

# Synthesis, Characterization and Antimicrobial Properties of New Poly(ether-ketone)s and Copoly(ether-ketone)s Containing Diarylidencycloalkanone Moieties in the Main Chain

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Received 4 March 2007; accepted 8 December 2007

DOI 10.1002/app.27963

Published online 29 February 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new category of linear poly(ether-ketone)s **IV**<sub>a-d</sub> and copoly(ether-ketone)s **V**<sub>a-f</sub> containing diarylidencycloalkanone moieties in the main chain has been synthesized by solution polycondensation of 4,4'-bis(chloroacetyl)diphenylether **I**, with different phenoxides of diarylidencycloalkanones **II**<sub>a-d</sub>. The model compound **III** was synthesized from the monomer **I** with sodium phenoxide in DMF and K<sub>2</sub>CO<sub>3</sub>, and its structure was confirmed by elemental and spectral analyses. The resulting polyketones and copolyketones were characterized by elemental and spectral analyses, beside solubility and viscometry measurements. The thermal properties of those polymers

were evaluated by TGA and DTA measurements and correlated to their structural units. X-ray analysis showed that polymers having some degree of crystallinity in the region  $2\theta = 5-60^\circ$ . In addition, the biological screening and morphological properties of selected examples of the polymers were tested. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3138–3147, 2008

**Key words:** synthesis; characterization; diarylidencycloalkanone; diaryl ether; poly(ether-ketone)s; copolymerization; thermal properties; morphology; high-performance polymers

## INTRODUCTION

Poly(ether-ketone)s are a desirable class of polymers, which are drawing attention of the researchers worldwide. However, new publications, mainly in the form of patents, are presented. This desirability stems from their extremely high thermal stability.<sup>1</sup> Poly(ether-ketone) blends are becoming important components in specific sectors of the polymer industry.<sup>2</sup> Surgical instruments are made from carbon-fiber-reinforced poly(ether-ketone)s.<sup>3</sup> The key application areas are the aerospace, electrical, nuclear, and oil industries; bearing films; coatings; and ultra-filtration membranes.<sup>4-8</sup> During the last decade, extensive work was carried out to prevent degradation of various chemical compounds using certain biocides, especially those based on the polymeric system.<sup>9</sup> A biocompatible polymeric material for medical application comprises of polymer having functionalized ketone groups.<sup>10</sup> Dubey et al.<sup>11</sup> synthesized a series of poly(ether-ether-ketone)s using K<sub>2</sub>CO<sub>3</sub> as a catalyst, and diphenyl sulfone as a solvent. Rao et al.<sup>12</sup> synthesized another polymer by

the nucleophilic substitution reaction of 4,4'-difluorobenzophenone with 4,4'-dihydroxy benzophenone and 4,4'-difluorodiphenyl benzophenone with anhydrous K<sub>2</sub>CO<sub>3</sub> in benzophenone medium.

In continuation of our interest in the study of synthesis, properties and applications of polyketones based on diarylidencycloalones,<sup>13-18</sup> we wish to report here a route for the synthesis of and characterization of some new poly(ether-ketone)s and copoly(ether-ketone)s based on diarylidene-cycloalkanones. The major aim of this work has been to investigate the effect of inclusion of cycloalkanone moieties on the polymer properties. In addition, other characteristic of these new polymers such as thermal stability, solubility, antimicrobial screening and crystallinity, were discussed.

## EXPERIMENTAL

### Measurements

Elemental analyses were carried out using VARIOEL, V<sub>2.3</sub> (Elemental Analyses system) July 1998 CHNS Mode. IR spectra were recorded on IR-470, Infrared spectrophotometer, Shimadzu (Japan) by using the KBr pellet technique. The <sup>1</sup>H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature in DMSO-d<sub>6</sub> or

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$\text{CDCl}_3$  using TMS as the internal reference. Mass spectra were recorded on a Jeol JMS<sub>600</sub> mass spectrometer. The solubility of polymers was examined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. The X-ray diffractographs of the polymers were obtained with a Philips X-ray pw 1710 diffractometer, and Ni-filtered  $\text{CuK}\alpha$  radiations. Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) analysis were carried out in air with TA 2000 thermal analyzer at heating rate of  $10^\circ\text{C}/\text{min}$  in air.

### Reagents and solvents

Diphenylether (Merck), cyclopentanone (Merck) and cyclohexanone (Merck) were used without purification. Aniline and Pyridine from El-Nasr Chemical Company (Egypt) were freshly distilled (b.p.  $183\text{--}184^\circ\text{C}$ , b.p.  $115\text{--}116^\circ\text{C}$ , respectively). Benzene and all other solvents were of high purity and were further purified by standard methods.<sup>19</sup>

### Monomers' syntheses

Bis (4-chloroacetyl) diphenylether **I** and diarylidene-cycloalkanones **II<sub>a-d</sub>** were prepared as described in our previous papers.<sup>14,15,17</sup>

### Synthesis of model compound

#### General procedure

A mixture of bis (4-chloroacetyl)diphenylether **I** (0.002 mol), sodium phenoxide (0.004 mol), 0.50 g anhydrous potassium carbonate and 20 mL DMF were introduced. The reaction mixture was stirred vigorously, while the temperature increased at  $160^\circ\text{C}$ , and was maintained for 18 h. After cooling to room temperature, the reaction mixture was precipitated in cold water. The precipitated products were isolated by filtration, then washed with water, and recrystallized from DMF/ $\text{H}_2\text{O}$  (m.p.  $> 360^\circ\text{C}$  (decompose, yield 65%).

Anal. Calcd. for  $\text{C}_{28}\text{H}_{22}\text{O}_5$ : Calcd %: C, 76.71; H, 5.02. Found %: C, 76.49; H, 4.88.

### Polymer syntheses

A solution polycondensation technique was used in the synthesis of poly(ether-ketone)s **IV<sub>a-d</sub>** as the following.

