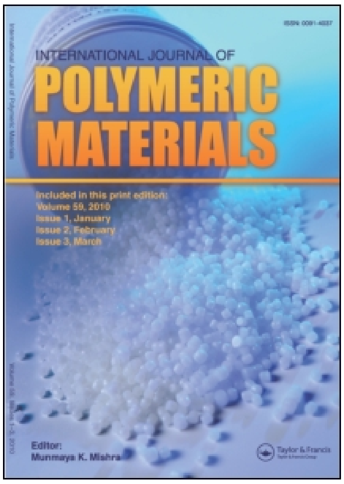

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Friedel–Crafts Polyketones: Synthesis, Thermal and Antimicrobial Properties

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Linear polyketones **A-D** and copolyketones **E**, **F** containing N-methylpiperidinone in the main chain were synthesized via Friedel-Crafts reaction through the polymerization of 2,6-bisfurfurylidene N-methyl piperidone (**2,6-BFNP**) with different diacid chlorides. The model compound was synthesized by reacting (**2,6-BFNP**) with benzoyl chloride and characterized by 1H-NMR, FTIR and elemental analyses. The resulting polyketones and copolyketones were identified by elemental and spectral analyses, and characterized by solubility, viscometry, X-ray and morphology measurements. The thermal properties of these polyketones and copolyketones were evaluated and correlated to their structural units by TGA and DTA measurements. All the polyketones were tested for their biological activity against bacteria, fungi and yeast. It was observed that the majority of the polyketones and the copolymers synthesized can be used as antibacterial and antifungal agents.

Keywords Friedel–Crafts, polyketones, synthesis and antimicrobial properties, thermal properties

INTRODUCTION

Recently, much attention has been focused on aromatic polyketones with excellent physical and chemical resistance in the fields of electronics, aerospace, and automobile industries [1–3]. Moreover, unsaturated polyketones derived from diarylidene cycloalkanones have attracted interest due to their potential applications [4–6]. Compared with conventional polyketones,

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e.g. poly(ether ether ketone) (PEEK), unsaturated polyketones exhibit unique optical properties and semiconductivity [4–7]. Therefore, in the past 20 years, a series of the polymers, containing the cycloalkanone moiety and oxygen or sulfur in the molecular backbone, were prepared and their properties were investigated [4–12].

During the last decade an extensive work was carried out towards prevention of biological degradation of useful materials such as textile fibers, food packaging materials, paints, marine coatings, electrical insulation and pharmaceutical materials using certain polymeric systems having biocidal properties [13–15]. It was therefore thought appropriate to synthesize the polyketones and copolyketones containing N-methylpiperidinone moiety and examine their biocidal properties against *Aspergillus flavus, Aspergillus niger, Candida albicans, Geotrichum candidum, Trichophyton rubrum, Escherichia coli, Pseudomonas aeruginosa*, and *Staphylococcus aureus*.

EXPERIMENTAL

Materials

Reagents

Furfural (Fluka, Germany) was freshly distilled at b.p. 162°C. N-methyl piperidone (Merck, Germany) was freshly distilled at b.p. 155°C, benzoyl chloride (Aldrich, Seelze, Germany) was used as purchased. Terephthaloyl chloride and isophthaloyl chloride (Aldrich, Seelze, Germany) were recrystallized twice from n-hexane (m.p. 83–84°C and 40°C, respectively). Adipoyl and sebacoyl dichlorides [16], freshly distilled at 125°C/11 Torr, and at 182°C/16 Torr, respectively, were used. Anhydrous aluminum chloride and sodium hydroxide (BDH, Leicestershire, England), were of analytical grade and were used as received.

Solvents

Methanol, 99.8%, ethanol, 99.9% (Hayman, Eastways Withan, England), acetone and N,N-dimethyl formamide (DMF), (BDH, Leicestershire, England), N-methyl-2-pyrrolidone (NMP) and benzene (Aldrich, Seelze, Germany) were extra pure solvents and were used as received. Carbon disulphide (Aldrich, Seelze, Germany) was a guaranteed reagent, dried over calcium hydride for 24 h, and followed by distillation under reduced pressure.

Methods

Monomer Syntheses: Synthesis of 2,6-bis furfurylidene N-methyl piperidone **(2,6-BFNP)**

A mixture of 0.1 mole N-methyl piperidone and 0.2 mole of furfural in warm ethanol was stirred, and few drops of NaOH (20% conc.) was added.

The reaction mixture was stirred at room temperature for 1 h, and the resulting solid was collected by filtration, washed with cold water, dried and recrystallized from ethanol as yellow needles; yield 95%, m.p. 141–2°C. Calculated for $C_{16}H_{15}O_3N$: C, 71.38; H, 5.58; N, 5.20%. Found: C, 70.96; H, 5.36; N, 5.02%. IR (KBr, cm^{-1}): at 1600 (s, C=C), at 1670 (s, C=O). ^{1}H-NMR ($CDCl_3$, ppm), at 7.0–8.0 (m, 6H of furfuryl moieties and 2H of 2CH=C); at 2.6 (s, 4H of $2CH_2$ piperidone moiety); and at 1.7 (s, 3H of N-methyl).

