

New Polymer Syntheses Part: 54 Novel Conducting Polymers and Copolymers Based on 4-Tertiary Butyl-Cyclohexanone Moiety in the Main Chain

Kamal I. Aly

Pittsburg State University, Kansas polymer Research Center, 1204 Research Rd., Pittsburg, Kansas 66762

Received 7 February 2010; accepted 14 January 2011

DOI 10.1002/app.34421

Published online 15 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A new interesting class of conducting polymer and copolymers based on 4-tertiary butyl-cyclohexanone in the main chain has been synthesized by solution polycondensation of terephthalaldehyde with 4-tertiary butyl-cyclohexanone and/or cycloalkanone derivatives. The model compound **I** was synthesized from the 4-tertiary butyl-cyclohexanone with benzaldehyde, and its structure was confirmed by elemental and spectral analyses. The resulting polymer and copolymers were characterized by elemental and spectral analyses including Fourier transform infrared spectrometer (FT-IR) and nuclear magnetic resonance ($^1\text{H-NMR}$), beside solubility and viscometry measurements. The thermal properties of those polymer and copolymers were evaluated by thermogravimetric analysis

(TGA) and differential scanning calorimeter (DSC) measurements and correlated to their structural units. X-ray analysis showed that it has some degree of crystallinity in the region $2\theta = 5\text{--}60^\circ$. The UV-visible spectra of some selected polymers were measured in dimethyl sulfoxide (DMSO) solution and showed absorption bands in the range 253–398 nm, due to $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ transition. The morphological properties of selected examples were tested by scanning electron microscope (SEM). Moreover, the electrical conductivities and the doping with iodine were tested. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3390–3401, 2012

Key words: synthesis; characterization; conducting polymers; thermal properties

INTRODUCTION

Conjugated polymers have attracted considerable attention in the last two decades because of their various applications in optoelectronic devices. π -Conjugated polymers have received much attention because of their attractive electronic and optical properties. In 1977, Heeger, MacDiarmid, and Shirakawa^{1–10} reported that conductivity of polyacetylene increased remarkably by doping with iodine. Up to now, a wide variety of *p*-conjugated polymers have been synthesized, and their physical and chemical properties have been investigated by many researchers. These materials are prepared by polymerization of simple monomers that are able to form a network of highly delocalized electrons. Moreover, conjugated organic polymers have gained increasing interest in recent years as electrically conducting polymers [e.g., poly(*p*-phenylene), polypyrrole, polythiophene, and others].^{11–14}

In previous works in our laboratory,^{15,16} polyconjugated polymers and copolymers were synthesized and studied. In this article, we present a route for the

synthesis and characterization of some new polymers and copolymers containing the methyl-cyclohexanone moiety in the polymer backbone. A major target of this work was to study the effect of the cycloalkanone moiety on the properties of polyconjugated polymers, including their thermal stability, solubility, electrical conductivity, morphology, and crystallinity.

EXPERIMENTAL

Materials

Reagents

4-Tertiary butyl-cyclohexanone (Fluka, Germany), b.p. 113–116°C/20 mmHg; m.p. 47–50°C. *N*-methylpiperidine (Merck, Germany) was freshly distilled at b.p. 155°C. Benzaldehyde from (Aldrich) was used as purchased. Cyclohexanone and cyclopentanone (Merck) were freshly distilled: cyclohexanone (b.p. 155°C) and cyclopentanone (b.p. 130–131°C). Terephthalaldehyde (Aldrich, Germany) m.p. 114–116°C. Potassium hydroxide and benzaldehyde (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

Correspondence to: K. I. Aly (kamalaly@yahoo.com or kali-ibr@pittstate.edu).

formamide (DMF; BDH, Leicestershire, England). *N*-Methyl-2-pyrrolidone (NMP) and benzene (Aldrich, Seelze, Germany) were extra pure solvents and were used as received. Tetrahydrofuran (THF; Aldrich, Seelze, Germany) was a guaranteed reagent, dried over calcium hydride for 24 h, and followed by distillation under reduced pressure.

Methods

Polymerization procedure

Synthesis of model compound I: 2,6-dibenzylidene-4-tertiary butyl-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 mol of 4-tertiary butyl-cyclohexanone and 2 mol of benzaldehyde in 50 mL absolute ethanol and vigorously stirred at room temperature. Then a few drops of a 10% alcoholic solution of KOH was 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 92% at a melting point (m.p. 140°C).

Infrared (IR; KBr, cm^{-1}): at 1685 (C=O of 4-tertiary butyl-cyclohexanone), at 3050 (C—H aromatic), at 2995 (C—H aliphatic), and at 1605 (C=C group). The nuclear magnetic resonance ($^1\text{H-NMR}$) spectrum (CDCl_3) for model compound I showed peaks at 0.95 ppm (s, 9H, 3 CH_3 of 4-ter. butyl-cyclohexanone), 1.55 ppm (pent, H, CH of cyclohexanone), 2.45 ppm (m, 4H, 2 CH_2 of cyclohexanone), and 7.2–7.9 ppm (m, 10H of Ar—H and 2H of CH=C—).

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 mmol (3.658 g) 4-tertiary butyl-cyclohexanone (for the polymer II) or 1.5 mmol (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 h. 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. By using the above general procedure,

the following polymer and copolymers were obtained:

Synthesis of polymer II. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde and 3 mol (3.658 g) 4-tertiary butyl-cyclohexanone for 3 h, as yellowish powder; yield: 83%.

Anal. Calc. for $(\text{C}_{18}\text{H}_{19}\text{O})_n$: C, 86.06; H, 7.57

Found %: C, 85.56; H, 7.03

Synthesis of copolymer III. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) 4-tertiary butyl-cyclohexanone, and 1.5 mmol (1.327 g) cyclopentanone for 3 h, as yellowish powder; yield: 89%.

Anal. Calc. for $(\text{C}_{23}\text{H}_{23}\text{O}_2)_n$: C, 83.38; H, 6.95

Found %: C, 82.97; H, 6.21

Synthesis of copolymer IV. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) 4-tertiary butyl-cyclohexanone, and 1.5 mmol (1.553 g) cyclohexanone for 3 h, as yellowish powder; yield: 83%.

Anal. Calc. for $(\text{C}_{24}\text{H}_{25}\text{O}_2)_n$: C, 83.48; H, 7.25

Found %: C, 82.27; H, 6.86

Synthesis of copolymer V. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) 4-tertiary butyl-cyclohexanone, and 1.5 mmol (1.6825 g) cycloheptanone for 4 h, as yellowish powder; yield: 83%.

Anal. Calc. for $(\text{C}_{25}\text{H}_{27}\text{O}_2)_n$: C, 83.57; H, 7.52

Found %: C, 84.84; H, 7.06.