#### General procedure

In a three-necked flask, equipped with a condenser, a magnetic stirrer and dry nitrogen inlet and outlet, a mixture of 4 bis (4-chloroacetyl)diphenylether **I** (0.002 mol), sodium salt of diarylidene-cycloalkanones **II<sub>a-d</sub>** (0.002 mol), 0.50 g anhydrous potassium carbonate and 20 mL DMF were introduced. The

reaction mixture was stirred vigorously, while the temperature increased at  $160^\circ\text{C}$ , and was maintained for 16–19 h. After cooling to room temperature, the reaction mixture was precipitated in ice-water/methanol. The formed polymer was isolated by filtration, then washed three times with water, hot methanol and finally with hot acetone then dried under reduced pressure (1 mm/Hg) at  $80^\circ\text{C}$  for 48 h.

By using the above general procedure the following poly(ether-ketone)s **IV<sub>a-d</sub>** were obtained.

#### Poly(ether-ketone) **IV<sub>a</sub>**

Obtained by the polymerization of 4-bis (4-chloroacetyl)diphenylether **I** 0.6435 g, (0.002 mol) with sodium salt of 2,5-bis(4-hydroxybenzylidene)cyclopentanone **II<sub>a</sub>** 0.672 g, (0.002 mol) for 16 h as brown powder; yield 69.3%.

Anal. Calcd. for  $(\text{C}_{35}\text{H}_{26}\text{O}_6)_n$ : Calcd %: C, 77.49; H, 4.79. Found %: C, 77.19; H, 4.89.

#### Poly(ether-ketone) **IV<sub>b</sub>**

Obtained by the polymerization of 4 bis (4-chloroacetyl)diphenylether **I** 0.6435 g, (0.002 mol) with sodium salt of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone **II<sub>b</sub>** 0.792 g, (0.002 mol) for 17 h as deep-brown powder; yield: 64.5%.

Anal. Calcd. for  $(\text{C}_{37}\text{H}_{30}\text{O}_8)_n$ : Calcd %: C, 73.75; H, 4.98. Found %: C, 73.98; H, 5.09.

#### Poly(ether-ketone) **IV<sub>c</sub>**

Obtained by the polymerization of 4 bis (4-chloroacetyl)diphenylether **I** 0.6435 g, (0.002 mol) with sodium salt of 2,6-bis(4-hydroxybenzylidene)cyclohexanone **II<sub>c</sub>** 0.7016 g, (0.002 mol) for 17 h as black powder; yield 69%.

Anal. Calcd. for  $(\text{C}_{36}\text{H}_{28}\text{O}_6)_n$ : Calcd %: C, 77.69; H, 5.03. Found %: C, 77.38; H, 4.92.

#### Poly(ether-ketone) **IV<sub>d</sub>**

Obtained by the polymerization of 4 bis (4-chloroacetyl)diphenylether **I** 0.6435 g, (0.002 mol) with sodium salt of 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone **II<sub>d</sub>** 0.8246 g, (0.002 mol) for 16 h as brown powder; yield 67%.

Anal. Calcd. for  $(\text{C}_{38}\text{H}_{32}\text{O}_8)_n$ : Calcd %: C, 74.02; H, 5.19. Found %: C, 73.85; H, 5.13.

### Synthesis of copolymers

A solution polycondensation technique was used in the synthesis of such copolymers as the following.

### General procedure

In a three-necked flask, equipped with a condenser, a magnetic stirrer and dry nitrogen inlet and outlet, a mixture of 4 bis(4-chloroacetyl)diphenylether **I** (0.004 mol), two different sodium salts of diarylidene-cycloalkanones **II<sub>a-d</sub>** (each one 0.002 mol), 0.50 g anhydrous potassium carbonate and 20 mL DMF were introduced. The reaction mixture was stirred vigorously, while the temperature increased at 160°C, and was maintained for 18–20 h. After cooling to room temperature, the reaction mixture was precipitated in ice-water/methanol. The formed polymer was isolated by filtration, then washed three times with water, hot methanol and finally with hot acetone then dried under reduced pressure (1 mm/Hg) at 80°C for 48 h.

By using the above general procedure the following copoly(ether-ketone)s **V<sub>a-f</sub>** were obtained.

#### Copoly(ether-ketone) **V<sub>a</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with sodium salt of 2,5-bis(4-hydroxybenzylidene)cyclopentanone **II<sub>a</sub>** 0.672 g, (0.002 mol) and sodium salt of 2,5-bis(4-hydroxy-3-methoxybenzylidene)-cyclopentanone **II<sub>b</sub>** 0.792 g (0.002 mol) for 18 h as brown powder; yield: 71.3%.

Anal. Calcd. for (C<sub>56</sub>H<sub>44</sub>O<sub>11</sub>)<sub>n</sub>: Calcd %: C, 75.33; H, 4.93. Found %: C, 75.71; H, 5.04.

#### Copoly(ether-ketone) **V<sub>b</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with sodium salt of 2,5-bis(4-hydroxybenzylidene)cyclopentanone **II<sub>a</sub>** 0.672 g, (0.002 mol) and sodium salt of 2,6-bis(4-hydroxy-benzylidene)cyclohexanone **II<sub>c</sub>** 0.70 g, (0.002 mol) for 18 h as pale brown powder; yield: 69.4%.

Anal. Calcd. for (C<sub>57</sub>H<sub>46</sub>O<sub>11</sub>)<sub>n</sub>: Calcd %: C, 75.49; H, 5.07. Found %: C, 75.29; H, 4.89.

#### Copoly(ether-ketone) **V<sub>c</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with sodium salt of 2,5-bis(4-hydroxybenzylidene)cyclopentanone **II<sub>a</sub>** 0.672 g, (0.002 mol) and sodium salt of 2,6-bis(4-hydroxy-3-methoxybenzylidene)-cyclohexanone **II<sub>d</sub>** 0.82 g, (0.002 mol) for 17 h as brownish powder; yield: 70%.