Synthesis of 2,6-bis(benzylidene) N-methyl Piperidone **(2,6-BBNP)**

This monomer was prepared as described previously [17].

Synthesis of Model Compound **(2,6-BDBNP)**

In a 250 ml round-bottomed flask equipped with a magnetic stirrer and a nitrogen inlet and outlet, was placed a solution of 1 mmole 2,6-bis furfurylidene N-methyl piperidone **(2,6-BFNP)** and 2 mmole of benzoyl chloride in 40 ml of dry carbon disulphide. The flask was purged with nitrogen while stirring and 20 mmole of anhydrous aluminum chloride was added portion wise to the solution. The solution was stirred for 24 h at 25°C, and the separated solid product was filtered off, washed with water and dried in vacuum at room temperature. An analytical sample was obtained by recrystallization from benzene as yellow needles, yield 75%, m.p. 179°C. Calculated for $C_{30}H_{23}O_5N$: C, 75.47; H, 4.82; N, 2.49. %. Found: C, 75.15; H, 4.51; N, 2.19%. IR (KBr, cm^{-1}): at 1665 (C=O of piperidone), at 1710 (C=O of benzoate group), at 1605 (C=C group). ^{1}H-NMR (DMSO-d_6, ppm), at 7.2–8.5 (m, 4H, furfuryl moiety, 10 H Ar-H, and 2H of 2CH=C), at 2.6 (s, 4H of $2CH_2$ piperidone moiety); and at 1.7 (s, 3H of N-methyl).

Polymerization Procedure

Synthesis of Polyketones **A-D**

Friedel-Crafts method was used for the preparation of all the polymers. All polymers and copolymers were synthesized by essentially the same experimental procedure, which will be given here for the preparation of polymer **A**. In a dry 250 ml three-necked round-bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet, was placed a solution of 1.614 g (6 mmole), 2,6-bis furfurylidene N-methyl piperidone **(2,6-BFNP)** and 1.218 g (6 mmole) of terephthaloyl chloride in 25 ml of dry carbon disulphide. The flask was purged with nitrogen while stirring and 2.660 g (20 mmole) of aluminum chloride was added during the nitrogen flash. The reddish brown reaction mixture was stirred for 24 h. Then it was filtered off and the separated product was triturated three times with a large excess of methanol.

The polymer was isolated by filtration, washed successively with methanol and acetone, and dried in a vacuum oven at 75°C to constant weight. Polymer samples were purified by repeated precipitation from their solutions in DMSO using methanol as a non-solvent. The precipitated polymers were isolated, washed, and dried to constant weights.

Synthesis of Copolyketones **E** *and* **F**

The same method applied in the synthesis of the polyketones, was also applied in the synthesis of the copolyketones.

Typically, in a 250-ml round-bottomed flask equipped with a magnetic stirrer and, nitrogen inlet and outlet, was placed a solution of 0.708 g (3 mmole), 2,6-bis furfurylidene N-methyl piperidone **(2,6-BFNP)** and 0.867 g (3 mmole) of 2,6-bis (benzylidene)-N-methyl piperidone **(2,6-BBNP)** and 1.208 g (6 mmole) of terephthaloyl chloride in 50 ml of dry carbon disulphide. The flask was purged with nitrogen while stirring, and 2.66 g (20 mmole) of aluminum chloride was added during the nitrogen flush. The reddish brown reaction mixture was stirred for 24 h. Then it was filtered off and the separated product was triturated three times with a large excess of methanol. The polymer was isolated by filtration, washed successively with methanol and acetone, and dried in a vacuum oven at 75°C to constant weight. Polymer samples were purified by repeated precipitation from their solutions in DMSO using methanol as a non-solvent. The precipitated polymers were isolated, washed, and dried to constant weights. This method was applied for the synthesis of copolyketone **F**.

Polymer Identification

Infrared spectra of the prepared polymers were measured on a Nicolet 6700 FT-IR Thermo Fisher Scientific Inc. (USA).The samples were powders of similar weight and mixed with KBr. All spectra were recorded within the wave number range of 4000–400 cm^{-1} at 25°C. Elemental analyses of the prepared monomers, model compound, and polymers were performed at the Micro Analytical Unit, Assiut University, Egypt.

Polymer Characterization

Viscosity

Inherent viscosity measurements were carried out on solutions of the polymers in NMP at 30°C using a suspended-level Ubbelohde viscometer with negligible kinetic energy correction. Flow times were measured on 0.5% and 4 lower concentrations of the polymer sample. All the plots obtained were linear. Inherent viscosity was determined by the usual extrapolation of $\eta_{\text{sp}}/\text{c}$ to zero concentration and expressed in deciliter per gram (dL g^{-1}).