Synthesis of copolymer VI. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) 4-tertiary butyl-cyclohexanone, and 1.5 mmol (1.7521 g) *N*-methylpiperidine for 3 h, as yellowish powder; yield: 78%.

Anal. Calc. for $(\text{C}_{24}\text{H}_{26}\text{O}_2\text{N})_n$: C, 80.00; H, 7.22; N, 3.89

Found %: C, 79.12; H, 6.83; N, 3.15

Synthesis of polymer VII. Obtained by the polymerization of a mixture of 3 mol (4.024 g) terephthalaldehyde, 1.5 mol (1.829 g) 4-tertiary butyl-cyclohexanone, and 1.5 mmol (1.6825 g) methyl-cyclohexanone for 4 h, as yellowish powder; yield: 87%.

Anal. Calc. for $(\text{C}_{25}\text{H}_{27}\text{O}_2)_n$: C, 83.57; H, 7.52

Found %: C, 84.89; H, 7.26

Polymer identification

FT-IR spectra of the prepared polymers were measured on a Nicolet 6700 Fourier transform infrared spectrometer (FT-IR) Thermo Fisher Scientific (NY, 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. 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 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 η_{sp}/c to zero concentration and expressed in deciliter per gram (dL g^{-1}).

Solubility. The solubility of polymers in various solvents such as DMF, dimethyl sulfoxide (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 was calculated as percent weight of the polymer per hundred milliliter of solvent (% w/v).

Electronic spectra. The electronic spectra were scanned on 2110 PC scanning spectrophotometer, Shimadzu in NMP as a solvent (Assiut University).

Scanning electron microscopy measurements. The morphology of polymers was examined by 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 15 kV using a low-dose technique (Assiut University).

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

Thermogravimetric analysis. Thermogravimetric analysis (TGA) curves were recorded on a Shimadzu TGA-50 H in air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ 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} .

Electrical properties. 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. Conductivities have been measured at room temperature under air using Keithly Electrometer (610°C).

RESULTS AND DISCUSSION

A new and unreported class of polyconjugated polymers, and copolymers based on 4-tertiary butyl-cyclohexanone moiety, were synthesized via solution poly-

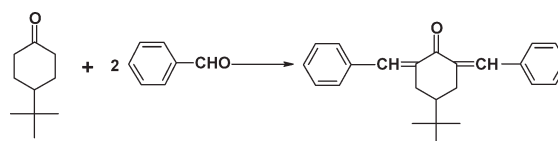
merization of terephthalaldehyde with 4-tertiary butyl-cyclohexanone to give polyconjugated polymers. A literature survey revealed that the interaction of dialdehyde (e.g., terephthalaldehyde) and diamines leads to polyimines as typically conjugated polymers by the step growth polycondensation. Thus, condensation of terephthalaldehyde with 4-tertiary butyl-cyclohexanone in alcoholic potassium hydroxide gave the polyconjugated polymer poly(benzylidene) 4-tertiary butyl-cyclohexanone. Copolycondensation of equimolar quantities of terephthalaldehyde with a mixture of cyclopentanone, cyclohexanone, cycloheptanone, *N*-methylpiperidine, or methylcyclohexanone gave copolymers **III**, **IV**, **V**, **VI**, and **VII**, respectively. The early precipitation of polymers within 20 min after mixing the monomers indicated that the polymers were insoluble in ethanol. The time of polymerization ranged from 2 to 3 h. All the polymers were yellow and intense yellow solids. Polymers were immediately isolated (see Experimental section) at the end of the reaction period. The resulting polymers were characterized by elemental analysis, IR spectra, $^1\text{H-NMR}$, solubility, viscometry, TGA, differential thermal analysis (DTA), X-ray analysis, conductivity measurements, and morphology.

Synthesis of model compound

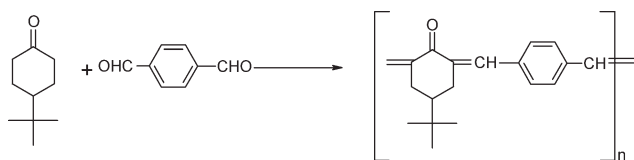
Before attempting polymerization, the model compound was synthesized by the interaction of 1 mol of 4-tertiary butyl-cyclohexanone with 2 mole of benzaldehyde in ethanol and KOH at room temperature as shown in Scheme 1. The structure of model compound was checked on the bases of good agreement between calculated and found analytical data, FT-IR, and $^1\text{H-NMR}$.

Polymer syntheses

Six novel polymer and copolymers containing 4-tertiary butyl-cyclohexanone in the main chain have been synthesized. The polymerization and copolymerization reactions were carried out at about 50°C in ethanol as a solvent and KOH as a catalyst. The reaction times varied from 2 to 3 h, and the polymers and copolymers were immediately isolated during the stirring, with yield in the range of 78–89%. The polymers were obtained as brown to yellow powder (Schemes 2–5).



Scheme 1 Synthesis of 2,6-dibenzylidene-4-tertiary butyl-cyclohexanone **I**.



Scheme 2 Synthesis of polymer II.

Polymer identification

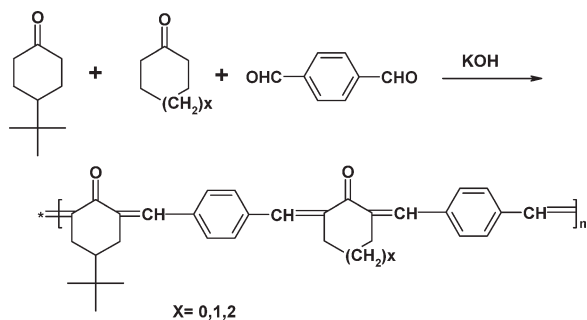
The structure of the prepared polymer and copolymers is proposed on the basis of their elemental analyses and IR spectra. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer; as shown in Experimental. It should be noted that the elemental analyses of these polymers deviated up to 1.27% from the theoretical values. However, it is common for polymers to trap solvent molecules within the polymer matrix.¹⁷

FT-IR spectroscopy

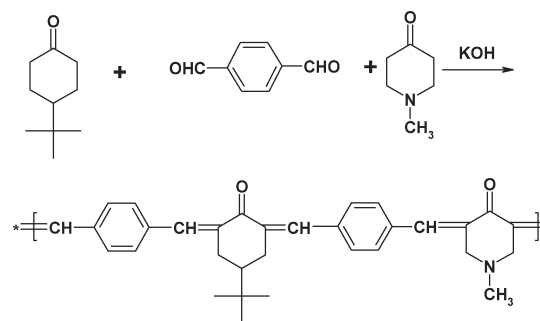
Figures 1 and 2 show FT-IR spectra of polymer II and copolymers III–VI, respectively. All the polymer and copolymers have a strong absorption near 1690 cm^{-1} , is attributed to $\text{C}=\text{O}$ of *t*-butyl-cyclohexanone moiety. The medium to strong absorption around 1600 cm^{-1} is attributed to $\text{C}=\text{C}$ 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 hydrogens.¹⁸ 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.¹⁹

$^1\text{H-NMR}$ spectra

The $^1\text{H-NMR}$ spectrum (CDCl_3) for polymer II showed peaks at $0.81\text{--}1.02\text{ ppm}$ (m, 9H, 3CH_3 of 4-ter. butyl-cyclohexanone), 1.55 ppm (pent, H, CH



Scheme 3 Synthesis of copolymers III–V.