Anal. Calcd. for (C<sub>59</sub>H<sub>50</sub>O<sub>13</sub>)<sub>n</sub>: Calcd %: C, 73.29; H, 5.17. Found %: C, 73.48; H, 5.10.

#### Copoly(ether-ketone) **V<sub>d</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with so-

dium salt of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone **II<sub>b</sub>** 0.792 g (0.002 mol) and sodium salt of 2,6-bis(4-hydroxybenzylidene)-cyclohexanone **II<sub>c</sub>** 0.70 g, (0.002 mol) for 18 h as brown powder; yield: 72%.

Anal. Calcd. for (C<sub>55</sub>H<sub>42</sub>O<sub>9</sub>)<sub>n</sub>: Calcd %: C, 75.65; H, 4.56. Found %: C, 75.69; H, 4.76.

#### Copoly(ether-ketone) **V<sub>e</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone **II<sub>b</sub>** 0.792 g (0.002 mol) and sodium salt of 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone **II<sub>d</sub>** 0.82 g, (0.002 mol) for 19 h as black powder; yield: 68.7%.

Anal. Calcd. for (C<sub>57</sub>H<sub>46</sub>O<sub>11</sub>)<sub>n</sub>: Calcd %: C, 75.49; H, 5.07. Found %: C, 75.27; H, 4.96.

#### Copoly(ether-ketone) **V<sub>f</sub>**

Obtained by the copolymerization of 4 bis(4-chloroacetyl)diphenylether **I** 1.293 g, (0.004 mol) with sodium salt of 2,6-bis(4-hydroxybenzylidene)cyclohexanone **II<sub>c</sub>** 0.70 g, (0.002 mol) and sodium salt of 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone **II<sub>d</sub>** 0.82 g, (0.002 mol) for 17 h as brown powder; yield: 71%.

Anal. Calcd. for (C<sub>58</sub>H<sub>48</sub>O<sub>11</sub>)<sub>n</sub>: Calcd %: C, 75.65; H, 5.21. Found %: C, 75.78; H, 5.18.

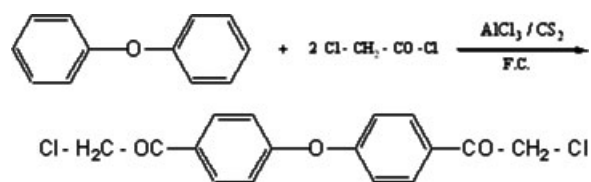
## RESULTS AND DISCUSSION

### Monomers' syntheses

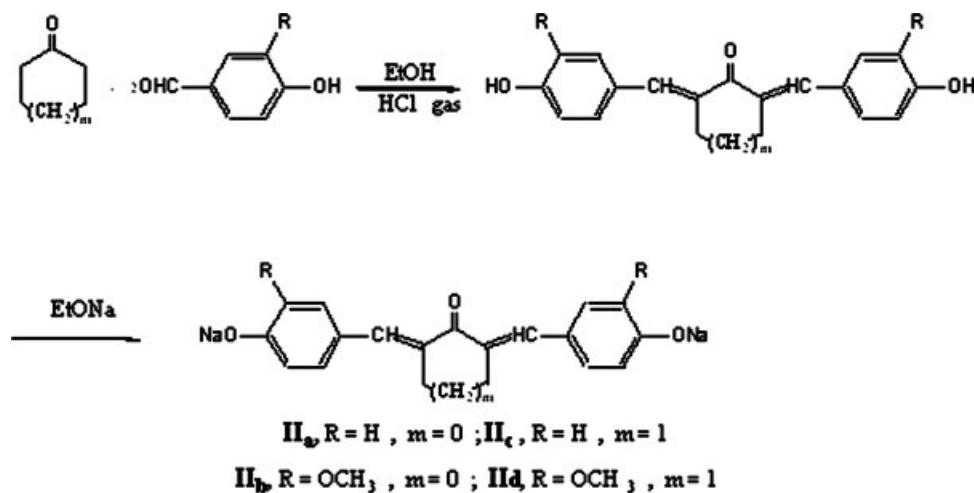
A new class of poly(ether-ketone)s which containing diaryl ether in the polymers main chain were synthesized. These polymers were necessitating the synthesizing of different monomers.

#### Synthesis of 4,4'-bis (chloroacetyl) diphenyl ether **I**

This monomer was synthesized in good yield by the interaction of 1 mol of diphenyl ether with 2 mol of chloroacetyl chloride using the normal condition of Friedel-Crafts reaction (anhydrous aluminum chloride and carbon disulphide) as shown in Scheme 1.



Scheme 1 Synthesis of monomer **I**.

Scheme 2 Synthesis of monomers  $\text{II}_{a-d}$ .

The synthesized monomer **I** was obtained as pale-yellow crystals and recrystallized twice or thrice before polymerization process. The structure of this monomer was confirmed by its elemental and spectral analyses (including IR,  $^1\text{H-NMR}$  and Mass spectra) as described in our previous paper.<sup>14</sup>

#### Synthesis of diarylidenecycloalkanones $\text{II}_{a-d}$

The preparation of diarylidenecycloalkane monomers by direct condensation of 1 mol of cycloalkane with two moles of *p*-hydroxybenzaldehyde or 4-hydroxy-3-methoxy-benzaldehyde in ethanol. The reaction of diarylidenecycloalkane monomers with sodium ethoxide gave easily their sodium salt  $\text{II}_{a-d}$  as shown in Scheme 2.

These monomers were purified by recrystallization twice or three times before using in the polymerization. Its structures were elucidated by correct elemental and spectral analyses as described in our previous work.<sup>14,15,17</sup>

#### Synthesis of model compound

Before attempting polymerization, the model compound **III** was synthesized by interacting 1 mol of 4,4'-bis(chloroacetyl)diphenyl ether **I** with two moles of sodium phenoxide in DMF and in the presence of anhydrous potassium carbonate according to Scheme 3.

