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ORIGINAL ARTICLE

Novel conducting terepolymers based on methyl-cyclohexanone moiety in the main chain: Synthesis and properties



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KEYWORDS

Synthesis; Characterization; Conducting polymers; Cycloalkanones; Electrical conductivity **Abstract** Five novel terepolymers based on methyl-cyclohexanone in the polymer main chain have successfully been synthesized via solution polycondensation technique. These terepolymers were prepared from the polycondensation of terephthalaldehyde with methyl-cyclohexanone and different cycloalkanone derivatives. They were characterized by viscosimetry, FT-IR, X-ray, thermal gravimetric analysis, and differential scanning calorimetry, UV–visible spectroscopy, SEM and electrical conductivities. X-ray analysis showed that it has some degree of crystallinity in the region $2\theta = 5-60^{\circ}$. The UV–visible spectra of some selected terepolymers were measured in DMF solution and showed absorption bands in the range 272–394 nm, due to $n-\pi^*$ and $\pi-\pi^*$ transition. The electrical conductivities in the $10^{-9}-10^{-8} \Omega^{-1} \text{ cm}^{-1}$ range were observed after doping with iodine. (© 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access

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1. Introduction

Polymers that exhibit high electrical conductivity have now been successfully synthesized and the past two decades have witnessed unabated interest in the synthesis and characterization of such conducting polymers, due to the potential technological applications of these materials (Skotheim, 1986;Bhadani et al., 1992; Alcacer, 1987; Salaneek et al., 1991). In 1977, Heeger, MacDiarmid, and Shirakawa reported that conductivity of polyacetylene increased remarkably by

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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 (Heeger, 2001; MacDiarmid, 2001; Shirakawa, 2001; Patil, 1988; Skotheim and Raynolds, 2006; Li et al., 2002, 2005; Konwer et al., 2011; Morita, 2011; Matru and Nayak, 2010; Muath and Bernadette, 2011; Libing et al., 2011). 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] (Rehahn et al., 1989; Gagnan et al., 1987; Ng et al., 1997; Skoog and West, 1971). In this article we present a route for the synthesis and characterization of some new terepolymers containing the methyl-cyclohexanone moiety in the polymer main chain. A major target of this work was to study the effect

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Scheme I Synthesis of terepolymer I.



Scheme II Synthesis of terepolymer II.



Scheme III Synthesis of terepolymer III.

of the cycloalkanone moiety upon the properties of polyconjugated polymers, including their thermal stability, solubility, electrical conductivity, morphology and crystallinity.

2. Experimental

2.1. Materials

Methyl-cyclohexanone (Fluka, Germany) was freshly distilled at b.p. 169–171 °C. *N*-methyl piperidone (Merck, Germany) was freshly distilled at b.p. 155 °C. Cyclohexanone, cyclopentanone and cycloheptanone (Merck) were freshly distilled: cyclohexanone (b.p. 155 °C), cyclopentanone (b.p. 130–131 °C), and cycloheptanone (b.p. 179 °C). *N*-methyl piperidone (Aldrich), b.p. 181–182 °C. Terephthalaldehyde (Aldrich, Germany) m.p. 114–116 °C. Potassium hydroxide and all other reagents were of analytical grade and were used as received.

2.1.1. Polymerization procedure

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



Scheme IV Synthesis of terepolymer IV.



Scheme V Synthesis of terepolymer V.

2.1.2. 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, 1 mol (1.219 g) methyl-cyclohexanone, and 1 mol for each other cycloalkanone 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 yellow 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 terepolymers were obtained:

Terepolymer I: Obtained by the polymerization of the following mixture: 3 mol (4.024 g) of terephthalaldehyde and 1 mol of each methyl-cyclohexanone, cyclohexanone and cyclopentanone for 4 h, as yellowish powder polymer in yield: 89%.

Terepolymer II: Obtained by the polymerization of the following mixture: 3 mol (4.024 g) of terephthalaldehyde and 1 mol for each methyl-cyclohexanone, cyclohexanone and cycloheptanone for 3 h, as yellowish powder; yield: 82%.

Terepolymer III: Obtained by the polymerization of the following mixture: 3 mol (4.024 g) of terephthalaldehyde and one mole for each methyl-cyclohexanone, cyclohexanone and *N*-methylpiperidinone for 3 h, as yellowish powder; yield: 87%.



Figure 1 Electronic spectra of terepolymers I–IV.

