New Polymer Syntheses Part: 55[#]. Novel Conducting Arylidene Polymers and Copolymers Based on Methyl-Cyclohexanone Moiety

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Abstract: A new interesting class of conducting polymers based on methyl-cyclohexanone in the polymer main chain has been synthesized by solution polycondensation of terephthalaldehyde with methyl-cyclohexanone. Copolymers containing different cycloalkanone moieties were also synthesized using solution polycondensation technique. The model compound **I** was synthesized by the interaction of methyl-cyclohexanone monomer with benzaldehyde, and its structure was confirmed by elemental and spectral analyses. The resulting new polymers and copolymers were characterized by elemental and spectral analyses, beside solubility and viscometry measurements. The thermal properties of those polymer and copolymers were evaluated by TGA, DrTGA and DTA measurements and correlated to their structural units. PDT as well as T_{10} was in the range from 205 to 370 ºC. In addition, T_{10} thermal stability for all the polymers was in the order: VI> II > III > IV > V. X– ray analysis showed that it has some degree of crystallinity in the region $2\theta = 5 - 60$ degree.The UV– visible spectra of some selected polymers were measured in DMSO solution and showed absorption bands in the range 265-397 nm, due to $n - \pi^*$ and $\pi - \pi^*$ transition. The morphological properties of copolymer IV as selected examples were tested by SEM. The electrical conductivities of the synthesized polymers and copolymers enhanced to become in the range of 10^{-9}-10^{-8} S cm^{-1} by doping with iodine.

Keywords: Synthesis, Characterization, Polycondensation, Conducting Polymers, Conducting Copolymers.

1. INTRODUCTION

Conjugated polymers have a great interest in variable fields due to their interesting optical and electronic properties. These properties, are mainly dependent upon the structure of the main backbone as well as the nature of attached side chains [1-4]. The enhance these properties is assumed to further extent of π-electron conjugation in the polymers chains. Different kinds of conducting polymers have been synthesized and investigated. An important point is these research has been archived in order to understand of the role of conjugation on the conductivity and the ability to tune this conductivity, based on substitution with various side chains and/ or cuts in conjugation [5-7]. From the other hand, Other research work are being conducted to examine how the illustrated structure can affect the conductivity

mechanism, including π -stacking effect [8]. According to the literature survey, there is much interest in the development of new design arylidene polymers *via* well known synthetic routes. It was incorporated into nearly almost all kinds of polymer architectures *via* solution polycondensation technique from polyester to polyimide and in some cases hybrid types of polymers such as poly(keto-amine)s and poly(keto-imine)s. These types of polymers are necessitating the synthesizing of corresponding monomers. Arylidene monomers and pre-monomers have considered as a corner stone for different types of interesting polymers and Diarylidenecycloalkanone derivatives, are considered as an important class of organic molecule, have both mesogenic and photo-active properties, and soon can be named as a versatile photo-active molecule. These types of compounds have already shown its potential for applications in chemistry, biology, materials science and technology. It is also having been studied as such for medical applications and by incorporating it into polymer architectures for harnessing its properties as a photo-active as well as a mesogenic unit. This photo-active molecule was introduced into a macromolecular architecture by

Borden *et al.* in 1969 [9, 10]. Arylidene polymers are widely used in various areas of interest. This kind of polymers have special characters such as photo-curing ability (for adhesives, photo-resists and holography), fluorescence, electronic conductivity, high thermal stability etc. As a continuation of the work reported in the literature concerning the variable studies on the synthesis and properties of different new polymers based on diarylidenecycloalkanones possessing an interesting properties, attractive morphology, higher thermal stability, liquid crystalline behavior, corrosion protection, conducting properties, antimicrobial activity and many other properties, which have been presented in the literature [11-18]. Furthermore, different arylidene conjugated polymers, copolymers and terpolymers were synthesized and studied [19-21]. In this research work we present a route for the synthesis and characterization of some new arylidene polymers, and copolymers containing methyl-cyclohexanone moiety in the polymer backbone. A major target of this work was to study the effect of the cycloalkanone moieties upon the properties of desired arylidene conjugated polymers, including their solubility and viscometry, crystallinity, thermal behavior and electronic spectra. Beside study the surface of selected polymers using scanning electron microscopy (SEM). Furthermore, study the effect of chemical structure on the electrical conductivity of these polymers at different temperatures.

2. EXPERIMENTAL

2.1. Reagents

Methyl-cyclohexanone (Fluka, Germany), was freshly distilled at b.p. 169-171 ^{o}C. N-methyl piperidone (Merck, Germany) was freshly distilled at b.p 155 ^{o}C, Benzaldehyde from (Aldrich) was used as purchased. Cyclohexanone and cyclopentanone (Merck) were freshly distilled: cyclohaxanone (b.p. 155 ^{o}C) and cyclopentanone (b.p. 130 -131 ^{o}C). Terephthalaldehyde (Aldrich, Germany) m.p. 114 - 116 ^{o}C. Potassium hydroxide (BDH, Leicestershire, England), were of analytical grade and were used as received.

2.2. Solvents

Methanol, 99.8%, Ethanol, 99.9% (Hayman, Eastways Withan, England), acetone and N,N-dimethylformamide (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.