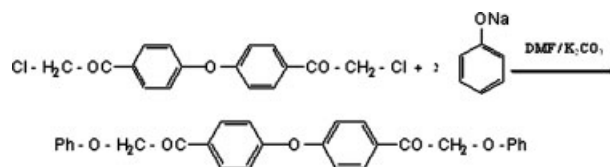
The structure of the model compound **III** was confirmed by correct elemental and spectral data. The IR spectrum showed the characteristic absorption bands at 1250–1270  $\text{cm}^{-1}$  due to C—O—C bonds (ether linkage). In addition, other characteristic bands at 1680  $\text{cm}^{-1}$  for the carbonyl of chloroacetyl group. The  $^1\text{H-NMR}$  spectrum of model compound (in  $\text{DMSO-d}_6$ , ppm) was in accordance with the proposed structure.

#### Synthesis of poly(ether-ketone)s

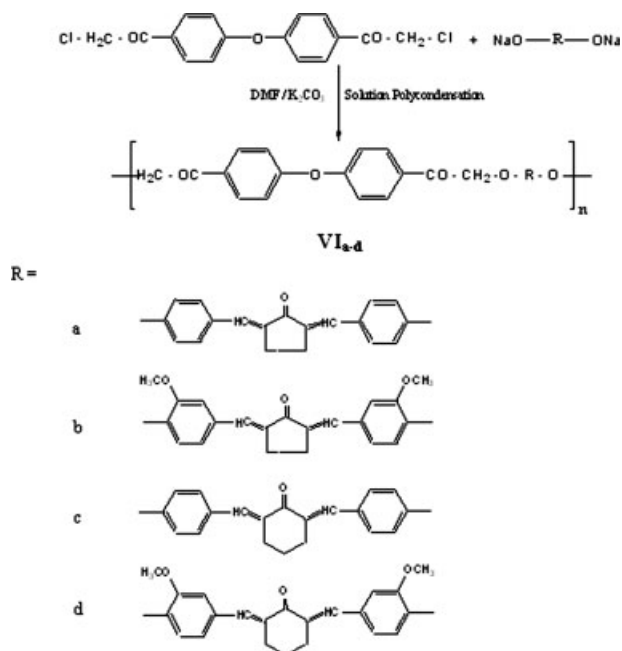
One of the aims of studies presented in this work is to synthesize a new series of poly(ether-ketone)s  $\text{IV}_{a-d}$  by using solution polycondensation technique.<sup>20</sup> These new polymers were synthesized by condensation of chloroacetyl monomer **I** with sodium salt of diarylidenecycloalkane monomers  $\text{II}_{a-d}$  in DMF and in the presence of anhydrous potassium carbonate as represented in Scheme 4.

The structure of these polymers was also established from elemental and spectral analyses. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer; the data are included in the experimental part. It should be noted that the elemental analyses of these polymers deviated up to 1.12% from the theoretical values. However, it is not uncommon for polymers to trap solvent molecules within the polymer matrix.

The IR spectra in KBr disks for all the obtained polymers showed the absorption new bands at 1660–1645  $\text{cm}^{-1}$  which attributed to C=O of the cycloalkane groups, absorption bands at 1250–1275  $\text{cm}^{-1}$  because of C—O—C linkage. Other characteristic absorption bands due to specific groups present in the various polymers were also shown, at 3050–3030  $\text{cm}^{-1}$  for (CH) stretching of aromatic ring, at 2920–2900  $\text{cm}^{-1}$  for (CH) stretching of (CH<sub>2</sub>) groups, and at 1680  $\text{cm}^{-1}$  for the carbonyl of chloroacetyl group.

Scheme 3 Synthesis of model compound **III**.





Scheme 4 Synthesis of poly(ketone-ether)s  $VI_{a-d}$ .

### Synthesis of copoly(ether-ketone)s

Our interest was focused on the synthesis and characterization of some new copoly(ether-ketone)s  $V_{a-f}$ , in addition to study the effect of inclusion of the diarylidencycloalkanone moieties in the polymers backbone. A new series of copoly(ether-ketone)s  $V_{a-f}$  was synthesized by interaction of a mixture containing 2 mol of two different sodium salts of diarylidencycloalkanone monomers  $II_{a-d}$  (1 : 1M ratio) together with two moles of chloroacetyl monomer I using solution polycondensation technique<sup>20</sup> in DMF and in the presence of anhydrous potassium carbonate as represented in Scheme 5.

The structure of these polymers was also established from elemental analyses and spectral data. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer. The IR spectra in KBr disks for all the obtained polymers showed the absorption new bands at  $1665\text{--}1640\text{ cm}^{-1}$  which attributed to  $C=O$  of the cycloalkanone groups, absorption bands at  $1245\text{--}1265\text{ cm}^{-1}$  because of  $C-O-C$  linkage. Other characteristic absorption bands because of specific groups present in the various polymers were also shown, at  $3040\text{--}3020\text{ cm}^{-1}$  for (CH) stretching of aromatic ring, at  $2940\text{--}2910\text{ cm}^{-1}$  for (CH) stretching of  $(CH_2)$  groups, and at  $1680\text{ cm}^{-1}$  for the carbonyl of chloroacetyl group.

### Polymers and copolymers characterization

The various characteristics of the resulting polymers and copolymers including solubility, X-ray diffraction analysis, TGA and DTA were also determined.

In addition, the biological screening of selected examples the resulting polymers were tested and all the data are discussed as described below.