Scheme 4 Synthesis of copolymer VI.

of cyclohexanone), 2.45 ppm (m, 4H, 2CH_2 of cyclohexanone), and $7.2\text{--}7.9\text{ ppm}$ (m, 4H of Ar-H and 2H of $\text{CH}=\text{C}$); Figure 3.

The $^1\text{H-NMR}$ spectrum (CDCl_3) for copolymer IV showed peaks at $0.82\text{--}0.89\text{ ppm}$ (m, 9H, 3CH_3 of 4-ter. butyl-cyclohexanone and 3H of CH_3 of *N*-methylpiperidine), $1.48\text{--}1.55\text{ ppm}$ (pent, H, CH of methylcyclohexanone and pent, H, CH of cyclohexanone), $2.45\text{--}3.277\text{ ppm}$ (m, 4H, 2CH_2 of *N*-methylpiperidine and m, 4H, 2CH_2 of cyclohexanone), and $7.30\text{--}7.97\text{ ppm}$ (m, 4H of Ar-H and 2H of $\text{CH}=\text{C}$); Figure 4.

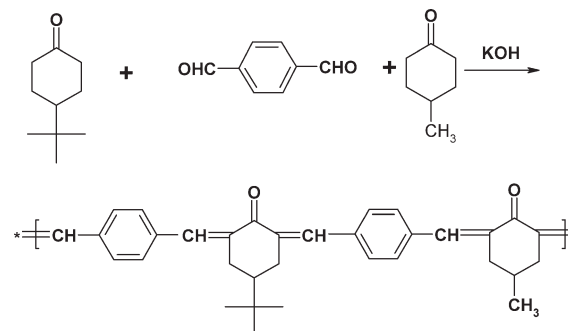
The $^1\text{H-NMR}$ spectrum (CDCl_3) for copolymer VII showed peaks at $0.80\text{--}1.01\text{ ppm}$ (m, 9H, 3CH_3 of 4-tertiary butyl-cyclohexanone and 3H of CH_3 of Methylcyclohexanone), $1.7\text{--}1.85\text{ ppm}$ (pent, H, CH of cyclohexanone), $1.9\text{--}2.1\text{ ppm}$ (m, 4H, 2CH_2 of 4-ter. butyl-cyclohexanone) $2.8\text{--}3.1\text{ ppm}$ (m, 4H of 2CH_2 , cyclohexanone), and $6.93\text{--}8.02\text{ ppm}$ (m, 4H of Ar-H and 2H of $\text{CH}=\text{C}$); Figure 5.

Polymer characterization

Viscosity

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

$$\eta_{\text{inh}} = [2.3 \log \eta / \eta_0] / C$$



Scheme 5 Synthesis of copolymer VII.

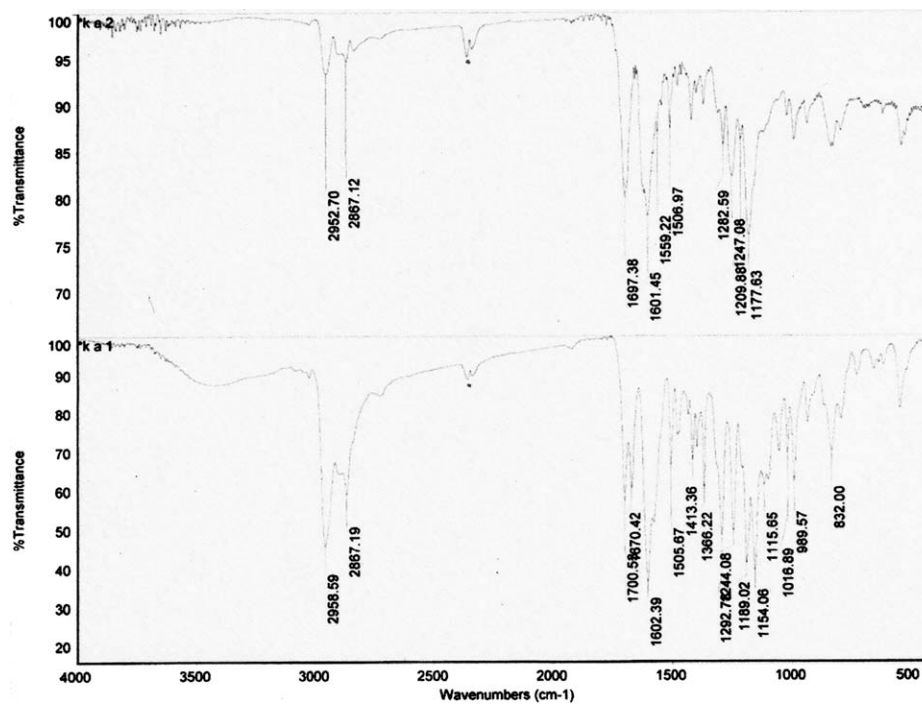


Figure 1 FT-IR figure of polymer II and copolymer III.

The solution concentration C is 0.5 g/100 mL and $\eta/\eta_0 =$ relative viscosity (or viscosity ratio). It can be shown from Table I that polymer II had high inherent viscosity (0.84 dL/g), and this may be attrib-

uted to high molecular weight of the polymer. But, the inherent viscosity of the copolymer V (0.56 dL/g) this may be attributed to low molecular weight of this polymer.