Solubility

The solubility of polymers in various solvents such as DMF, DMSO, and NMP was determined at room temperature (30°C). It was performed by gradual addition of the polymer to the solvent and stirred well till saturation. The maximum solubility of the polymers were calculated as percent weight of the polymer per hundred milliliter of solvent (% w/v).

Scanning Electron Microscopy Measurements

The morphology of polyketone **A** as example was examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) curves were recorded on a Shimadzu TGA-50 H in air atmosphere at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ and a heating range from room temperature to 700°C. The sample weights ranged from 3 to 5 mg, and the gas flow rate was $30\,\mathrm{ml\,min^{-1}}$.

X-ray Measurements

X-ray diffractographs of the polymers were obtained with a Philips X-ray pw 1710 diffractometer. X-ray source was Cu Ka (40 kV/15 mA). The samples were maintained stationary while scattering angles (2θ) from 5° to 60° were scanned in the reflection mode at a scanning rate of $1^\circ\,\mathrm{min^{-1}}$.

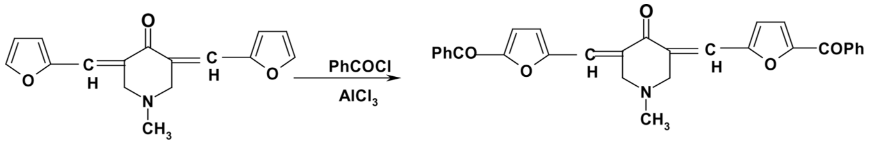
Antimicrobial Properties

The antimicrobial screening of polyketones and copolyketones (**A-D**, **E**, **F**) were performed using the standard agar diffusion method, against different organisms (fungal and bacterial species) including: *Aspergillus flavus, Aspergillus niger, Candida albicans, Geotrichum candidum, Trichophyton rubrum, Escherichia coli, Pseudomonas aeruginosa,* and *Staphylococcus aureus*. The fungal species were maintain on sabourand dextrose agar (SDA) whereas the bacterial species were maintain on nutrient agar (NA).

RESULTS AND DISCUSSION

Synthesis of Model Compound

Before attempting polymerization, the model compound was synthesized by the interaction of one mole of 2,6-bis furfurylidene N-methyl piperidone **(2,6-BFNP)** with two moles of benzoyl chloride via Friedel-Craft reaction at room temperature as shown in Scheme 1.



Scheme 1: Synthesis of model compound.

The structure of the model compound was checked on the basis of good agreement between calculated and found analytical data, FTIR and ^{1}H-NMR (see experimental part).

Polymer Syntheses

Six novel polyketones and copolyketones polymers containing N-methylpiperidinone in the main chain have been synthesized. In order to determine an adequate catalyst for the this synthesis, Friedel-Crafts polycondensation of 2,6-bis furfurylidene N-methyl piperidone **(2,6-BBNP)** with terephthaloyl chloride (as an example) (polymer **A**) was carried out in the presence of various Lewis acids such as: $FeCl_3$, $SbCl_5$, and $AlCl_3$. It appeared that anhydrous $AlCl_3$ gave the best result with respect to yield and degree of polymerization. The favorable mole ratio of catalyst to each reactant was ca. 2.0. The polymerization and copolymeriztion reactions were carried out at room temperature in carbon disulphide as a solvent and anhydrous aluminum chloride as a catalyst. The reaction times varied from 20 to 24 h and the polymers and copolymers were immediately isolated when the reaction mixtures were poured into methanol/water mixture, with yield in the range of 68–85%. The polymers were obtained as brown to black-brown powders. Brown color is the characteristic of a Friedel–Craft products obtained from benzene and its derivative [18].

Polymer Identification

The structure of the prepared polymers is proposed on the basis of their elemental analyses and IR spectra. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer, as shown in Table 1. It should be noted that the elemental analyses of these polymers deviated up to 1.90% from the theoretical values. However, it is not uncommon for polymers to trap solvent molecules within the polymer matrix. On the other hand, FTIR data supported the chemical structure of the repeating unites in the polymers as shown in reaction Schemes 2 and 3. All the polymers have a strong absorption near 1690 cm^{-1}, which is assigned to C=O stretching of aromatic ketone and absorption near 1670 cm^{-1}, which is assigned to C=O stretching of N-methylpiperidinone [19]. The medium to strong absorption

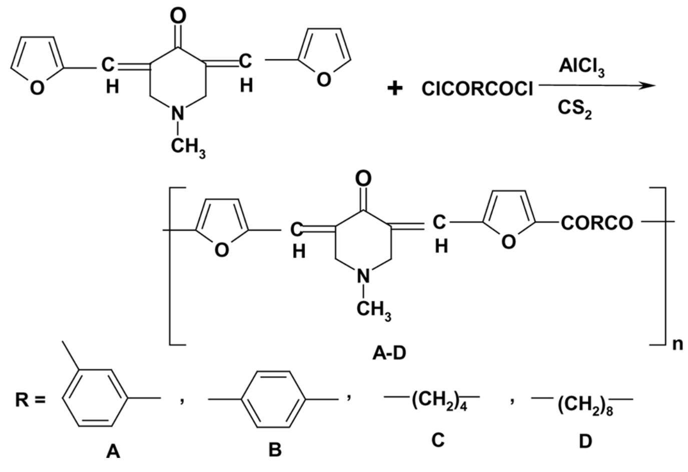
Table 1: Elemental analyses, inherent viscosity, yield and color of polyketones **A-D** and copolyketones **E** and **F**.