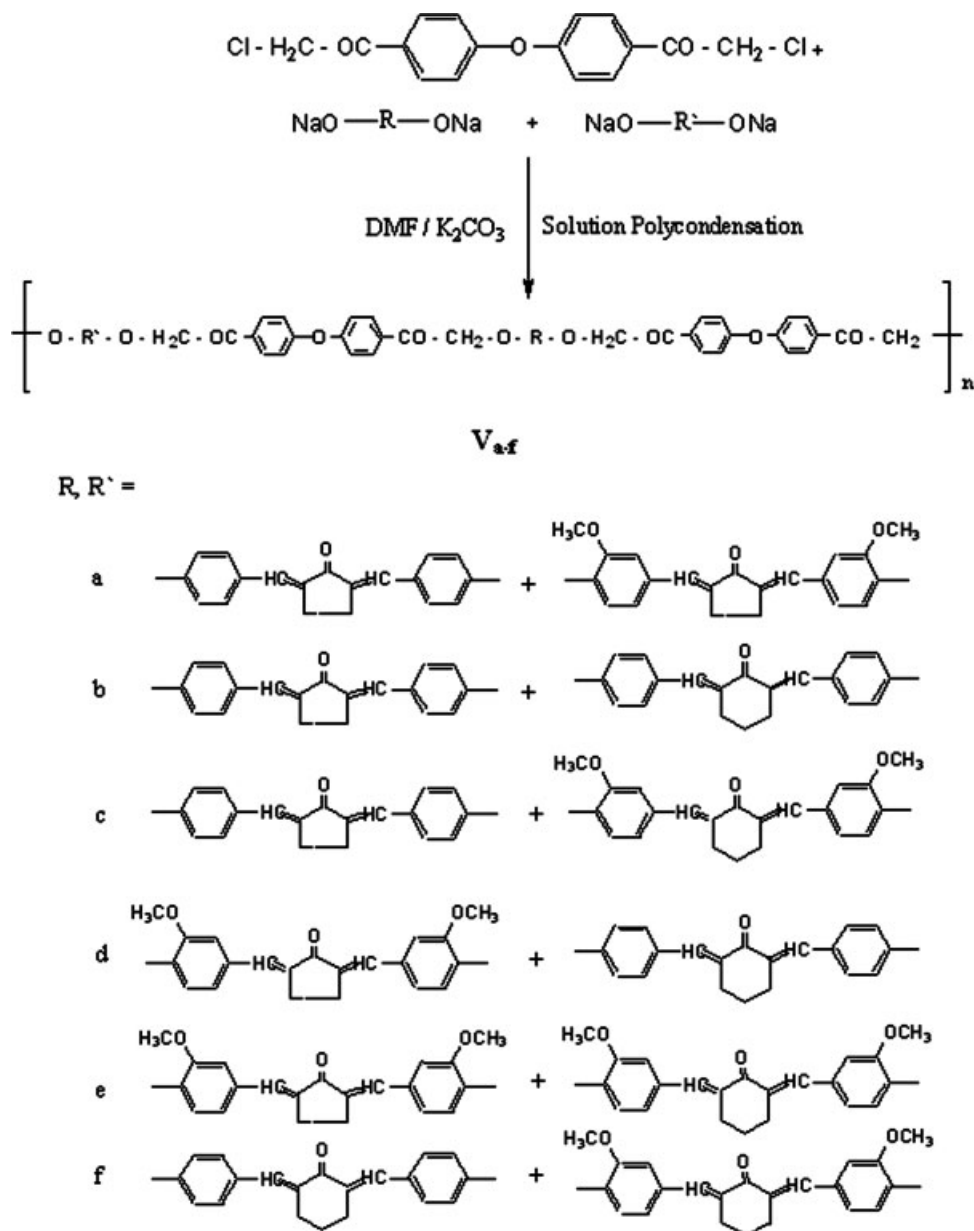
### Solubility

Room temperature solubility characterizations of poly(ether-ketone)s  $IV_{a-d}$  and copoly(ether-ketone)s  $V_{a-f}$  were tested using various solvents including : DMF, DMSO, DMA, 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 can be clarified from Table I that all the poly(ether-ketone)s  $IV_{a-d}$  were insoluble in most simple 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 I that, the majority of the polymers and copolymers were partially soluble in DMSO except polymers,  $IV_{a,b}$  which are completely insoluble. In other polar aprotic solvents such as DMF, DMA it was found that the majority of the polymers and copolymers were partially soluble except polymers  $IV_{a-c}$  which are completely insoluble. Moreover, it was found that all the polymers  $IV_{a-d}$  and majority of the copolymers were completely insoluble in chloroform–acetone mixture and methylene chloride except copolymers  $V_{a,c,f}$  which are partially soluble. On comparison between the solubility of the polymers based on diarylidencyclopentanone with those based on diarylidencyclohexanone, it was found that, the latter series are slightly more soluble in aprotic solvents (e.g., DMSO, DMF, DMA) than the former polymers. This may be attributed to the higher flexibility of the cyclohexanone moiety as described in our previous works.<sup>21,22</sup>

Furthermore, on comparison between all the synthesized polymers and copolymers, it was found that the latter are slightly more soluble than the former, which appear clearly in (DMSO, DMF, DMA, methylene chloride and chloroform–acetone mixture).

### X-ray analysis

The X-ray diffractograms of selected examples of poly(ether-ketone)s  $IV_{b,d}$  and copoly(ether-ketone)s  $V_{b,d,e}$  are shown in Figure 1. It can be clarified from this figure, the polymer  $IV_d$  showed a halo pattern in the region  $2\theta = 5\text{--}60^\circ$ ; this indicates that this polymer was amorphous, whereas the X-ray diffractogram of polymer  $IV_b$  showed a halo-pattern in the region  $2\theta = 5\text{--}30^\circ$ , and few low intensity peaks in the region  $2\theta = 30\text{--}60^\circ$ , which indicated that this polymer was semicrystalline. Moreover, the presence of  $C=O$ ,  $C=C$ , polar groups, induces some order between two adjacent chains of the polymers, leading to some extended of crystallinity.<sup>23</sup>

Scheme 5 Synthesis of copoly(ether-ketone)s  $\text{V}_{a-f}$ .