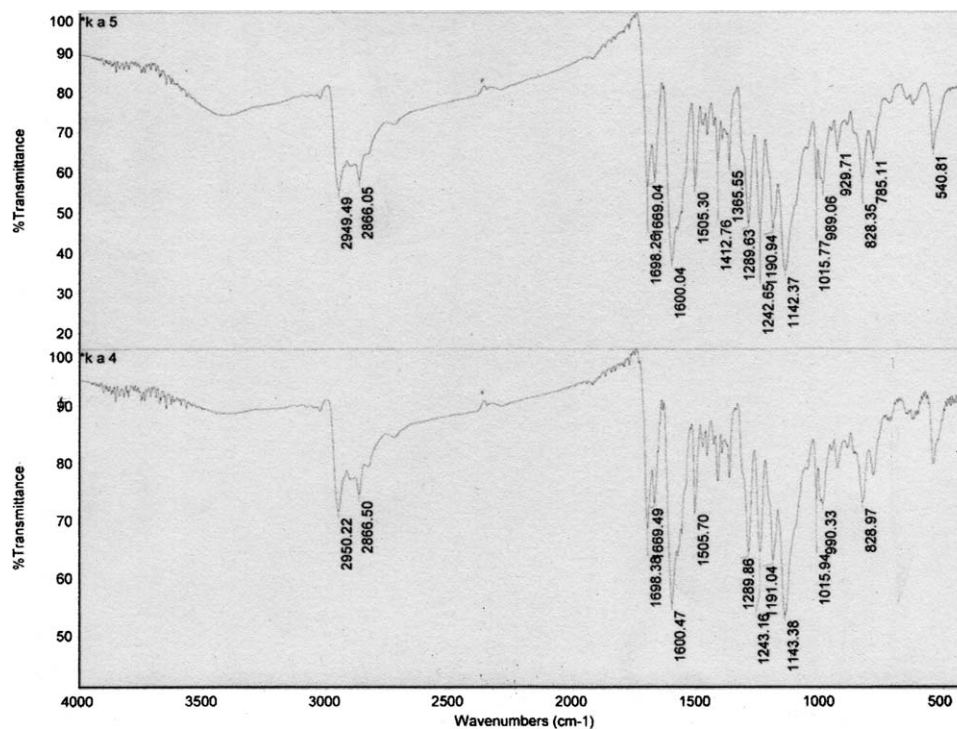


Figure 2 FT-IR figure of copolymers VI and VII.

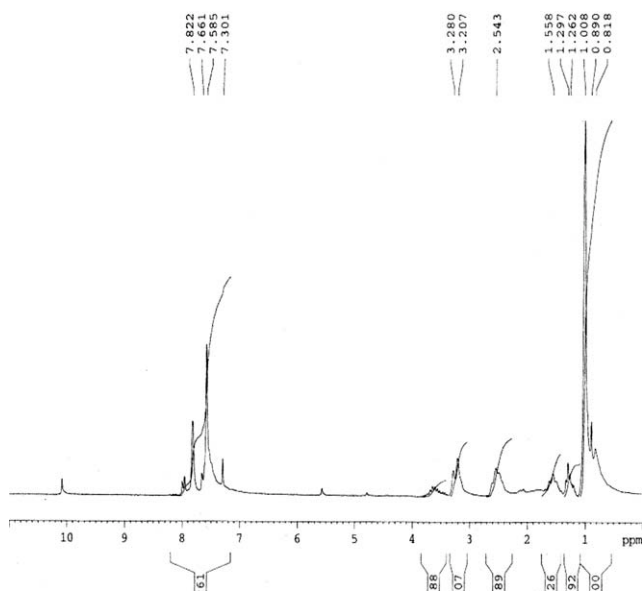


Figure 3 ¹H-NMR spectrum of polymer II.

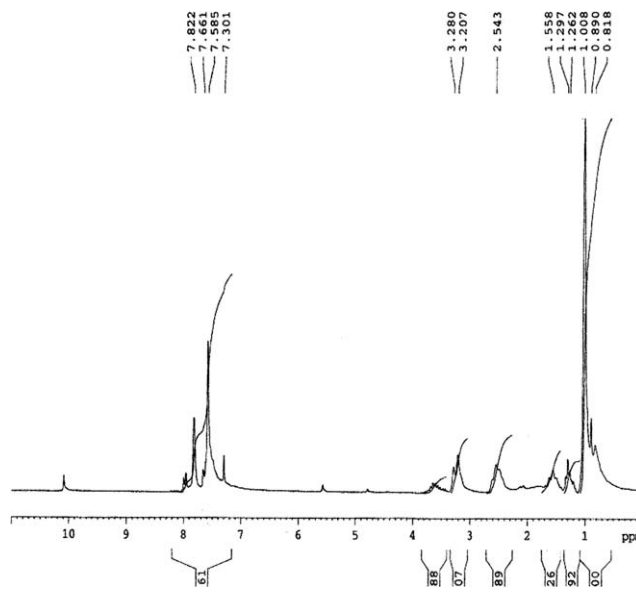


Figure 4 ¹H-NMR spectrum of copolymer IV.

Solubility

The solubility behavior of all polymer and copolymers is summarized in Table I. Almost all polymers were soluble in both polar a protic solvents, such as NMP, dimethylacetamide (DMAc), DMF, and DMSO, and less polar solvents, including acetone-chloroform mixture, THF, and *m*-cresol, except copolymers IV and V were easily soluble in less

polar solvents. It is well known that conjugated polymers generally have limited solubility in most organic solvents because of their rigid chain structure.²⁰ However, several attempts have been made to obtain polyconjugated polymers with improved solubility by introducing flexible bonding or bulky groups in the polymer backbone.²¹ Our polymers

Thermal Analysis Result

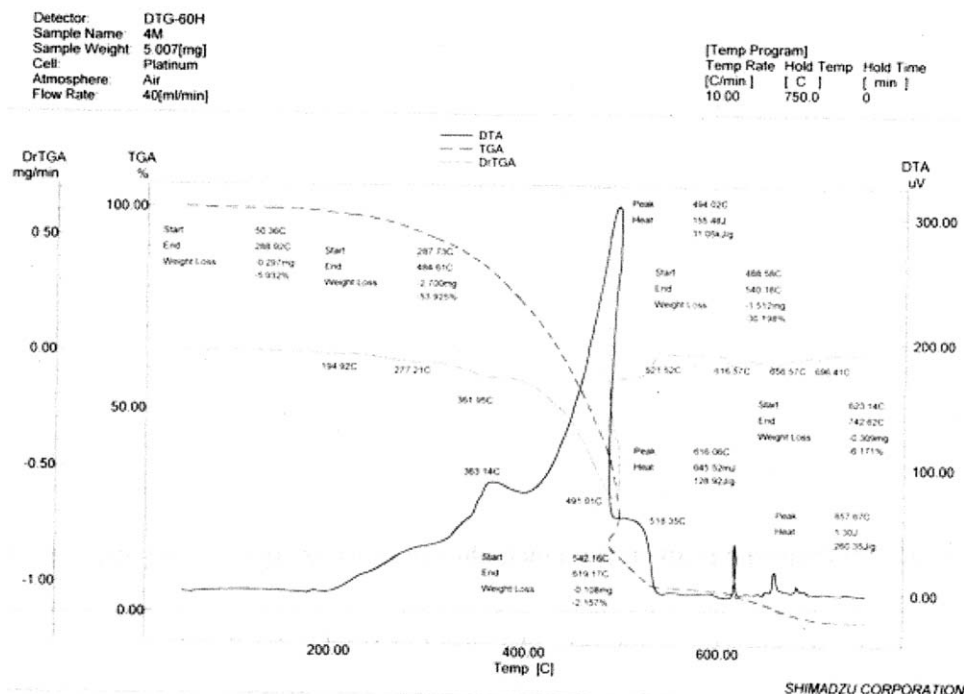


Figure 5 ¹H-NMR spectrum of copolymer VII.