Polymer Code	Repeating unit	C%		H%		N%		η_{inh} (dL/g)	Yield %	Appearance of polymer
		Calcd.	Found	Calcd.	Found	Calcd.	Found			
A	$C_{24}H_{17}O_5N$	72.18	71.43	4.26	4.02	3.51	3.19	0.48	68	brownish
B	$C_{24}H_{16}O_5N$	72.18	70.92	4.26	3.89	3.51	3.26	0.53	73	brownish
C	$C_{22}H_{20}O_5N$	69.66	71.56	5.54	5.22	3.69	3.41	0.65	76	brownish
D	$C_{26}H_{28}O_5N$	71.72	70.24	6.67	6.37	3.22	2.89	0.69	69	brownish
E	$C_{51}H_{34}O_8N_2$	76.12	74.87	4.48	4.18	3.48	3.07	—**	85	brownish
F	$C_{47}H_{42}O_8N_2$	73.82	72.72	5.76	5.25	3.66	3.35	0.57	81	deep-brown

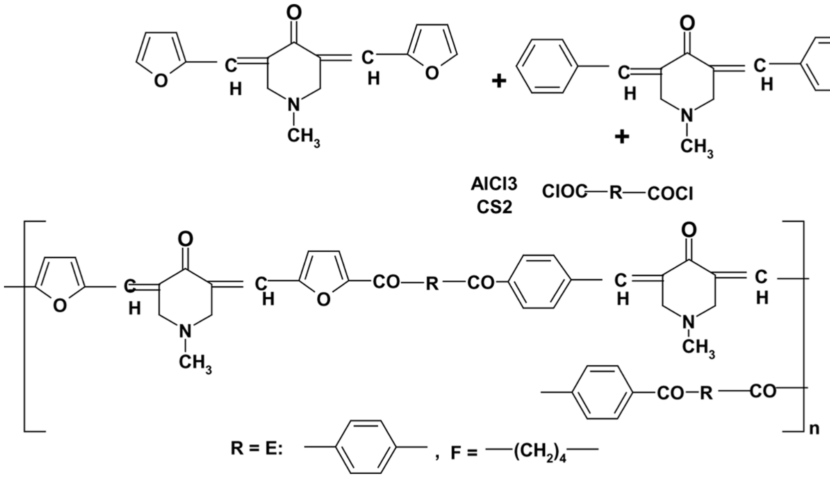
*η Inherent viscosity measured in NMP at 30°C.
**Partially soluble in NMP.

around 1590 cm^{-1} is attributed to C=C stretching. The phenyl ring vibrations are assigned to absorption near 1600 and 1500 cm^{-1}. The CH_3 asymmetric and symmetric bending modes are traced to 1450 and 1350 cm^{-1}, respectively. The CH_2 bending mode also appears around 1455 cm^{-1}. The medium strong peak at 830 cm^{-1} may be assigned to CH out-of-plane bending in the benzene ring having two adjacent hydrogen [20]. The absorption at 770 cm^{-1} has variable intensity. This peak is attributed to CH out-of-plane bending in benzene ring having two adjacent hydrogens [21].

Moreover, it would be expected that all of these polymers have similar structural formula except for the presence of methylene linkage $-(CH_2)_4-$, $-(CH_2)_8-$ or aromatic nuclei in their main chains. This expectation was evidenced experimentally by comparing the IR spectra of these polymers in the region of 3100–2990 cm^{-1}, which is characteristic for stretching vibration bands of these groups. Furthermore, polymers **A**, **B**, and **D** showed bands at



Scheme 2: Synthesis of polyketones **A-D**.



Scheme 3: Synthesis of copolyketones **E** and **F**.

1275 and 1150 cm^{-1}, which correspond to the asymmetric and symmetric stretching of the C-H aromatic groups, respectively. Thus, the results of elemental analyses coupled with the results of IR spectra seemed to be in good agreement with the expected structures of the prepared polymers, which are illustrated in Schemes 2 and 3.

Polymer Characterization

Viscosity

The inherent viscosities (η_{inh}) of polyketones **A-D** and copolyketones **E**, **F** were determined in NMP at 30°C with an Ubbelohde suspended level viscometer The inherent viscosity value is defined as:

$$\eta_{\mathrm{inh}} = [2.3\ \log \eta/\eta_{\mathrm{o}}]/\mathrm{C}$$

The solution concentration C is 0.5 g/100 ml, η/η_{o} = relative viscosity (or viscosity ratio). It can be seen from Table 1 that polyketone **D** had high viscosity (0.69 dL/g) and this may be attributed to high molecular weight of the polymer. But the inherent viscosity of the polyketone **A** (0.48 dL/g) may be attributed to the low molecular weight of this polymer.