On the other hand, the X-ray diffractograms of selected copolymers  $\text{V}_{b,d,e}$  in Figure 1 indicated that copolymer  $\text{V}_e$  showed the same behavior which observed in previous polymer  $\text{IV}_b$ , in the same region; this indicated that this copolymer was semi-crystalline, whereas the copolymers  $\text{V}_{b,d}$  showed high intensity peaks in the region  $2\theta = 5\text{--}60^\circ$ , which also indicated that the resulting copolymers were crystalline. On comparison between all the selected polymers and copolymers, it was found that the presence of methoxy group as a substituent in the polymers backbone caused some hindering between the repeating units and enforced it to unsymmetrical orientation in the polymer chain and reduced the crystallinity.<sup>15</sup>

#### Thermal analyses

The thermal properties of the poly(ether-ketone)s  $\text{IV}_{a-d}$  and copoly(ether-ketone)s  $\text{V}_{a-f}$  were evaluated by thermogravimetric analysis (TGA), DTG and by differential thermal analysis (DTA) in air at a heating rate of  $10^\circ\text{C min}^{-1}$ . TGA curves of these polymers and copolymers were given in Figures 2 and 3, and Table II gives the temperature for various percentage of weight loss. The temperatures for (10%) weight loss are considered to be the polymers decomposition temperatures (PDT).<sup>24</sup> For the poly(ether-ketone)s  $\text{IV}_{b,d}$  the thermograph of polymer  $\text{IV}_b$  as selected example in (Fig. 2) showed a small weight loss in the range 2–4% starting at  $80^\circ\text{C}$  until  $109^\circ\text{C}$ , which may

TABLE I  
Solubility Characteristics and Inherent Viscosity of Poly(ether-ketone)s and Copoly(ether-ketone)s IV<sub>a-d</sub> and V<sub>a-f</sub>

Polymer number	DMF	DMSO	DMA	Chloroform + acetone (1 : 1 v/v)	CH <sub>2</sub> Cl <sub>2</sub>	HCOOH	Conc. H <sub>2</sub> SO <sub>4</sub>
IV <sub>a</sub>	–	–	–	–	–	+	++
b	–	–	–	–	–	+	++
c	–	+	–	–	–	+	++
d	+	+	+	–	–	+	++
V <sub>a</sub>	+	+	+	+	+	+	++
b	+	+	+	–	–	+	++
c	+	+	+	+	+	+	++
d	+	+	+	–	–	+	++
e	+	+	+	–	–	+	++
f	+	+	+	+	+	+	++

++, Soluble at room temperature (RT); +, partially soluble at (RT); –, insoluble.

be attributed to loss of absorbed moisture and entrapped solvents. The thermographs of poly(ether-ketone)s IV<sub>b,d</sub> indicated that the polymers decompose in three stages. The first step is slow and ranges between 125 and 272°C; the expected nature of decomposition depends upon the nature of these polymers, which may be due to a pyrolytic oxidation of C=C bonds, scission of many bonds.<sup>25</sup> The second step is the main step of degradation and ranging between 230 and 460°C. The expected nature of decomposition in this step is cleavage of ether linkage, scission of many bonds, in addition to formation of char as an end product. The rate of degradation becomes maximal at 507 °C for polymer IV<sub>b</sub> and at 412 °C for polymer IV<sub>d</sub>. Moreover, the degradation is nearly complete at around 550 °C.

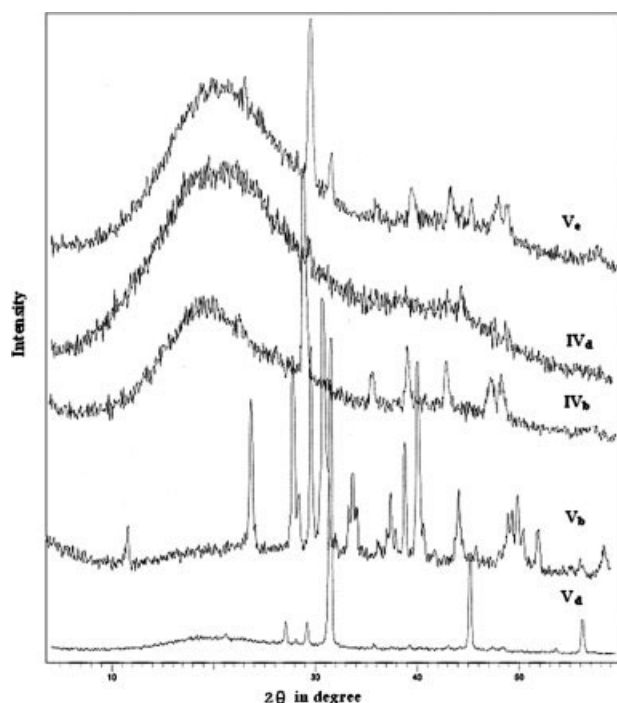


Figure 1 X-ray Diffraction patterns of polymers IV<sub>b,d</sub> and V<sub>b,d,e</sub>.