TABLE I
Solubility Characteristics of Polymer II and Copolymers III–VII

Polymer code	DMSO	DMF	NMP	Chloroform	THF	Methylene chloride	Trifluoroacetic acid	H ₂ SO ₄	η_{inh}^a (dl/g)
II	+	±	+	±	±	±	+	+	0.84
III	+	+	+	+	±	+	+	+	0.65
IV	+	+	+	+	±	+	+	+	0.71
V	+	+	+	+	±	+	+	+	0.56
VI	+	+	+	+	±	+	+	+	0.74
VII	±	±	±	±	±	±	+	+	0.69

+, soluble at room temperature RT; ±, partially soluble at RT.

^a η inherent viscosity measured in NMP at 30°C.

with cycloalkanones moieties (II–VII) were insoluble in common organic solvents like alcohol, benzene, and acetone, but soluble in halogenated solvents like methylene chloride and chloroform. They also dissolved completely in concentrated sulfuric acid giving a deep brown color, except for polymer VI that was a yellowish color.

Electronic spectra

The electronic spectra of model and undoped polymer and copolymers were obtained in NMP acid at a concentration of $2.6 \times 10^{-6}M$. These displayed two absorption bands with λ_{max} near 258 nm, which was due to the $\pi-\pi^*$ transition within the benzenoid system, and with λ_{max} near 365 nm, which was due to the $\pi-\pi^*$ 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 polymer chain, and the delocalization of π electrons also contributes to the formation of the polymer-iodine adducts.

Scanning electron microscopy measurements

The morphology of the synthesized polymer II and copolymer VII (as example) was examined by 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, as described in our previous work.²² 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 polymer II showed that the surface of polymer II [Fig. 6(a), magnification $X = 3500$] consisted of porous kidney shape

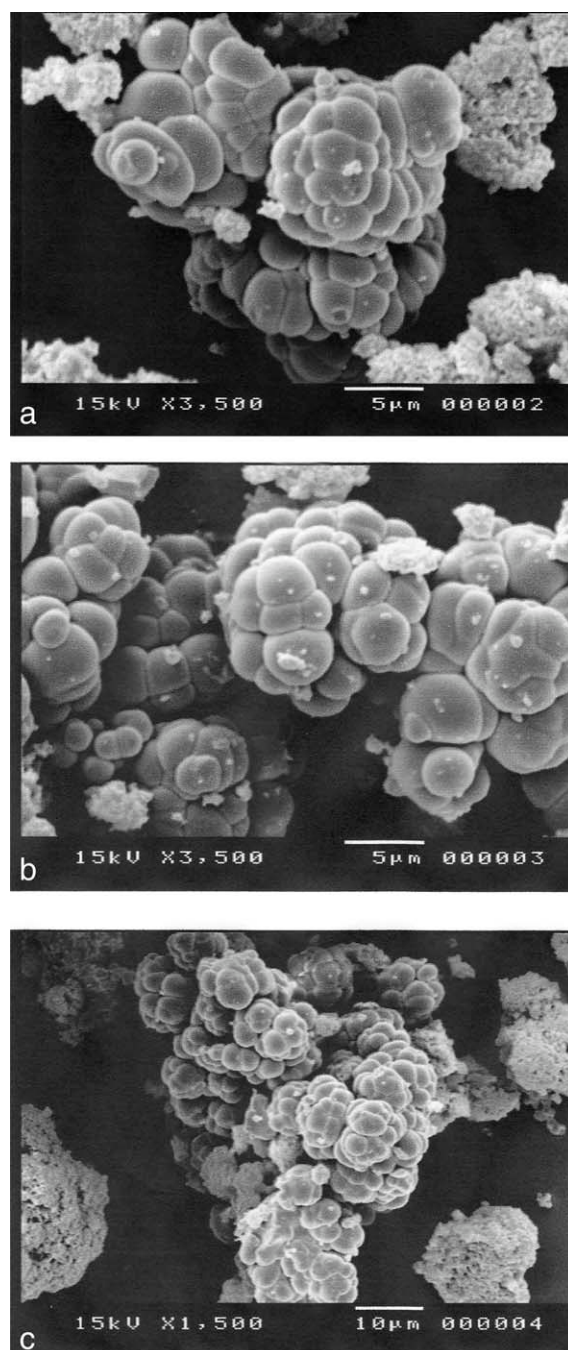


Figure 6 The SEM images of the polymer surface of polymer II (a, $X = 3500$; b, $X = 3500$; c, $X = 1500$).

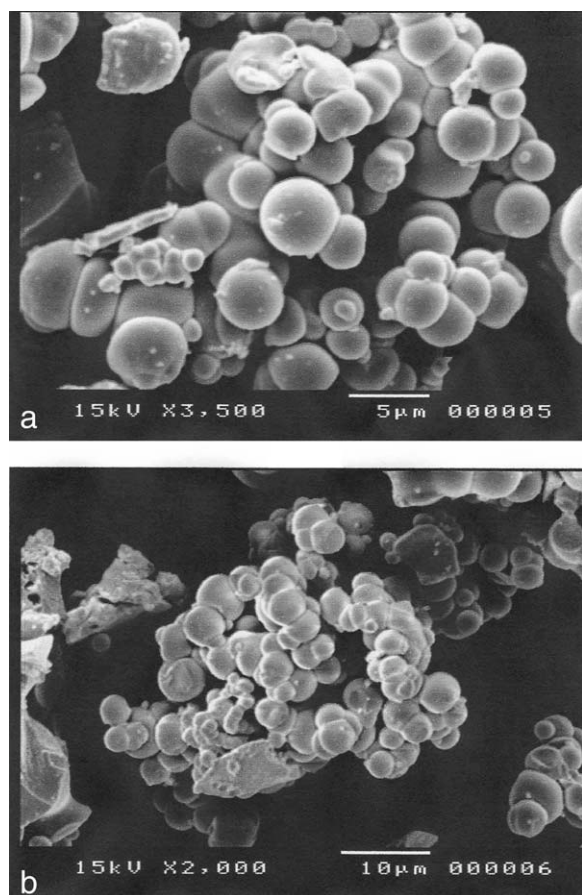


Figure 7 The SEM images of the polymer surface of copolymer VII (a, $X = 3500$; b, $X = 2000$; c, $X = 2000$).

accumulative merged particles, with lower magnification $X = 1500$ [Fig. 6(c)] showed grape fruit like shape. For copolymer VII showed that the surface

like globules in Figure 7(b,c). The higher magnifications in Figure 4(a) show that the globular and subglobular structures appeared in a continuous chain with some coalescence present. Moreover, the study of the morphological properties of these polymers is in progress and the results will be published in the near future.