On comparing the inherent viscosity, η_{inh} values for all the synthesized polyketones, it was found that η_{inh} values varied from series to another series, where polyketones containing aliphatic chain (polymers C,D) had higher values than those containing aromatic chain. The order of higher η_{inh} values is: polyketones **D** > **C** > **F** > **B** > **A**, this may indicate that the these polymers had difference in their molecular weight.

Solubility

Room temperature solubility characterizations of polyketones **A-D** and copolyketones **E**, **F** were tested using various solvents including : DMF, DMSO, NMP, chloroform–acetone (1:1; v/v), methylene chloride, formic acid and conc. H_2SO_4. A 5% (w/v) solution was taken as a criterion for solubility. It is clear from Table 2 that all the polyketones **A-D** were insoluble in most common organic solvents such as alcohols, benzene, and acetone but dissolved completely in concentrated sulfuric acids giving an orange to red colors. It can be clarified from Table 2 that, the majority of the polymers and copolymers were partially soluble in polar aprotic solvents like DMSO and DMF except copolyketone F which is completely soluble. In other polar aprotic solvents such as NMP it was found that all the polymers and copolymers were completely soluble except polymer **E** which is partially soluble. Moreover, it was found that all the polymers and copolymers were completely insoluble in chloroform–acetone mixture and methylene chloride except polymer D which is completely soluble.

On comparison between the solubility of the polymers based on aliphatic chains with those based on aromatic, it was found that, the former series is slightly more soluble in aprotic solvents (eg. DMSO, DMF, DMA) than the latter polymers. This may be attributed to the higher flexibility of the aliphatic chains as described in our previous works [22,23].

Scanning Electron Microscopy Measurements

The morphology of the synthesized polyketone **A** (as example) was examined by scanning electron microscopy (SEM). The sample was prepared by putting a smooth part of polymer powder on a copper holder and subsequently coating it with gold palladium alloy. SEM images were taken on a penta Z Z-50 P Camera with Ilford film at an accelerating voltage of 15 Kv using a low-dose technique [24]. This technique gives us the ability to show the

Table 2: Solubility characteristics of polyketones **A-D** and copolyketones **E** and **F**.

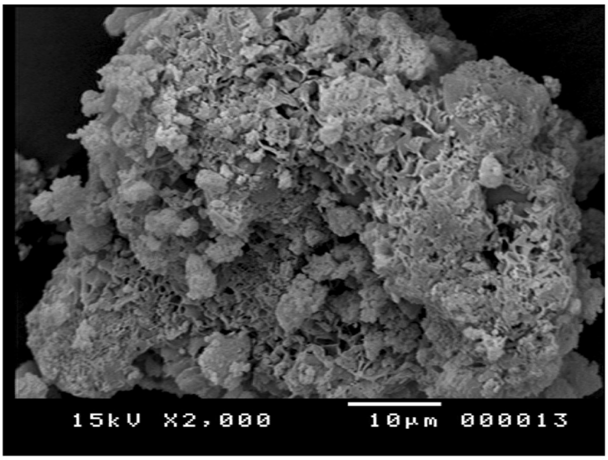
Polymer code	DMSO	DMF	NMP	Chloroform acetone	THF	Methylene chloride	Triflouroacetic acid	H_2SO_4
A	±	±	+	±	±	±	+	+
B	±	±	+	±	±	−	+	+
C	±	±	+	±	±	−	+	+
D	+	+	+	+	±	±	+	+
E	±	±	±	±	±	±	+	+
F	+	+	+	±	±	±	+	+

(+) Soluble at room temperature RT.
(±) Partially soluble at RT.
(−) Insoluble.

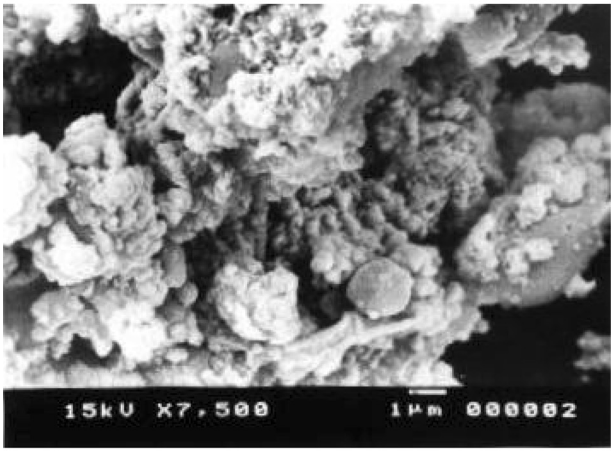
surface of the polymers and to study the effect of structure on the surface of the selected polymer by comparison the images in each case. The study of selected polymer **A** showed that the surface of polyketone **A** (Figure 1a magnification X = 2000) consisted of porous cavities among the aggregated particles, with higher magnification X = 7500 (Figure 1b) shows a similar nature.