For the copoly(ether-ketone)s v<sub>a,b</sub>, the thermographs of these copolymers showed a big twisted exothermic peak in the range 450 to 460°C (Fig. 3), which may be attributed to the rapid degradation of these copolymers. The thermographs also indicated that the selected copolymers decompose in two overlapped stages. The first step is slow and ranges between 240 and 420°C; the expected nature of decomposition depends upon the nature of these polymers which may be due to a pyrolytic oxidation of C=C bonds, scission of many bonds.<sup>25</sup> The second step is a fast degradation between 330 and 496°C. The expected nature of decomposition in this step is cleavage of ether linkage, scission of many bonds, in addition to formation of char as an end product. The (PDT) for all the selected polymers and copolymers ranged from 240 to 281°C. Therefore, the data in Table II indicate that the thermal stabilities of these polymers and copolymers were in the order IV<sub>b</sub> > V<sub>a</sub> > IV<sub>d</sub> > V<sub>b</sub>. The comparison of T<sub>40</sub> and T<sub>50</sub> values of polymer IV<sub>d</sub> showed low significant temperatures of degradation than the others, which may be attributed to the less thermal stability of that polymer than other polymer and copolymers. Moreover, it can also be seen from Table II that polymer IV<sub>b</sub> is more thermally stable than the others, which appeared clearly in T<sub>40</sub> and T<sub>50</sub>.

The determination of glass transition temperature T<sub>g</sub> by using DTA measurements is a well-known technique. Most long chain synthetic polymers show characteristic sequence of changes as they are heated. For polymer IV<sub>b</sub>, (as a selected example) showed T<sub>g</sub> at 211.75°C and T<sub>m</sub> at 350°C (cf. Fig. 2). On the other hand, the disappearance of T<sub>g</sub> and T<sub>m</sub> of copolymers V<sub>a,b</sub> may be attributed to the rapid decomposition.<sup>14</sup>

#### Antimicrobial screening

The antimicrobial screening of selected examples of poly(ether-ketone)s and copoly(ether-ketone)s was performed using the standard agar diffusion

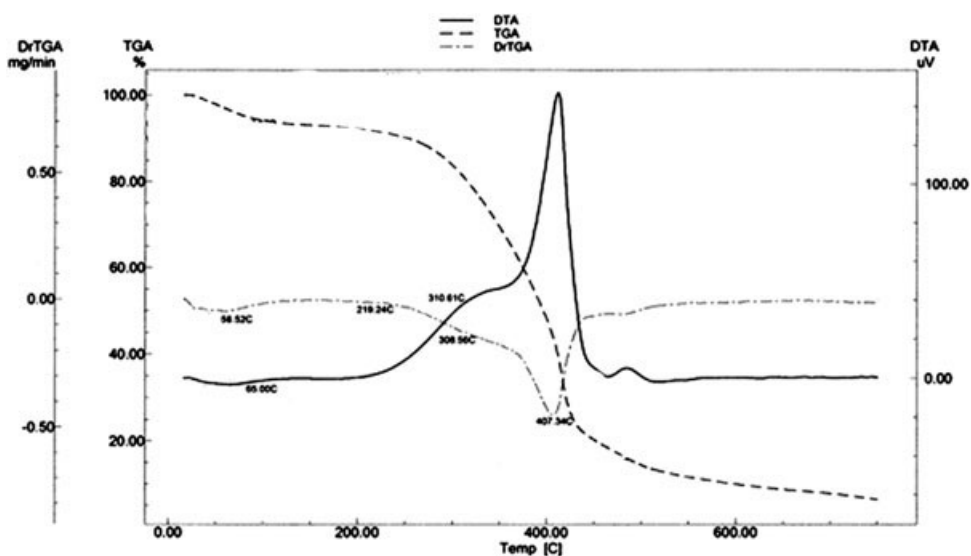


Figure 2 The TGA, DTG, and DTA traces of polymer IV<sub>d</sub> in air at a heating rate of 10°C/min.

method, against different organisms (fungal and bacterial species) including: *Aspergillus flavus*, *Aspergillus niger*, *Candida albicans*, *Geotrichum candidum*, *Scopulariopsis brevicaulis*, *Trichophyton rubrum*, *Bacillus cereus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Serratia marcescens*, and *Staphylococcus aureus*. The fungal species were maintained on sabouraud dextrose agar (SDA) whereas the bacterial species were maintained 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<sup>26</sup> pointed out that chlorine-containing polyketones exerted a very close inhibitory effect against some fungi, yeast, and bacteria including: *A. niger*, *Penicillium chrysogenum*, *R.*

*minuta*, *S. cerevisiae*, *P. stipitis*, *P. fluorescens*, *B. subtilis*, and *E. coli* species.

Antifungal and antibacterial activities of the tested polymers were determined as described before<sup>27,28</sup>; the size of the resulting inhibition zone was determined in Table III. It can be seen from the Table III that all the selected poly(ether-ketone)s and copoly(ether-ketone)s showed no significant influence antifungal activity against the selected fungi.

On the other hand, it was clear to show that the majority of the selected polymers and copolymers showed a moderated antibacterial activity against *T. rubrum*, *B. cereus*, *S. marcescens*, and *S. aureus* except copolymers V<sub>a,b,d</sub> against *T. rubrum*, copolymer V<sub>a</sub> against *B. cereus*, polymer IV<sub>b</sub> against *S. marcescens*

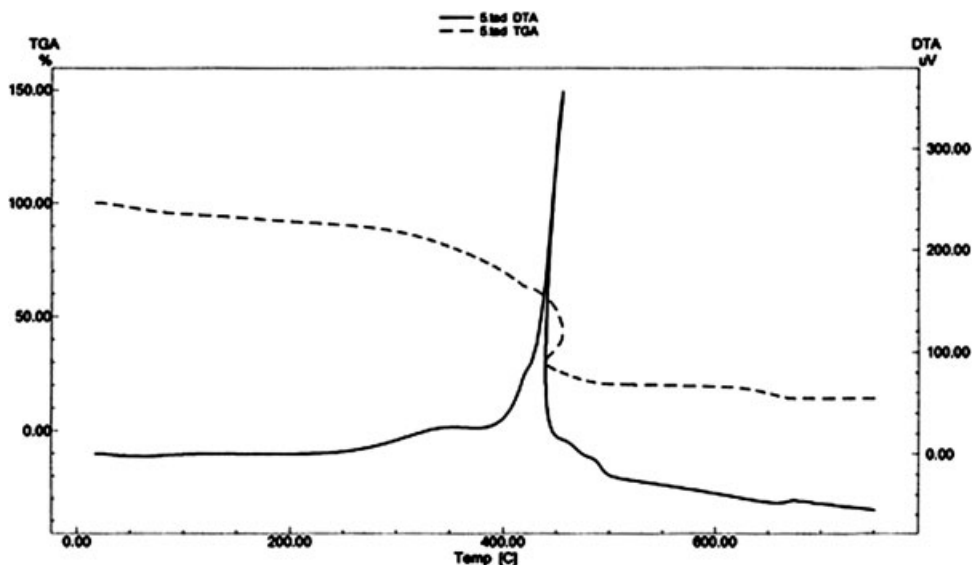


Figure 3 The TGA and DTA traces of copolymer V<sub>a</sub> in air at a heating rate of 10°C/min.