Terepolymer IV: Obtained by the polymerization of the following mixture: 3 mol (4.024 g) of terephthalaldehyde and one mole for each methyl-cyclohexanone, cyclopentanone and

Table 1 Solubility characteristics of terepolymers I–V.												
Terepolymer codes	DMSO	DMF	NMP	Chloroform:acetone (1:1)	THF	Methylene chloride	Triflouro-acetic acid	H_2SO_4	$\eta_{inh} (dL g^{-1})^a$			
I	+	+	+	±	±	±	+	+	0.79			
II	+	+	+	+	+	+	+	+	0.63			
III	+	+	+	±	±	+	+	+	0.71			
IV	+	+	+	+	±	+	+	+	0.66			
V	+	+	+	±	±	+	+	+	0.68			
(+) Soluble at room temperature PT												

(+) Soluble at room temperature RT.

 (\pm) Partially soluble at RT.

^a η inherent viscosity measured in DMF at 25 °C.

N-methylpiperidinone for 4 h, as yellowish powder; yield: 93%.

Terepolymer V: Obtained by the polymerization of the following mixture: $3 \mod (4.024 \text{ g})$ of terephthalaldehyde and one mole for each methyl-cyclohexanone, cycloheptanone and *N*-methylpiperidinone for 4 h, as yellowish powder; yield: 91%.

2.1.3. Polymer characterization

2.1.3.1. Viscosity. Inherent viscosity measurements were carried out on 0.5% solutions of the polymers in DMF 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).

2.1.3.2. Solubility. The solubility of polymers in various solvents was determined at room temperature (25 °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).

2.1.3.3. *Electronic spectra*. The electronic spectra were scanned on 2110 PC scanning spectrophotometer, Shimadzu in DMF as a solvent.

2.1.3.4. 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.

2.1.3.5. 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 Ka (40 kV/15 mA). The samples were maintained at a stationary state while scattering angles (2θ) from 5° to 60° were scanned in the reflection mode at a scanning rate of 1° min⁻¹.

2.1.3.6. 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.

2.1.3.7. 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).

3. Results and discussion

A new and unreported class of polyconjugated terepolymers based on methyl-cyclohexanone moiety, were synthesized via solution polymerization of terephthalaldehyde with methylcyclohexanone and different cycloalkanones derivatives 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 cycloalkanones in alcoholic potassium hydroxide gave the polyconjugated polymer. Terepolymerization of equimolar quantities of terephthalaldahyde with a mixture of methyl-cyclohexanone with (cyclohexanone + cyclopentanone), (cyclohexanone + cycloheptanone), (cyclohexanone + N-methylpiperidinone), (cyclopentanone + Nmethylpiperidinone) and (cycloheptanone + N-methylpiperidinone) gave the terepolymers I, II, III, IV and V, respectively, as shown in Schemes I-V.

The early precipitation of terepolymers within 30 min after mixing the monomers indicated that the polymers were insoluble in ethanol. The time of polymerization ranged from 3 to 4 h. All the terepolymers were yellow and intense yellow solids. Polymers were immediately isolated at the end of the reaction period. The resulting terepolymers were characterized by FT-IR spectra, 1H-NMR, solubility, viscometry, TGA, DTA, X-ray analysis, conductivity measurements, and morphology.

3.1. Polymer characterization

3.1.1. FT-IR spectroscopy

FT-IR spectra of all the terepolymers I–V showed a strong absorption near 1660–1690 cm⁻¹, attributed to C=O groups which are present in all the cyclolakanones moieties. The medium to strong absorption around 1600 cm⁻¹ is attributed to C=C stretching. The phenyl ring vibrations are assigned to absorption near 1600 and 1500 cm⁻¹. The CH₃ asymmetric and symmetric bending modes are traced to 1450 and



Figure 2 X-ray diffractogram of terepolymer I.



Figure 3 X-ray diffractogram of terepolymer II.

1350 cm⁻¹, respectively. The CH₂ bending mode also appears around 1455 cm⁻¹. The medium strong peak at 830 cm⁻¹ may be assigned to CH out-of-plane bending in the benzene ring having two adjacent hydrogen.

3.1.2. 1H-NMR Spectra

The 1H-NMR spectrum (d_6 /DMSO) for terepolymer I showed peaks at 1.0–1.26 ppm (m, 3H, CH₃ of methyl-cyclohexanone); 1.29–1.55 ppm (pent, H, CH of cyclohexanone), 2.45–2.56 ppm



X-ray diffractogram of terepolymer III. Figure 4



Figure 5 X-ray diffractogram of terepolymer V.