2.3. Synthesis of Model Compound: 2,6-Dibenzylidenemethyl-cyclohexanone (I)

In a 100 ml round-bottomed flask equipped with a magnetic stirrer, and a nitrogen inlet and outlet, was placed a solution of 1 mmole of methyl-cyclohexanone and 2 mmole of benzaldehyde in about 50 mL absolute ethanol and vigorously stirred at room temperature. Then a few drops of a 10% alcoholic solution of KOH were added and the temperature was allowed to rise to 50 °C over 30 min. At the end of the reaction a bright yellow solid separated out that was filtered off, washed with water, and recrystallized from ethanol. Yellowish needles were obtained with a yield of 89% at a melting point (mp 138 °C). Anal. Calc. For $(C_{21}H_{20}O)_n$:C, 87.50; H, 6.94. Found %: C, 86.49; H, 6.37. FT-IR (KBr, cm^{-1}): at 1685 (C=O of methyl-cyclohexanone), at 3050 (C-H aromatic), at 2995 (C-H aliphatic) and at 1605 (C=C group). ^{1}H-NMR for compound **I** (CDCl$_3$, δ ppm): δ at 7.14-7.38 (m, 10 H of 2 Ph-, 2 H of CH=C-), at 1.92-2.22 (m, 4 H of 2 CH$_2$, 2H CH$_2$ of cyclohexanone), and at 1.06 (3H, CH$_3$). ^{13}C-NMR (CDCl$_3$, δ ppm) δ at: 190.0 (1C), 149.5 (2C), 139.4 (2C), 136.7 (2C), 132.7 (4C), 130.0 (2C), 128.4 (4C), 44.5 (1C), 42.4 (1C), 25.2 (1C)

2.4. Polymerization Procedure

A solution polycondensation technique was used in the synthesis of these conjugated polymer and copolymers which described as following:

General Procedure

In a three-necked flask equipped with a condenser, a magnetic stirrer, and a dry nitrogen inlet and outlet, a mixture of 3 mol (4.024 g) terephthalaldehyde and 3 mol (3.658 g) methyl-cyclohexanone (for the polymer II) or (1.5 mol for the copolymers III-VI), was dissolved in 50 mL of absolute ethanol and vigorously stirred at room temperature. Then few drops of a 15% alcoholic solution of KOH was added, the temperature was allowed to rise to 80 °C over 30 min, and the reflux was continued for 3-4 hrs. At the end of that time a colored polymer had precipitated. The formed polymer was filtered off, washed with water, hot alcohol, and hot acetone, and dried under reduced pressure (1 mmHg) at 70 °C for 2 days.

Using the above general procedure the following polymer and copolymers were obtained:

2.4.1. Synthesis of Polymer II

Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde and 3 mol (3.658 g) methyl-cyclohexanone for 3 hrs, as yellowish powder; yield: 83%. Anal. Calc. For $(C_{15}H_{14}O)_n$:C, 85.71; H, 6.66. Found %: C, 85.26; H, 6.13. FT-IR (KBr, cm^{-1}): at 1605 (C=C group), nearly at 1500 and 1600 cm^{-1} (phenyl ring vibrations), at 1685 (C=O of methyl-cyclohexanone), at 3040 (C-H aromatic), at 2990 (C-H aliphatic).

2.4.2. Synthesis of Copolymer III

Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) methyl-cyclohexanone and 1.5 mol (1.327 g) cyclpentanone for 3 hrs, as yellowish powder; yield: 89 %. Anal. Calc. for $(C_{28}H_{24}O_2)_n$:C, 85.71; H, 6.12. Found %: C, 84.97; H, 5.71. FT-IR (KBr, cm^{-1}): at 1595 (C=C group), nearly at 1500 and 1600 cm^{-1} (phenyl ring vibrations), at 1687 (C=O of methyl-cyclohexanone), at 3044 (C-H aromatic), at 2992 (C-H aliphatic).

2.4.3. Synthesis of Copolymer IV

Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) methyl-cyclohexanone and 1.5 mol (1.553 g) cyclhexanone for 3 hrs, as yellowish powder; yield: 81%. Anal. Calc. for $(C_{29}H_{26}O_2)_n$:C, 85.71; H, 6.40. Found %: C, 83.27; H,5.94. FT-IR (KBr, cm^{-1}): at 1600 (C=C group), nearly at 1500 and 1600 cm^{-1} (phenyl ring vibrations), at 1683 (C=O of methyl-cyclohexanone), at 3048 (C-H aromatic), at 2990 (C-H aliphatic).

2.4.4. Synthesis of Copolymer V

Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) methyl-cyclohexanone and 1.5 mol (1.6825 g) cycloheptanone for 4 hrs, as yellowish powder; yield: 79%. Anal. Calc. for $(C_{30}H_{28}O_2)_n$: C, 85.71; H, 6.66. Found %: C, 83.84; H, 6.06. FT-IR (KBr, cm^{-1}): at 1600 (C=C group), nearly at 1500 and 1595 cm^{-1} (phenyl ring vibrations), at 1690 (C=O of methyl-cyclohexanone), at 3035 (C-H aromatic), at 2985 (C-H aliphatic).

2.4.5. Synthesis of Copolymer VI

Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) methyl-cyclohexanone and 1.5 mol (1.7521 g) N-methylpiperidinone for 3 hrs, as yellowish powder; yield: 68%. Anal. Calc. for $(C_{29}H_{27}O_2N)_n$: C, 82.66; H, 6.41; N, 3.33. Found %: C, 81.12; H, 6.53; N, 3.95. FT-IR (KBr, cm^{-1}): at 1590 (C=C group), nearly at 1500 and 1600 cm^{-1}

(phenyl ring vibrations), at 1685 (C=O of methyl-cyclohexanone), at 3050 (C-H aromatic), at 2985 (C-H aliphatic).