X-ray analysis

The X-ray diffractogram of polyconjugated of polymer II and copolymers III and IV containing 4-tertiary butyl-cyclohexanone unit in Figures 8–10 show a few reflection peaks that are intermediate between crystalline and amorphous interference in the region $2\theta = 5\text{--}60^\circ$. This indicates that there is a large class of structures that are intermediate in the ordered states between crystals (with pronounced long-range order) in the arrangement of their atoms and molecules. Moreover, the presence of high C=C bond levels induces some order between two adjacent chains in the polymer, leading to some extent of crystallinity. Also, the diffractograms indicated that polymer II has a high degree of crystallinity in comparison with copolymers III and IV. 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.²³

Thermogravimetric analysis

The thermal properties of polymer II and copolymers III–VII containing 4-tertiary butyl-cyclohexanone unit thus obtained were investigated with

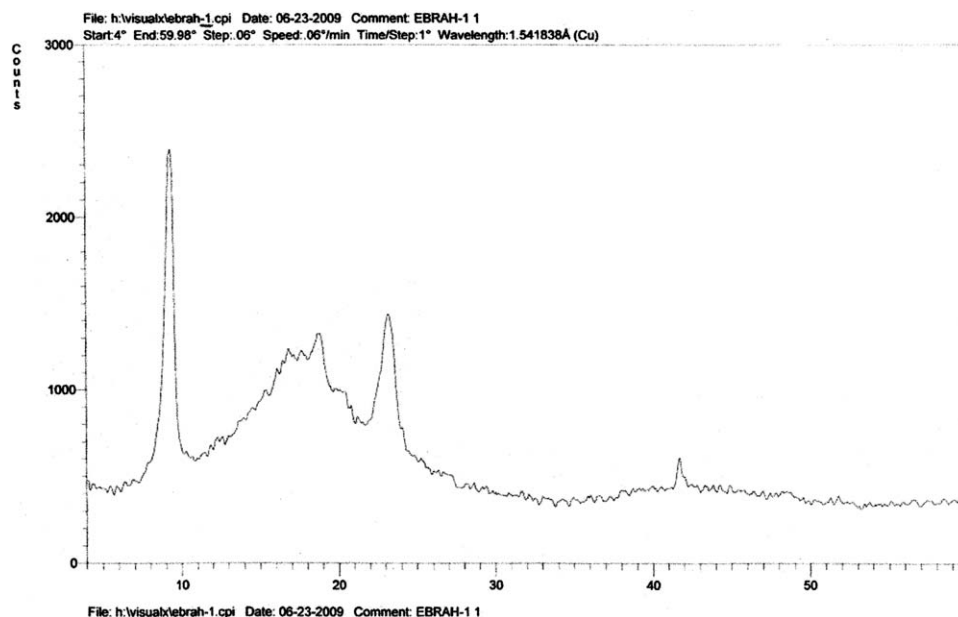


Figure 8 X-ray diffractogram of polymer II.

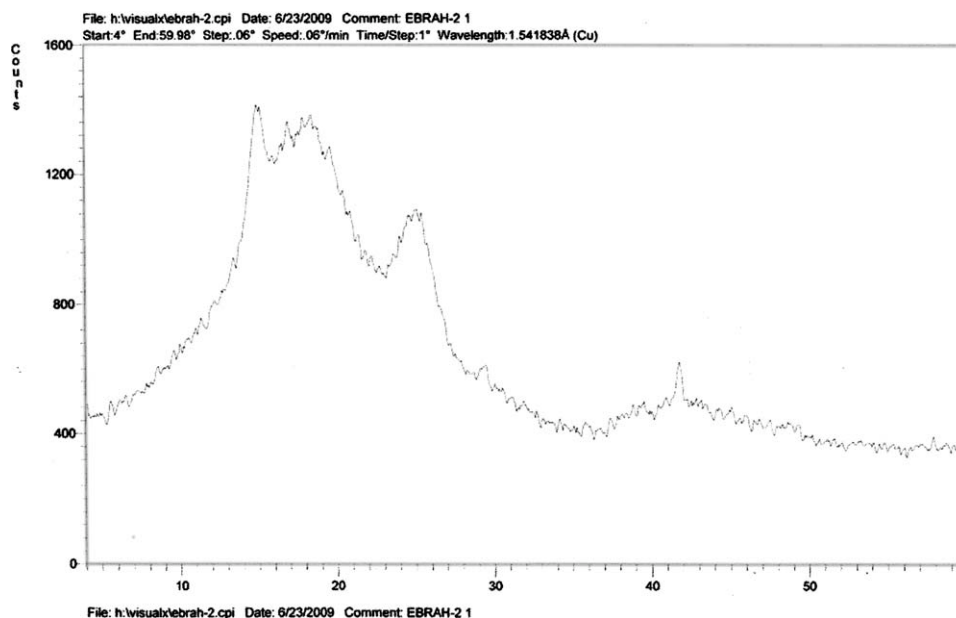


Figure 9 X-ray diffractogram of copolymer III.

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 6–8 for polymer II and copolymers VI and VII (as examples), also Table II gives the temperature of various percentages of weight loss. In Figure 11, TGA curve of polymer II shows 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 one stage. This stage, which is rapid stage between

400°C and 430°C, depends on the nature of the polymer and copolymers. The rate of degradation in the first stage is somewhat faster than in the second stage. Moreover, the data indicated that the copolymer V is more thermally stable than the copolymer VII, and this may be attributed to the presence methyl group in the polymer main chain in the later copolymer, and this decrease the stability.