(m, 4H, 2CH₂ of methyl-cyclohexanone and 4H, 2CH₂ of cyclopentanone); 3.20-3.28 ppm (m, 4H of 2CH₂, cyclohexanone), 7.3-7.8 ppm (m, 4H of Ar-H and 2H of CH=C-). The 1H-NMR spectrum (d_6 /DMSO) for terepolymer III showed peaks at 1.00-1.02 ppm (m, 3H, CH₃ of methyl-cyclohexanone and 3H of CH₃ of N-methylpiperidone), 1.40-1.87 ppm (m, H, CH of cyclohexanone), 1.9-2.1 ppm (m, 4H, 2CH2 of cyclohexanone) 2.53-3.27 ppm (m, 4H of 2CH₂, cyclohexanone, and 4H of cyclopentanone moiety), 7.3-7.97 ppm (m, 4H of Ar-H and 2H of CH=C-).

3.1.3. Viscosity

The inherent viscosities (η_{inh}) of the terepolymers I-V were determined in DMF at 25 °C with an Ubbelohde suspended-level viscometer. The inherent viscosity value is defined as

$$\eta_{inh} = [2.3 \log \eta/\eta^0]/C$$







(B)



Figure 6 The SEM images of the polymer surface of terepolymer I: (a) $\times 1500$, (b) $\times 5000$ and (c) $\times 7500$.

The solution concentration *C* is 0.5 g/100 ml, η/η^0 = relative viscosity (or viscosity ratio). It can be shown from Table 1 that terepolymer I had high inherent viscosity (0.79 dL g⁻¹) and this may be attributed to high molecular weight of the polymer, but, the inherent viscosity of the terepolymer III (0.63 dL g⁻¹) may be attributed to low molecular weight of this polymer.



Figure 7 The SEM images of the polymer surface of terepolymer III: (a) $\times 2000$, (b) $\times 3500$ and (c) $\times 5000$.

3.1.4. Solubility

The solubility behavior of all the terepolymers is summarized in Table 1. All the polymers were soluble in polar aprotic solvents, such as NMP, DMF, and DMSO, and also completely soluble in the acids like concentrated sulphuric acid and triflouro-acetic acid. In less polar solvents, like acetone–chloroform mixture, THF, and most of them were partially soluble. In halogenated solvent like methylene chloride, the majority of the polymers are completely soluble except polymer **I**, which



Figure 8 TGA and DTA diagrams of terepolymer I in air at a heating rate of 10 °C min⁻¹ (TGA: ----, DTA: -.-.-).



Figure 9 TGA and DTA diagrams of terepolymer III in air at a heating rate of 10 °C min⁻¹ (TGA: -----, DTA: -----).

Terepolymer numbers	Polymer weig	ght loss (%) at temp	Electrical conductivity S cm ⁻¹			
	300 °C	400 °C	500 °C	550 °C	Before doping	After doping
I	14	18	78	82	4.1×10^{-12}	4.7×10^{-8}
II	11	19	74	81	8.6×10^{-12}	6.4×10^{-9}
III	9	28	79	82	5.8×10^{-11}	10.5×10^{-8}
IV	15	32	75	85	7.2×10^{-11}	8.9×10^{-8}
V	11	36	75	79	6.7×10^{-11}	5.5×10^{-8}

^a Heating rate 10 °C min⁻¹.

may be attributed to the presence of cyclopentanone ring as a rigid moiety, this decreases the solubility. It is well known that conjugated polymers generally have limited solubility in most organic solvents because of their rigid chain structure (Aly and Kandeel, 1996).

3.1.5. Electronic Spectra

The electronic spectra in Fig. 1 of terepolymers **I–IV** as selected samples were obtained in DMF at a concentration of 2.6×10^{-6} M. These displayed two absorption bands with λ max near 275–287 nm, which was due to the π – π * transition within the benzenoid system, and with λ_{max} near 331–406 nm, which was due to the π – π * excitation of C=O or C=N groups. The diagram shows 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.

3.1.6. X-ray analysis

The X-ray diffractogram of polyconjugated terepolymers I-III and V in Figs. 2-5, respectively, shows few reflection peaks that are intermediate between crystalline and amorphous interference in the region $2\theta = 5-60^{\circ}$. 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 terepolymer V has a high degree of crystallinity in comparison with terepolymers I-III, this may be attributed to the presence of the cycloheptanone beside the N-methyl-cyclohexanone moieties as flexible moieties in the main chain. Moreover, the presence of C=O, C=C, as polar groups, induces some order between two adjacent chains of the polymers, leading to a certain extent of crystallinity (Mandelkern, 1964).