2.5. Polymer Identification

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

2.6. Polymer Characterization

2.6.1. Solubility

The solubility of polymers in various solvents including: dimethylsulfoxide (DMSO), dimethylforma-mide (DMF), n-methylpyrrolidone (NMP), chroloform – acetone mixture (1:1), terahydrofurane (THF), m-cresol, n,n-dimethylacetamide (DMAc) and sulfuric acid. The solubility test for the powder polymers was determined at room temperature (30 °C). It was perfor-med by gradual addition of the polymer to the solvent and stirred well till saturation. The maximum solubility of the polymers was calculated as percent weight of the polymer per hundred milliliter of solvent (% w/v).

2.6.2. Viscosity

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

2.6.3. UV-Visible

The electronic spectra were scanned on 2110 PC scanning spectrophotometer, Shimadzu in DMSO as a solvent.

2.6.4. Scanning Electron Microscopy Measurements

The morphology of polymers was examined by a Scanning electron microscope (SEM) using a Jeol-

JSM-5400 LV-SEM. The SEM sample was prepared by putting a smooth part of polymer powder on a copper holder and then coating it with a gold-palladium alloy. SEM images were taken using a Pentax Z-50P Camera with Ilford film at an accelerating voltage of 15kV using a low dose technique.

2.6.5. Thermal Analyses

Thermogravimetric analysis (TGA) differential thermo-gravimetric (DTG) and differential thermal analysis (DTA) measurements were recorded on a Shimadzu TGA-50 H in air atmosphere at a heating rate of 10 °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 ml min^{-1}.

2.6.6. X-Ray Measurements

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

2.6.7. Electrical Properties

The electrical resistivity measurements [22] were carried out using the circuit, by using an apparatus consists of vacuum system, vacuum chamber and specimen holder. It is provided with an equipment and means of measuring the required parameters. Pellets for electrical conductivity measurements have been pressed at constant pressure 1500 psi using IR die-silver paste was used to make contacts and sandwiched between the polymer pellets and two graphite electrodes. The samples prepared in the shape of disk 25-mm diameter and 3-5 mm thickness to be most suitable for the electrical properties investigation. The sample faces were polished and lapped parallel. The resistance of the sample is measured by an electrometer of type (Keithly 610C).

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis

A new and unreported class of arylidene conjugated polymers, and copolymers based on methyl-cyclohexanone moiety, has been synthesized *via* solution polymerization of terephthalaldehyde with methyl-cyclohexanone. A literature survey revealed that the interaction of dialdehyde (e.g., terephthalaldehyde) with di-amines leads to polyimines as typically conjugated polymers by the step growth polycondensation. Thus, condensation of terephthalaldehyde with methyl-cyclohexanone in alcoholic potassium hydroxide solution gives the corresponding arylidene conjugated polymer or by other words poly(benzylidene)methyl-cyclohexanone **II**. Copolycondensation process of equimolar quantities of terephthalaldahyde with a mixture of cyclopentanone and cyclohexanone or cyclopheptanone, and n-methylpiperidone gives the corresponding conjugated arylidene copolymers **III, IV, V and VI** respectively. The early precipitation of polymers within 20 min after mixing the monomers indicates that the new polymers are insoluble in ethanol. Polymers are immediately isolated (see the experimental section) at the end of the reaction period. Before attempting the polymerization, the model compound **I** is synthesized by the interaction of one mole of methyl-cyclohexanone with two moles of benzaldehyde in ethanol and KOH at room temperature to optimize the polymerization condition as shown in Figure **1**. The structure of the new model compound is conferment and checked on the bases of the good agreement between calculated and found analytical data, FT-IR and ^{1}H-NMR (see experimental part). Five novel polymers and copolymers containing methyl-cyclohexanone in the main chain have been synthesized. The polymerization and copolymerization reactions are carried out using the optimum condition as shown for model compound (stirring at room temperature in absolute ethanol as a
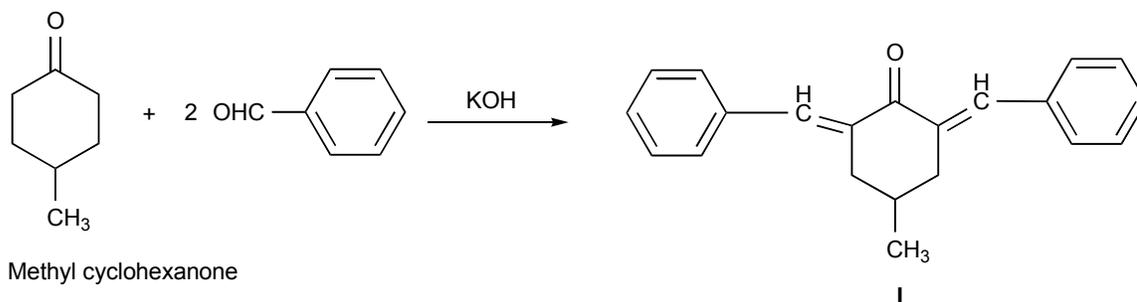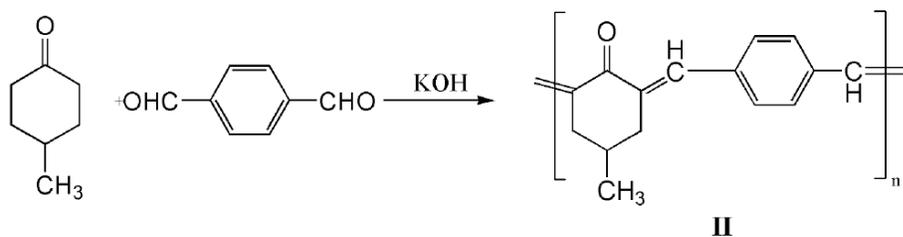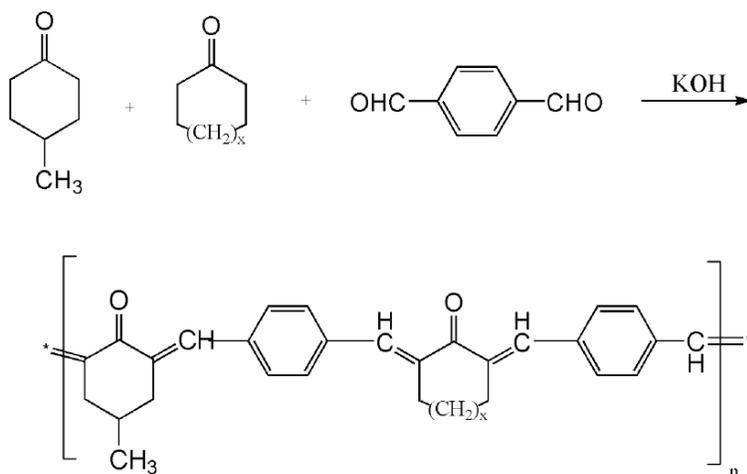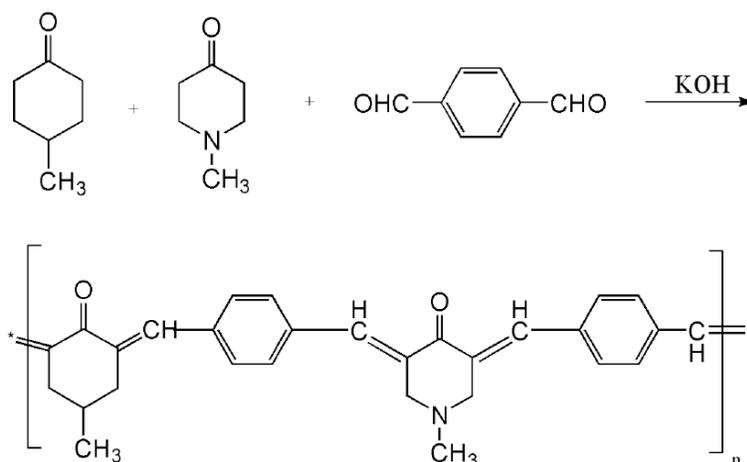

