reactivity ratios of the three systems were calculated by two methods which gave close results. The thermal properties of the copolymers were measured by TGA analysis and showed that the homopolymer and the copolymers have relatively high thermal stability. Activation energy of degradation for the homopolymer and the copolymers was measured. The homopolymer has low antibacterial activity but when copolymerized with about 18% VA its antibacterial capacity increases dramatically as evident from inhibitory zone and minimum inhibition concentrations data. It seems that the monomer sequence distribution plays certain role in enhancing the bacterial activity.

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