3.1.7. Scanning electron microscopy measurements

The morphology of the synthesized polymers I and III (as examples) was examined by scanning electron microscopy (SEM). The sample was prepared by putting a smooth part of polymer powder on a copper holder and subsequently coating it with gold palladium alloy. SEM images were taken on a penta Z Z-50 P Camera with Ilford film at an accelerating voltage of 15 kV using a low-dose technique (Tager, 1972). This technique gives us the ability to show the surface of the polymers at different magnification. The study of selected terepolymer I showed that the surface of this polymer (Fig. 6a, magnification ×1500) consisted of globules shape accumulative merged particles, with higher magnification ×5000 and ×7500 (Fig. 6b and c) showed that globules like needles shape. For polymer III showed that the surface like the cauliflower in Fig. 7a where the $\times 2000$, with higher magnifications in Fig. 7b and c the cauliflower shape structures appeared in a continuous chain.

3.1.8. Thermogravimetric analysis

The thermal properties of terepolymers I-V based on methylcyclohexanone unit thus obtained, were investigated with the aids of thermogravimetric analysis TGA and DTA in air at a heating rate of 10 °C min⁻¹. The thermographs of these polymers are given in Figs. 8 and 9 for terepolymers I and III (as example), also Table 2 gives the temperature of various percentages of weight loss. In Fig. 8, TGA curve of polymer I shows a weight loss in the range 6–15% starting at 150–190 °C, which may be attributed to the loss of absorbed moisture and entrapped solvents. The thermograph also indicates that the terepolymer decomposes in one stage. This stage which is the rapid stage between 390 °C and 440 °C depends upon the nature of the terepolymer.

In Fig. 9, TGA curve of polymer III shows a weight loss in the range 9–18% starting at 130–180 °C, which may be attributed to the loss of absorbed moisture and entrapped solvents. The thermograph also indicates that the terepolymer decomposes in one stage. This stage which is the rapid stage between 370 °C and 410 °C depends upon the nature of the terepolymer. Moreover, the data indicated that the terepolymer I is more thermally stable than the terepolymer III and this may be attributed to the presence cyclopentanone as a rigid moiety in the polymer main chain in the latter terepolymer, and this decreases the stability.

More particularly, terepolymers I and IV, which were based on the cyclopentanone ring, were slightly more thermally stable than II, III and V that contain the cyclohexanone or cycloheptanone moieties. This was attributed to the flexibility of the latter moiety. Most long chain synthetic polymers show a characteristic sequence of changes as they are heated. For DTA trace of terepolymer I, in Fig. 8, a broad endothermic at 460 °C (T_m). For terepolymer III in Fig. 9, a broad endothermic at 430 °C (T_{m_1}) and 470 °C (T_{m_2}).

3.1.9. Electrical conductivity

The electrical conductivity of the terepolymers I-IV ranged from 5.8×10^{-11} to 4.1×10^{-12} S cm⁻¹ at 25 °C (Table 2). Terepolymers I and IV, which contain cyclopentanone moiety, were the most conductive among these examined polymers. The doping with iodine as an electron acceptor was performed until the polymer was saturated with iodine. The doped terepolymers (I-IV), which had an affinity (absorbed amount) of about 10 wt.% toward iodine, were light to dark brown in color. Those with more than 63 wt.% were black after being left overnight whereas the undoped ones were yellow to orange solids. Polymers I and III absorbed 80 and 71 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 10.5×10^{-8} S cm⁻¹ upon iodine doping of about 68 wt.%. Thus, the polyconjugated polymers with cycloalkanone moieties are good insulators, but they are converted into semiconductors by doping with iodine.

4. Conclusions

Five novel terepolymers based on methyl-cyclohexanone have successfully been synthesized via solution polycondensation technique. The properties of the polymers were affected by their chemical structure. In general, the presence of the methyl pendant group leads to a polymer of a higher solubility in most organic solvents particularly the polar solvents. All the prepared terepolymers are highly thermally stable and thermogravimetric analyses showed that the terepolymers containing the cyclopentanone (polymers I and IV) were somewhat more thermally stable than other terepolymers due to its rigidity. Upon doping with iodine, the synthesized polymers became semiconductors $(10^{-8}-10^{-9} \text{ S cm}^{-1})$.

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