Figure 1: Synthesis of 2,6-dibenzylidene-methyl cyclohexanone **I**.

(A) Synthesis of polymer II

(B) Synthesis od copolymer III - V

III, X = 0　;　**IV,** X = 1　;　**V,** X = 2

(C) Synthesis od copolymer VI

Figure 2: Synthesis of conducting polymer **II** and copolymer **III-VI**.

solvent and KOH as a catalyst as) illustrated in Figure **2**. The reaction times varied from 2-3 hr and the polymers and copolymers were immediately isolated during the stirring, with yield in the range of 68 - 89 %. All the polymers and copolymers have obtained as brownish to deep yellow powder. The structure of the new polymers and copolymers was confirmed by elemental and spectral analyses. The structure of the prepared polymer and copolymers 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 experimental part. It should be noted that the elemental analyses of these polymers deviated up to 1.44% from the theoretical values. However, it is not uncommon for polymers to trap solvent molecules within the polymer matrix. FT-IR spectra show that, all the polymer and copolymers have a strong absorption near 1680 - 1690 cm^{-1} is attributed to carbonyl of methyl-cyclohexanone. The medium to strong absorption around 1610 cm^{-1} is attributed to C=C stretching. The phenyl ring vibrations are assigned to absorption near 1600 and 1510 cm^{-1}. The CH$_3$ asymmetric and symmetric bending modes are traced to 1455 and 1350 cm^{-1}, respectively. The CH$_2$ bending mode also appears around 1460 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 atoms [23]. The absorption at 775 cm^{-1} has variable intensity. This peak is attributed to CH out-of-plane bending in benzene ring having two adjacent hydrogen atoms [24].

3.2. Polymer Characterization

The solubility behavior of all polymer and copolymers is summarized in Table **1**. It is well known that conjugated polymers generally have limited solubility in most organic solvents because of their rigid chain. However, several attempts have been made to obtain nearly similar polymers with improved solubility by introducing flexible bonding or bulky groups in the polymer [25-27]. Our targeted polymer and copolymers that based methylcyclohexanone moiety **(II– VI)** are insoluble in common organic solvents like alcohol, benzene, acetone, but soluble in halogenated solvents like methylene chloride, and chloroform. Furthermore, all the synthesized polymers are dissolved completely in concentrated sulfuric acid as good example for protonic solvent giving a deep brown color, except for polymer **VI** that give yellowish color. The same behavior is observed in DMAc. Almost all polymers are

soluble in the tested polar aprotic solvents, such as NMP, DMF, and DMSO except copolymer **VI** which is partially soluble and polymer **II** which is partially soluble in DMF. While in THF, all the polymers are completely soluble. The majority of the polymers are partially soluble in less polar solvents, including; acetone-chloroform mixture, THF, and m-cresol, except copolymers, **III** and **V** that show easy soluble behavior in these solvents. Copolymer **III** is completely soluble in m-creasol and copolymer **V** is completely soluble in m-cresol & acetone- chloroform mixture.