**TABLE II**  
Thermal Properties of Poly(ether – ketone)s IV<sub>a-d</sub>  
and Copoly(ether-ketone)s V<sub>a-f</sub>

Polymer number	Temperature (°C) for various percentage decompositions <sup>a</sup>				
	10%	20%	30%	40%	50%
IV <sub>b</sub>	281	390	454	485	508
IV <sub>d</sub>	248	320	375	367	400
V <sub>a</sub>	261	358	400	420	453
V <sub>b</sub>	240	360	415	430	456

<sup>a</sup> The values were determined by TGA at a heating rate of 10°C min<sup>-1</sup>.

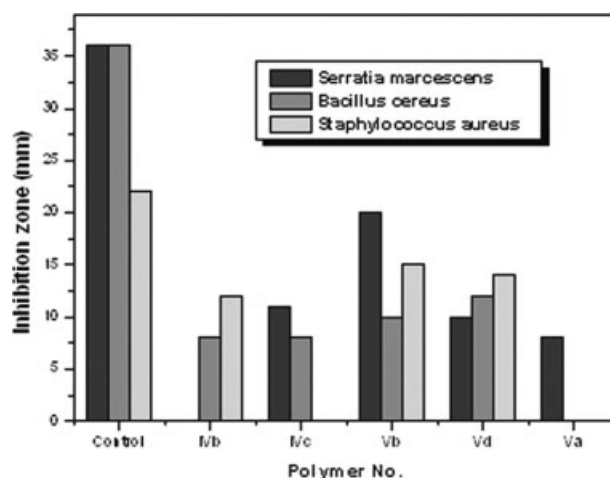
and polymer IV<sub>c</sub> and copolymer V<sub>a</sub> against *S. aureus*, which have no significant influences. Although only polymers IV<sub>b,c</sub> showed a strong antibacterial activity against *T. rubrum* compared with the controlled values (13, 17/24 respectively), copolymer V<sub>b</sub> showed strong antibacterial activity against *S. marcescens* (20/36), and copolymers V<sub>b,d</sub> showed strong antibacterial activity against *S. aureus* (15, 14/22, respectively), on the other hand, the rest of selected polymers and copolymers showed week significant influences.

Figure 4 provides a comparative account of the effect of the poly(ether-ketone)s on the growth of bacteria (*S. marcescens*, *B. cereus* and *S. aureus*). These results indicate that the poly(ether-ketone)s significantly inhibit the growth of microorganisms. It can be clarified from this figure that, the control culture (without polymer sample) generally exhibits maximum growth. On the other hand, the polymers samples gave different growth which may be attributed to polymer structures. The synthesized poly(ether-ketone)s showed as reported previously by Patel et al.<sup>29</sup> We believe that more work is needed to identify the moiety that is most important in the different

**TABLE III**  
Results of Antimicrobial Screening of Poly(ether-ketone)s IV<sub>a-d</sub> and Copoly(ether-ketone)s V<sub>a-f</sub>

Organism	Polymer inhibition			Number zone (mm)		
	IV <sub>b</sub>	IV <sub>c</sub>	V <sub>a</sub>	V <sub>b</sub>	V <sub>d</sub>	Control
<i>Aspergillus flavus</i>	0	0	0	0	0	22
<i>Aspergillus niger</i>	0	0	0	0	0	16
<i>Candida albicans</i>	0	0	0	0	0	28
<i>Geotrichum candidum</i>	0	0	0	0	0	22
<i>Scopulariopsis brevicaulis</i>	0	0	0	0	0	0
<i>Trichophyton rubrum</i>	13	17	0	0	0	24
<i>Bacillus cereus</i>	8	8	10	12	0	36
<i>Escherichia coli</i>	0	0	0	0	0	24
<i>Pseudomonas aeruginosa</i>	0	0	0	0	0	16
<i>Serratia marcescens</i>	0	11	20	10	8	36
<i>Staphylococcus aureus</i>	12	0	15	14	0	22

Control: (antibacterial, chloramphenicol; antifungal, tro-syd).



**Figure 4** Effect of poly(ether-ketone)s on the growth of bacteria.

structures for higher antimicrobial activity, which will be done in our next work.

## CONCLUSIONS

A new series of poly(ether-ketone)s IV<sub>a-d</sub> and copoly(ether-ketone)s V<sub>a-f</sub> was synthesized using solution polycondensation technique. The various characteristics of the resulting polymers and copolymers were tested. The presence of methoxy group as substituent in the polymer backbone reduced the crystallinity and caused some hindering between the repeating units and enforced it to an unsymmetrical orientation in the polymer chain. The majority of the selected polymers and copolymers showed a moderate antibacterial activity against all the selected bacteria, whereas polymers IV<sub>b,c</sub> showed a strong antibacterial activity against *T. rubrum*, copolymer V<sub>b</sub> showed strong antibacterial activity against *S. marcescens* (20/36), and copolymers V<sub>b,d</sub> showed strong antibacterial activity against *S. aureus* (15, 14/22, respectively).

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