X-ray Measurements

The typical wide-angle X-ray diffraction patterns of polyketones **A-D** are shown in Figure 2. It can be clarified from this figure, all the polyketones showed a halo pattern in the region $2\theta = 10–50^\circ$, this indicate that all these polymers are amorphous. While, the X-ray diffractogram of polymer **D** showed



(a)



(b)

Figure 1: SEM image of polyketone A: (a, X = 2000 and b, X = 7500).

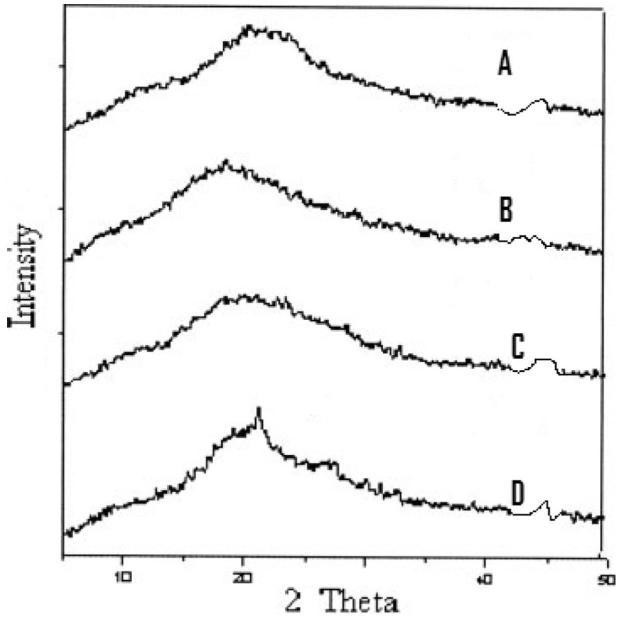


Figure 2: X-ray diffractograms of polyketones **A-D**.

low degree of crystallinity, in the region $2\theta = 10–50°$. This indicates that this polymer is semicrystalline, due to the presence of flexible aliphatic chain (eight methylene groups) in the polymer main chain. Moreover, the presence of C=O, C=C, polar groups, induces some order between two adjacent chains of the polymers, leading enhancement of crystallinity [25].

Thermogravimetric Analysis

The thermal properties of polyketones **A-D** and copolyketones **E** and **F** containing N-methylpiperidinone unit thus obtained were investigated with the aid of thermogravimetric analysis (TGA), DTG and DTA in air at a heating rate of 10°C/min. The thermographs of these polymers are given in Figure 3 (Polymer A as example), also Table 3 gives the temperature of various percentages of weight loss. In Figure 3, TGA curve of polyketone **A** show a weight loss in the range 8–19% starting at 160–200°C which may be attributed to loss of absorbed moisture and entrapped solvents. The thermographs also indicate, the polymers decompose in two stages. The first stage which is rapid stage between 400 and 430°C depends upon the nature of the polyketones. This result is in good agreement with decomposition of ketone-linkage observed by Swedo and Marvel [26]. The second stage of degradation of polyketones occurred between 435 and 550°C. The rate of degradation in the first stage is somewhat faster than in the second stage. A comparison of the weight loss values (at 300–700°C) of polyketones **A**, **B** containing aromatic moiety showed

Table 3: Characteristic temperature for thermal degradation of polyketones **A-D** and copolyketones **E**, **F** evaluated from TGA.

Polymer number	Polymer weight loss (%) at temperature up to 700°C				
	300°C	**400°C**	**500°C**	**600°C**	**700°C**
A	8	17	76	82	89
B	7	19	74	81	88
C	12	28	79	82	93
D	14	32	75	85	90
E	10	22	79	83	93
F	13	34	79	87	92

better thermal stability than others based on aliphaticmoiety **C**, **D**. Moreover, the data indicated that the copolyketone **E** is more thermally stable than the copolyketone **F** and this may be attributed to the presence polymethylene groups $(CH_2)_4$ in as flexible spacers in the polymer main chain in the later copolyketone, which decreases the stability. Most long chain synthetic polymers show characteristic sequence of decomposition stages as they are heated. For DTA trace of polyketone A, in Figure 3, a broad endothermic at 480°C (T_1), at 510°C (T_2) and at 530°C (T_3).

Antimicrobial Screening

The antimicrobial screening of polyketones **A-D** and copolyketone **E** were performed, using the standard agar diffusion method, against different organisms (fungal and bacterial species) including: *Aspergillus flavus, Aspergillus niger, Candida albicans, Geotrichum candidum, Trichophyton rubrum, Escherichia coli, Pseudomonas aeruginosa,* and *Staphylococcus aureus*.