The inherent viscosities (η_{inh}) of polymer **II** and copolymers **III-VI** are determined in NMP at 30°C with an Ubbelohde suspended level viscometer The inherent viscosity value is defined as:

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

The solution concentration C is 0.5g/100 ml, η/η_o = relative viscosity (or viscosity ratio). It can be shown from Table **1** that polymer **II** has high inherent viscosity (0.84 dL/g) and this may be attributed to high molecular weight of the polymer. But, the inherent viscosity of the copolymer **V** is (0.56 dL/g) and this may be attributed to low molecular weight of this polymer.

The electronic spectra of model and undoped polymer and copolymers are obtained in NMP at a concentration of 2.6 X10^{-6} *M.* These displayed two absorption bands with l max near 258 nm, which is due to the π- π* transition within the benzenoid system, and with λ_{max} near 365 nm, which is attributed to the π- π* excitation of C=O or C=N groups. The electronic spectra of polymers **II–VI** show broadening absorption bands and a small bathochromic shifting of both bands, indicating a highly conjugated system. Moreover, the electric conducting properties of the undoped and doped polymers are therefore related to the presence of extensively delocalized *p* electrons along the

Table 1: Solubility Characteristics of Polymer II and Copolymers III-VI

Polymer Code	DMSO	DMF	NMP	Chloroform Acetone (1:1)	THF	m-cresol	DMAc	H$_2$SO$_4$	η^*_{Inh} (dl/g)
II	+	±	+	±	±	±	+	+	0.84
III	+	+	+	±	±	+	+	+	0.65
IV	+	+	+	±	±	±	+	+	0.71
V	+	+	+	+	±	+	+	+	0.56
VI	±	±	±	±	±	±	+	+	0.69

(+): Completely soluble at room temperature (RT).
(±): Partially soluble.
(−): Insoluble.
*η Inherent viscosity measured in NMP at 30 °C.

polymer chain, and the delocalization of π electrons also contributes to the formation of the polymer-iodine adducts.

The morphological properties of the synthesized copolymer **IV** (as selected example) are examined by scanning electron microscopy (SEM). The sample is prepared by putting a smooth part of polymer powder on a copper holder and subsequently coating it with gold palladium alloy. SEM images are taken on a penta Z Z-50 P Camera with Ilford film at an accelerating voltage of 15 Kv using a low-dose technique [28]. This technique gives us the ability to show the 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 copolymer **IV** shows that the surface of the copolymer (Figure **3a**, magnification X= 3500) consisted of porous kidney shape accumulative merged particles, with higher

magnification X= 7500 (Figure **3b**) shows grape fruit like shape, again with higher magnification X = 10,000 (Figure **3c**) shows the porous like balls. The particle sizes for the selected copolymer have expansion slots in the range 2.0 - 4.0 μm. Moreover, the further studies of the morphological properties of these polymers are in progress and the results will be published in the near future.

The typical wide-angle X-ray diffraction patterns of the new arylidene conjugated polymer and copolymers **II, III, V** and **VI** are given in the range 2θ = 5° - 60° and diffractograms are shown in Figures **4**, **5**. It can be clarified from these figures that the polymer **II** and copolymer **VI** shows halo pattern in the region 2θ =10-50°, this indicate that all these polymers are amorphous to semi-crystalline. While, the X-ray diffractogram of copolymers **III** and **V** shows a sharpness peaks in the region 2θ =20-30°, this
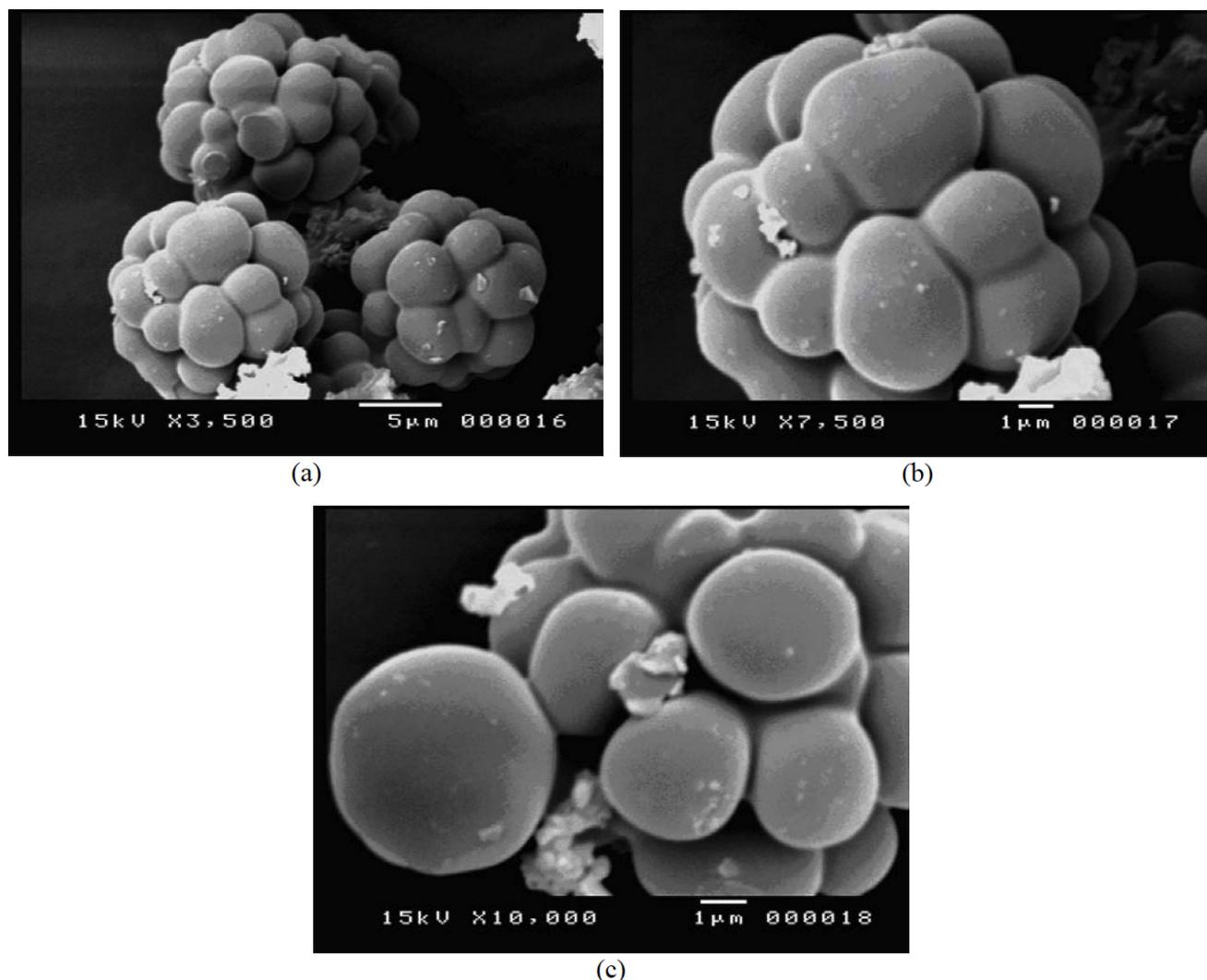