More particularly, copolymer III, which was based on the cyclopentanone ring, was slightly more thermally stable than copolymers IV and V that contain

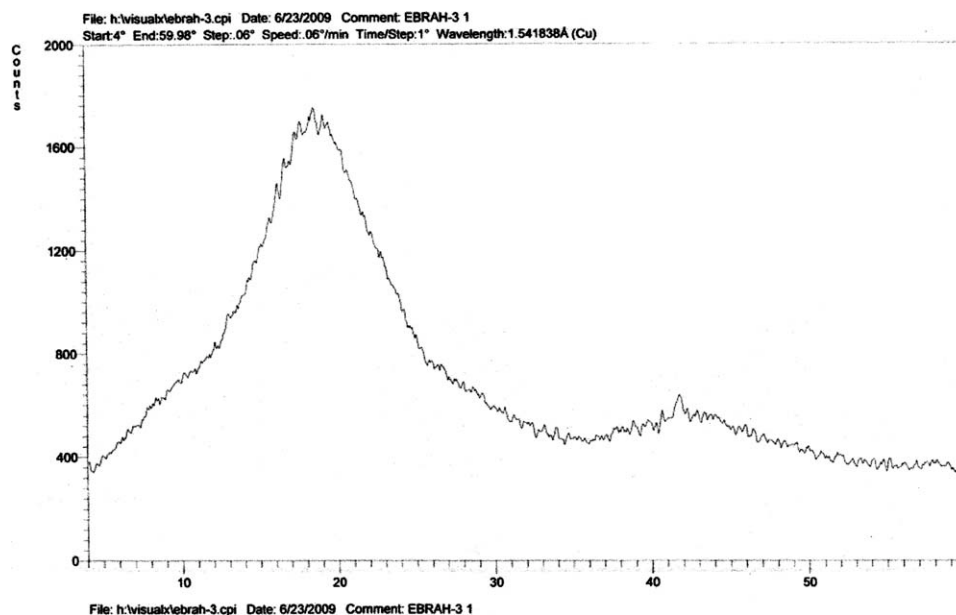


Figure 10 X-ray diffractogram of copolymer IV.

TABLE II
Characteristic Temperature for Thermal Degradation and Electrical Conductivity (Doped and Non-Doped) of Polymer II and Copolymers III–VII

Polymer number	Polymer weight loss (%) at temperature ^a up to 700°C					Electrical conductivity S cm ⁻¹	
	300 °C	400°C	500°C	600°C	700°C	Before doping	After doping
II	8	17	76	82	89	4.2×10^{-12}	4.7×10^{-8}
III	7	19	74	81	88	8.6×10^{-12}	6.4×10^{-9}
IV	12	28	79	82	93	6.8×10^{-11}	10.5×10^{-8}
V	14	32	75	85	90	7.5×10^{-11}	9.2×10^{-9}
VI	10	22	79	83	93	12.1×10^{-12}	8.9×10^{-8}
VII	13	34	79	87	92	2.2×10^{-11}	2.5×10^{-9}

^a Heating rate is 10°C/min.

the cyclohexanone or cycloheptanone moieties. This was attributed to the flexibility of the latter moiety. Most long-chain synthetic polymers show characteristic sequence of changes as they are heated. For DTA trace of polymer II, in Figure 6, a broad endothermic at 500°C (T_m). For copolymer VI in Figure 12, a broad endothermic at 480°C (T_{m1}) and 550°C (T_{m2}). For copolymer VII in Figure 13, a broad endothermic at 520°C (T_{m1}) and 550°C (T_{m2}).

Electrical conductivity

The electrical conductivity of the polymer and copolymers II–VII ranged from 10.2×10^{-11} to 8.8×10^{-12} S cm⁻¹ at 25°C (Table II). Polymers III and IV, which contain cyclopentanone and cyclohexanone, respectively, were the most conductive among these exam-

ined polymers. The doping with iodine as an electron acceptor was performed until the polymer was saturated with iodine. The doped polymers (II–VII), which had an affinity (absorbed amount) of about 12 wt % toward iodine, were light to dark brown in color. Those with more than 65 wt % were black after being left overnight, whereas the undoped ones were yellow to orange solids. Polymers II and VI absorbed 82 and 73 wt % of iodine per polymer, respectively. As can be seen from Table II, the electric conductivities were successfully raised by iodine doping and reached as high as 4.7×10^{-8} S cm⁻¹ on 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. Moreover, the study of the electrical conductivity temperature dependence, curing, and

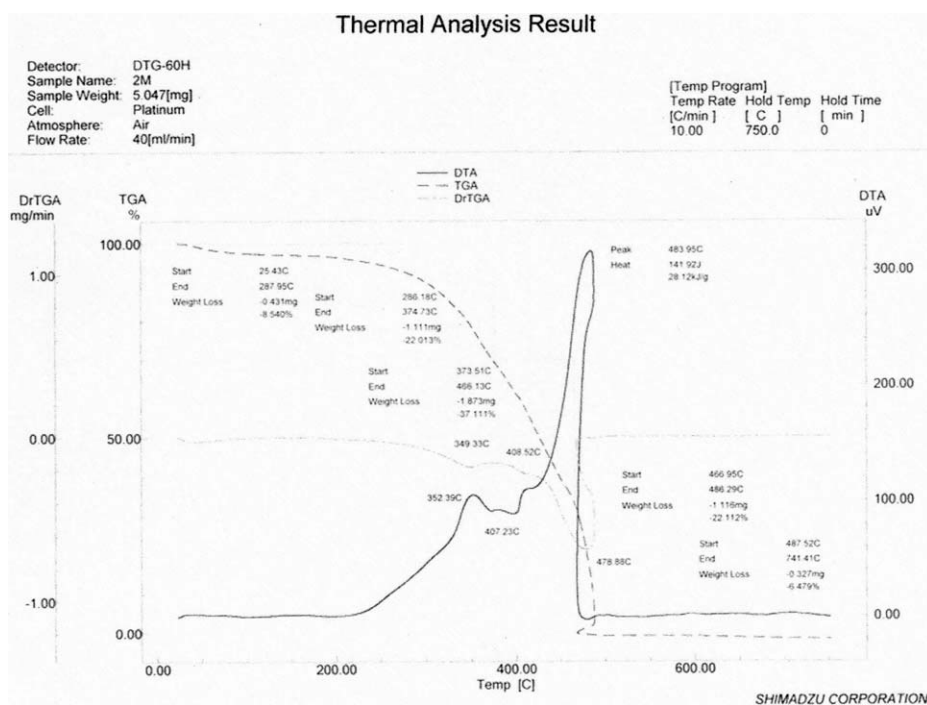


Figure 11 The TGA and DTA traces of polymer II in air at a heating rate of 10°C/min.