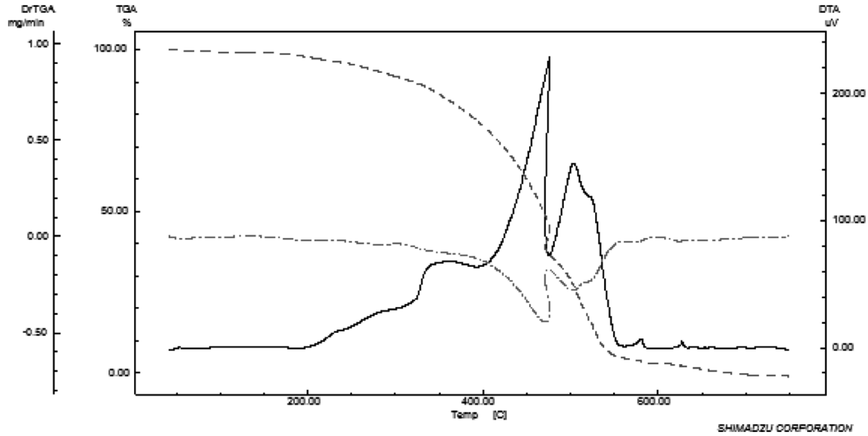


Figure 3: TGA, DTA DrTGA curves of polyketone A (TGA:__, DrTGA:—, DTA:__).

The fungal species were maintain on sabourand dextrose agar (SDA) whereas the bacterial species were maintain on nutrient agar (NA). Similar inhibitory effects were obtained by several authors who dealt with antifungal and antibacterial activities of different polyketone derivatives. Patel and Patel [27] pointed out that chlorine containing polyketones exerted an inhibitory effect against some fungi, yeast and bacteria including: *Aspergillus niger, Penicillium chrysogenum, R. minuta, S. cerevisiae, P. stipitis, P. fluorescens, B. subtils* and *E. coli species*.

Antifungal and antibacterial activities of the tested polymers were determined as described before [28,29]; the size of the resulting inhibition zone is shown in Table 4. It can be seen from Table 4 that all the selected polyketones and copolyketones showed no significant antifungal activity against the selected fungi.

On the other hand, it was clear that the majority of the selected polyketones and copolyketones showed a moderate antibacterial activity against *Trichophyton rubrum, Bacillus cereus, Serratia marcescens* and *Staphylococcus aureus*, except polyketones **D** and **E** against *Trichophyton rubrum*, polyketone **E** against *Aspergillus flavus*, polyketone **A** against *Geotrichum candidum* and polyketone **E** against *Staphylococcus aureus*. Only polyketones **A**, **B**, **E** showed a strong antibacterial activity against *Trichophyton rubrum* compared with the control values (13, 17/8, respectively). Polyketones **B**, **C**, **D**, **E** showed strong antibacterial activity against Geotrichum candidum (11/20/10/8 respectively), and polyketones **A**, **B**, **C**, **D** showed strong antibacterial activity against Staphylococcus aureus (14, 8/15/14 respectively). On the other hand, the rest of the selected polymers and copolymers showed weak significant influences.

These results, graphically shown in Figure 4, indicate that the polyketones significantly inhibit the growth of some microorganisms. It is clear from this Figure that the control culture (without polymer sample) generally

Table 4: Effect of polyketones **A**, **C**, **D** and copolyketones **E**, **F** on the growth of fungal and bacterial species.

	Polyketone number inhibition zone (mm)					
Type of organism	**A**	**C**	**D**	**E**	**F**	**Control**
Aspergillus niger	0	0	0	0	0	18
Candida albicans	0	0	0	0	0	28
Trichophyton rubrum	13	17	0	0	8	24
Aspergillus flavus	8	8	10	16	0	25
Escherichia coli	0	0	0	0	0	24
Pseudomonas aeruginosa	0	0	0	0	0	16
Geotrichum candidum	0	11	20	10	8	32
Staphylococcus aureus	14	8	15	14	0	22

Control: (Antibacterial = Chloramphenicol, Antifungal = Trosyd).

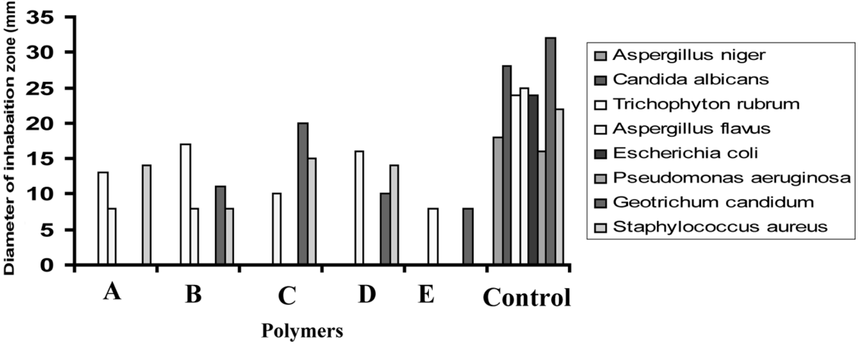


Figure 4: Effect of polyketones and copolyketones on the growth (%) of bacteria.

exhibits maximum growth. On the other hand, the polymers samples give different growth which may be attributed to polymer structures. We believe that more work is needed to identify the moiety that is most important in the different structures for higher antimicrobial activity. This will be done in our next work.