(a)

(b)

(c)

Figure 3: The SEM images of the polymer surface of copolymer **IV**. (**a**, X = 3500, **b**, X = 7500 and **c**, X = 10,000).

indicated that this polymer was crystalline and have high degree of crystallinity. 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 [29].
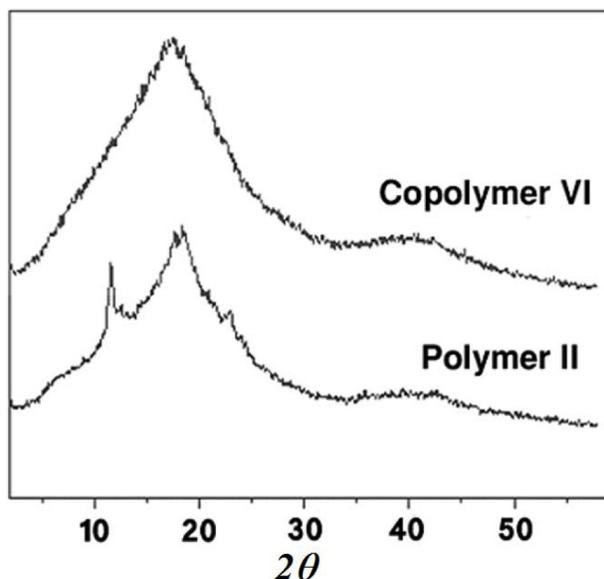

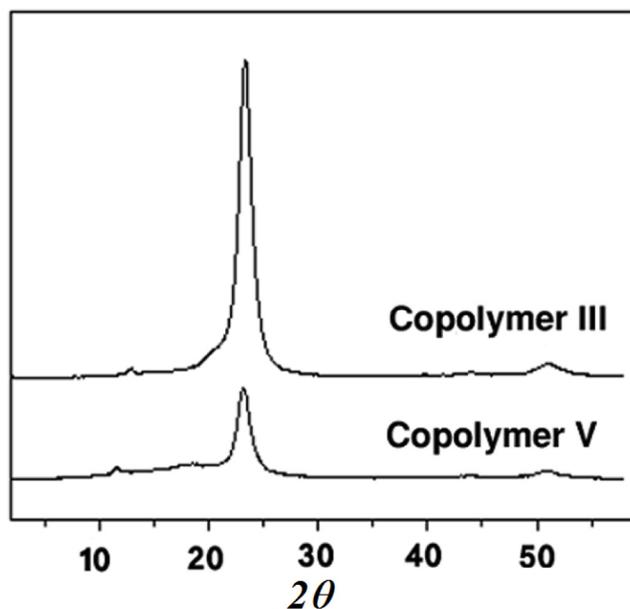**Figure 4:** X- ray Diffraction patterns of polymer **II** & copolymer **VI**.

Figure 5: X- ray Diffraction patterns of copolymers **III** & **V**.

The thermal behavior of polymer **II** and copolymers **III-VI** containing methyl-cyclohexanone unit are obtained and investigated with the aids of TGA, DTG and DTA in air at a heating rate of 10°C /min. The thermographs of these polymers are given in Figures **6**, **7** and **8** for polymer **II** and copolymers **III** and **V** (as selected examples), also Table **2** shows the

temperature of various percentages of weight losses at 10%, 20%, 30%, 40% and 50% weight losses that represented in the form T_{10}-T_{50} values. Figure **6**, TGA curve of polymer **II** shows a weight loss in the range 4 - 8% starting at 110-120°C, which may be attributed to loss of absorbed moisture and entrapped solvents. The thermographs also indicate, the polymer decompose mainly in one stage. A rapid decomposition is observed and is ranged between 390°C and 420 °C; this may be attributed to the nature of these polymers and copolymers. Similarly, copolymer **III** shows nearly the same TG curve and hence the same thermal behavior. Whereas, copolymer **V** shows different pattern of decomposition.
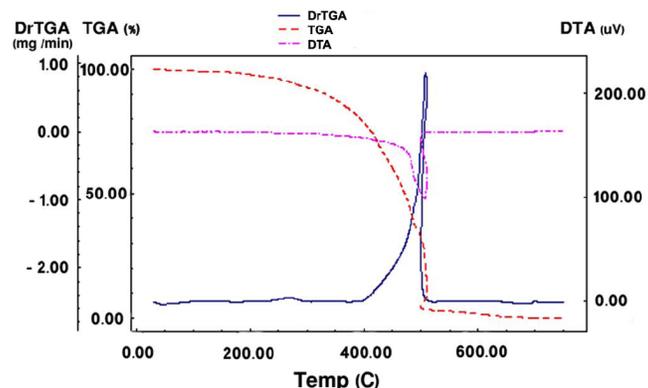