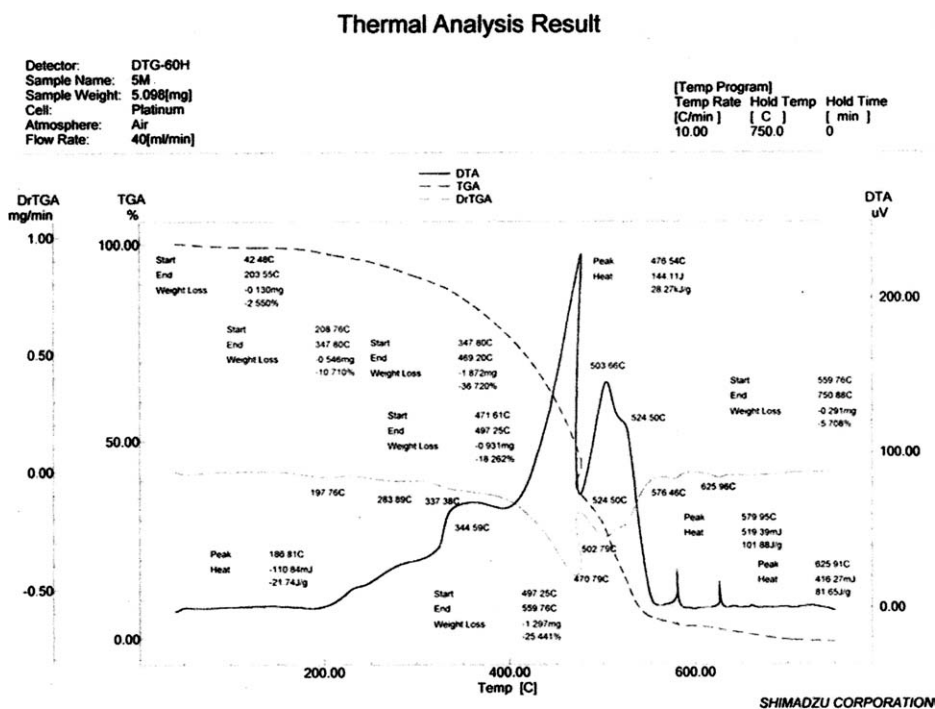


Figure 12 The TGA and DTA traces of copolymer VI in air at a heating rate of 10°C/min.

irradiation of these polymers is in progress, and the results will be published in the near future.

CONCLUSIONS

Six novel polymer and copolymers based on 4-tertiary butyl-cyclohexanone have successfully been syn-

thesized via solution polycondensation technique. Polymers properties were strongly affected by their structural differences. In general, the presence of the aliphatic group like tertiary butyl(CH₃)₄— leads to polymer of a higher solubility in most organic solvents particularly the polar solvents and halogenated solvents. All the prepared polymers are highly

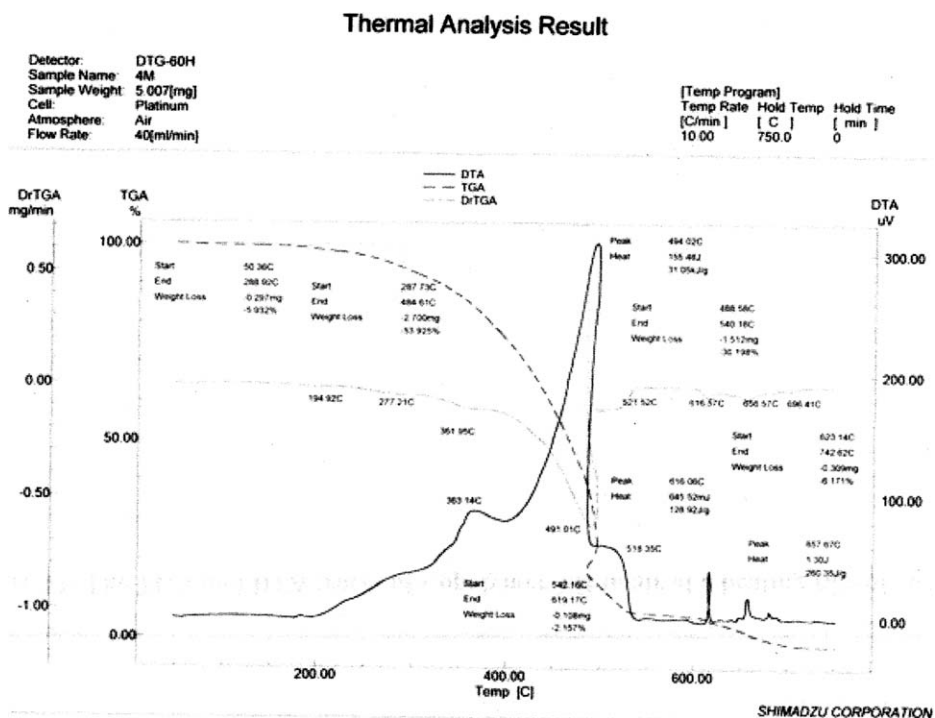


Figure 13 The TGA and DTA traces of copolymer VII in air at a heating rate of 10°C/min.

thermally stable and TGAs showed that the copolymers which contain the cyclopentanone moiety were somewhat more thermally stable than other copolymers due to its rigidity. On doping with iodine, the synthesized polymers became semiconductors (10^{-8} – 10^{-9} S cm $^{-1}$).

References

1. Heeger, A. J. *Angew Chem Int Ed* 2001, 40, 2591.
2. MacDiarmid, A. G. *Angew Chem Int Ed* 2001, 40, 2581.
3. Shirakawa, H. *Angew Chem Int Ed* 2001, 40, 2575.
4. Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem Rev* 1988, 88, 183.
5. Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers*, 3rd ed.; Marcel Dekker: New York, 2006.
6. Nalwa, H. S. *Handbook of Organic Conductive Molecules*; Wiley: Chichester, 1997.
7. Salaneck, W. R.; Clark, D. T.; Samuelsen, E. J. *Science and Applications of Conducting Polymers*; Adam Hilger: Bristol, 1991.
8. Li, X. G.; Huang, M. R.; Duan, W.; Yang, Y. L. *Chem Rev* 2002, 102, 2925.
9. Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kanar, R. B.; Science 1991, 252.
10. Li, X. G.; Hua, Y. M.; Huang, M. R. *Chem Eur J* 2005, 11, 4247.
11. Rehahn, M.; Schluter, A. D.; Weger, G.; Feast, W. J. *Polymer* 1989, 30, 1054.
12. Rehahn, M.; Schluter, A. D.; Weger, G.; Feast, W. J. *Polymer* 1989, 30, 1060.
13. Gagnan, D. R.; Capistran, J. D.; Karaz, F. E.; Lenz, R. W.; Antoun, S. *Polymer* 1987, 28, 567.
14. Ng, S. C.; Chan, H. S. O.; Yu, W. L. *J Mater Sci Lett* 1997, 16, 809.
15. Aly, K. I. *J Appl Polym Sci* 1999, 74, 2369.
16. Aly, K. I.; Khalaf, A. A. *J Appl Polym Sci* 2000, 77, 1218.
17. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1974.
18. Skoog, D. A.; West, D. M. *Principles of Instrumental Analysis*; Holt, Rinhart, Winston: New York, 1971.
19. Aly, K. I.; Mostafa, H.; Wahdan, A.; Hussein, J. *J Appl Polym Sci* 2009, 112, 513.
20. Aly, K. I.; Monem M. I. A. *J Appl Polym Sci* 2005, 98, 2394.
21. Aly, K. I.; Hussein, M. A. *J Polym Res* 2009, 112, 620.
22. Al-Muaikel, N. S.; Aly, K. I.; Hussein, M. A. *J Appl Polym Sci* 2008, 108, 3138.
23. Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.