CONCLUSION

Six novel polyketones and copolyketones based on 2,6-bis furfurylidene N-methylpiperidone have successfully been synthesize via Friedel–Crafts reaction. Polymers properties were strongly affected by their structural differences. In general, the introduction of the flexible aliphatic linkages leads to polymer of a higher solubility in NMP. X-ray diffraction analyses indicated that most of the polymers are amorphous. All the prepared polymers are highly thermally stable and thermogravimetric analyses showed that the polyketones based aliphatic chains were somewhat less thermally stable than the aromatic based polymers. All the polymers showed antimicrobial activity.

REFERENCES

[1] Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R. J., Rose, J. B., and Staniland, P. A. *Polymer* **22**, 1096 (1981).

[2] Staniland, P. A., Eastmond, G. C., Ledwith, A., Russo, S., and Sigwalt, P. (Eds.), (1989). *Comprehensive Polymer Science*, vol. 5, Pergamon Press, Oxford, UK, p. 483.

[3] Yonezawa, N. *J. Synth. Org. Chem. Jpn.* **53**, 172 (1995).

[4] Abd-Alla, M. A., Aly, K. I., and Hammam, A. S. *High Perform Polym.* **1**, 23 (1989).

[5] Abd-Alla, M. A., and EI-Shahawy, A. S. *Polymer* **33**, 1525 (1992).

[6] EI-Shahawy, A. S., and Abd-Alla, M. A. *Macromolecules* **24**, 5528 (1991).

[7] Abd-Alla, M. A., El-Zohry, M. F., and Osaman, M. A. *Polym Bull.* **25**, 287 (1991).

[8] Aly, K. I., and Khalaf, A. A. *J Appl Polym Sci.* **77**, 1218 (2000).

[9] Osaman, M. A., Othman, A., and Abd-Alla, M. A. *Polymer* **33**, 52 (1992).

[10] Abd-Alla, M. A., Hammam, A. S., Kandeel, M. M., and Aly, K. I. *J Macromol Sci-Chem.* **27**, 5 (1990).

[11] Aly, K. I., Abbady, M. A., Mahgoub, S. A., and Hussein, M. A. *Polym Int.* **51**, 1253 (2002).

[12] Aly, K. I. *Polym Int.* **47**, 483 (1998).

[13] Kuchkov, B. P., Finn, G. R., Entsova, L. L., and Mozgina, A. A. *Tr. Volgogr. Gos. Med. Inst.* **21**, 486 (1968).

[14] Ackant, W. B., Camp, R. L., Wheelright, and Byck, W. L. J. S. *J. Biomed. Mater. Res.* **9**, 55 (1975).

[15] Tarason, V. N., and Boldasov, V. K. *Voen.-Med. Zh.* **9**, 3 (1967).

[16] Vogel, A. (1967). *Text Book of Practical Organic Chemistry*, Longmans Green, London, 1, p. 464.

[17] Aly, K. I., and Al-Muaikel, N. S. *European Polymer Journal* (Submitted).

[18] Aly, K. I. *Journal of Applied Polymer. Science.* **94**, 1440 (2004).

[19] Colthup, N. B., Daly, L. H., and Wiberley, S. E. (1990). *Introduction to Infrared Spectroscopy*, Academic Press, New York.

[20] Bellamy, L. J. (1975). *Infrared Spectra of Complex Molecules*, Chapman & Hall, London.

[21] Williams, D. H., and Fleming, I. (1988). *Spectroscopic Methods in Organic Chemistry*, 4th Ed, Tata McGraw Hill, New Delhi.

[22] Aly, K. I., Wahdan, M. H., and Hussein, M. A. *Journal of Applied Polymer Science* **112**, 513 (2009).

[23] Aly, K.I., Abbady, M. A., Mahgoub, S. A., and Hussein, M. A. *Journal of Applied Polymer Science* **112**, 620 (2009).

[24] Tager, A. (1972). *Physical Chemistry of Polymers*, Mir, Moscow.

[25] Mandelkern, L. (1964). *Crystallization of Polymers*, McGraw-Hill, New York.

[26] Swedo, R. J., and Marvel, C. S. *J. Polym. Sci.* **17**, 2815 (1979).

[27] Patel, B. T., and Patel, R. M. *Intern. J. Polymeric Mater* **41**, 199 (1998).

[28] Namba, T., Tsunezuka, M., and Masao, H. *Planta Medica* **44**, 100 (1982).

[29] Pai, S. T., and Platt, M. W. *Letters in App. Microbiology* **20**, 14 (1995).