Figure 6: TGA, DTA and DrTGA traces of polymer **II** in air at a heating rate of 10 °C / min.
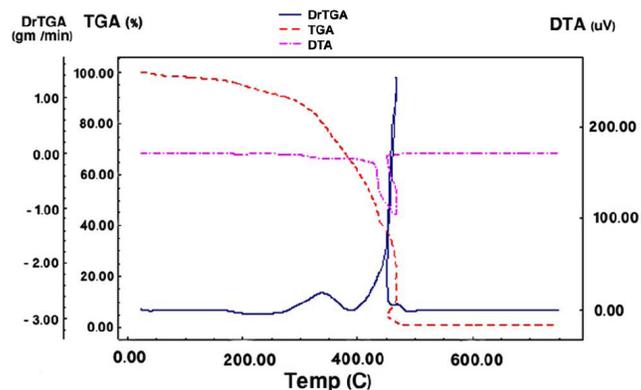

Figure 7: TGA, DTA and DrTGA traces of copolymer **III** in air at a heating rate of 10 °C / min.

It is noteworthy that the decomposition occurs mainly in three steps. The first step ranged from 220 to 374 ºC, the second step of degradation occurs between 412 and 530 ºC; while the third step of degradation occurs between 544 and 638 ºC. The rate of degradation in the third step is somewhat faster than that in the first and second steps. The expected nature of decomposition is dependent upon the nature of arylidene polymers which may be due to a pyrolytic
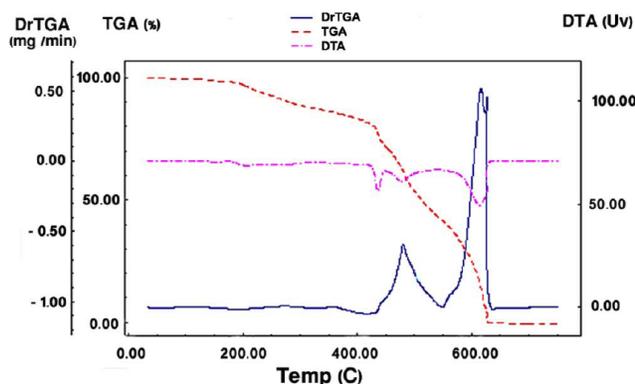
Figure 8: TGA, DTA and DrTGA traces of copolymer **V** in air at a heating rate of 10 °C / min.

oxidation of C=C bonds, scission of many bonds as reported in the literature and as mentioned in our previous studies [11-13, 30]. T_{10}, in the range from 205 to 370 ºC, is considered as polymer decomposition temperature (PDT) [31, 32]. Therefore, the data in Table **2** indicate that all investigated polymers have high thermal stability at T_{10} (higher than 200 ºC). The thermal stability at T_{10} is in the order: **VI> II > III > IV > V**. The final decomposition temperature (FDT) corresponds to the temperature at which the rate of degradation that may occur is nearly completed. It can be clarified from the TG curves that the FDT for all polymers is nearly completed at around 454-630 °C. Moreover, the data given in Table **2** is also indicated that copolymer **VI** is more thermally stable than the copolymers **III - V** and this may be attributed to the presence of n-methylpiperidone moiety in the polymer main chain. More particularly, copolymer **III**, which is based on the cyclopentanone ring, was slightly more thermally stable than copolymers **IV, V** that contain the cyclohexanone or cycloheptanone moieties respectively. This is may be attributed to higher rigidity of cyclopentanone moiety compared to the higher flexibility for both cyclohexanone and cycloheptanone

moieties. Most long chain synthetic polymer and copolymers show the characteristic sequence of changes as they are heated. For DTA trace of polymer **II**, in Figure **6**, a broad endothermic at 510 °C due to (T_m). For copolymer **III** in Figure **7**, a broad endothermic at 480 °C (*Tm*) is presented. For copolymer **V** in Figure **8**, a broad endothermic at 420 °C (T_{m1}) and 500°C (T_{m2}).

The electrical conductivity of the polymer and copolymers **II -VI** ranged from 10.2 x 10^{-11} to 8.8 x10^{-12} S cm^{-1} at 30°C as represented in Table **2**. Copolymers **III** and **IV**, which contain cyclopentanone and cyclohexanone, respectively, are the most conductive among these examined polymers. The doping with iodine as an electron acceptor is performed until the polymer is saturated with iodine. The doped polymers **(II–VI),** which have an affinity (absorbed amount) of circa 15 wt % toward iodine, were light to dark brown in colour. Those with more than 68 wt % were black after being left overnight whereas the undoped ones are yellow to orange solids. Polymers **II** and **VI** absorb 82 and 73 wt % of iodine per polymer, respectively. As can be seen from Table **2**, the electric conductivities were successfully raised by iodine doping and reached as high as 9.2 x 10^{-7} S cm^{-1} upon iodine doping of circa 65 wt %. Thus, the polyconjugated polymers with cycloalkanones moieties are good insulators, but they are converted into semiconductors by doping with iodine.

Furthermore, it is known that, there is a direct association of electrical resistivity with temperature. This is observed in the field of correlation of resistivity with heat flow, [30, 31]. It is well documented in the laboratory that the equation:

$\rho = \rho_0 \ exp \ (E/k_BT)$, applies to nearly all minerals. Here ρ is electrical resistivity (usually expressed in

Table 2: Characteristic Temperature for Thermal Degradation and Electrical Conductivity (Doped and Non-Doped) of Polymer II and Copolymers III-VI

Polymer Code	Electrical Conductivity (S cm^{-1}) [a]		Polymer Weight loss (%) at temperature up to 700ºC [b]				
	Before doping	After doping	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}
II	10.2x10^{-11}	6.8x10^{-7}	300	350	385	445	470
III	9.6x10^{-11}	7.4x10^{-8}	250	265	285	330	390
IV	8.8x10^{-12}	10.5x10^{-8}	210	255	280	320	375
V	9.5x10^{-12}	9.2x10^{-7}	205	250	275	305	340
VI	10.1x10^{-11}	7.8x10^{-7}	370	420	455	470	495

[a]Determined from Kithly 610C (the resistance of the samples were determined first).
[b]The values were determined by TGA at heating rate of 10°C min^{-1}.

ohm. cm), ρ_0 is pre-exponential factor, k_B is the Boltzmann constant, T absolute temperature and E the activation energy in eV. The electrical resistivity was measured in the temperature range from RT to 300 °C. A typical temperature dependence of the electrical resistivity of specimens in the temperature range from RT to 300 °C is shown in Figure **9** which shows three regions of temperature dependence of electrical resistivity. The first region lies in the range from room temperature up to 125 °C, the second region lies in the range from 125 to 225 °C and the third region lies in the range from 225 to 300 °C. This result indicates that there are three conduction mechanisms. It is found that, in the beginning of the temperature rise a very small weight loss is recorded as indicated in the TG curves, which is ascribed to the evolution of the few percentage of free water from the samples. As the temperature increases the structurally bound water start to release from the samples at about 125 °C which leads to the weight loss of the samples. In the first region of all curves the electrical resistivity decreases slightly with increasing temperature which may be attributed to that the only conduction mechanism is the impurity doping ions in the sample. In the second region the electrical resistivity decreases rapidly with increasing temperature, which may be attributed to, the structural change can be taken place at high temperatures, which enhances the electrical conductivity (decreases the electrical resistivity).
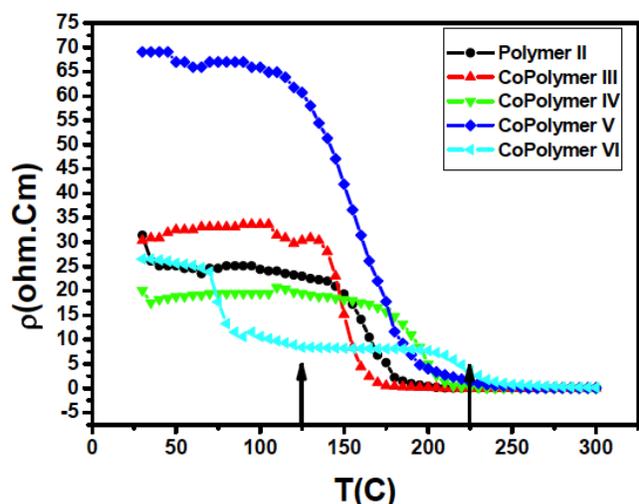

Figure 9: A typical temperature dependence of the measured electrical resistivity of polymer II and copolymers **III-VI**.

In the third region the electrical resistivity behaves as constant for all the studied samples, which may be ascribed to that, at this range of temperature all the structural water were evaluated. In the temperature range from 225 to 300 °C there is some kind of consistency in the behavior between all the studied samples which may be attributed to that, as the temperature increases, the major charge carriers in this temperature range are the lattice ions which may have the same effect on the electrical resistivity in all samples. Usually, impurity ions provide the charge carriers. The binding energy of impurity ions is somewhat less than the binding energy of regular lattice ions and, as a result, they are available for conduction at lower temperatures.

4. CONCLUSIONS

Five Novel polymer and copolymers based on methyl-cyclohexanone have successfully been synthesized *via* solution polycondensation technique. Polymers properties were strongly affected by their structural differences. In general, the presence of the aliphatic group like alkyl group leads to polymer of a higher solubility in most organic solvents particularly the polar solvents. All the synthesized polymers are dissolved completely in concentrated sulfuric acid as good example for protonic solvent. The electronic spectra of these polymers show broad absorption bands and a small bathochromic shift, indicating a highly conjugated system. All the prepared polymers are highly stable. Thermogravimetric analyses show that the copolymer which contains the cyclopentanone moiety is somewhat more thermally stable than other copolymers due to its rigidity. The final decomposition temperature for all polymers is nearly completed at around 454-630 °C. SEM images, shows the particle sizes for copolymer **IV** have expansion slots in the range 2.0 - 4.0 µm. Upon doping with iodine, the synthesized polymer and copolymers became semiconductors (10^{-8}–10^{-9} S cm^{-1}). The presence of such cycloalkanone moieties in the back bone of these polymer and copolymers enhances the electrical conductivity.

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