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# Syntheses and Characterization of New Conjugated Polymer Containing 4-Phenylcyclohexanone as a Pendent Group

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A new interesting category of polyconjugated polymer, poly(2,6-dibenzylidene)-4-phenylcyclohexanone was prepared by condensation of 4-phenylcyclohexanone with terephthalaldehyde at ambient temperature. The polymer was characterized by elemental analyses, IR, <sup>1</sup>H-NMR spectra, UV and visible spectra and X-ray analysis. The inherent viscosity was found to be 0.85 dl/g and showed good solubility in various aprotic polar solvents. The thermal behavior of the synthesized polymer was evaluated by TGA analyses and correlated with their structure. The morphology of the polymer was examined by a scanning electron microscope. Electrical conductivity in the range of  $10^{-8} \Omega^{-1} \text{ cm}^{-1}$  at room temperature and the doping with iodine showed good conductivity after doping, well within the semiconducting region.

**Keywords:** syntheses; characterization; conjugated; 4-phenylcyclohexanone; conductivity

## 1 Introduction

For more than 20 years, electrical conduction in organic solids has been one of the most fascinating topics for organic chemists and solid-state physicists. Synthesis and characterization of conjugated polymers have attracted much attention because of academic interest and practical applications such as electronics (1), nonlinear optical (NLO) materials (2, 3). Conjugated polymers are prepared by polymerization of simple monomers that are able to form a network of highly delocalized electrons usually prepared in the form of intractable films, gels, or powders that are insoluble in common organic solvents. For example, polyacetylene is typically synthesized by the polymerization of gaseous acetylene monomer using a soluble Ziegler-Natta catalyst system such as  $\text{Ti}(\text{OBu}')_4\text{-4AlEt}_3$  in nonpolar solvents such as toluene or cyclohexane (4). Depending on the reaction conditions, the polyacetylene is obtained as an insoluble film, precipitate, or gel. On the other hand, polypyrrole and polyaniline are usually synthesized using chemical oxidants [e.g.,  $\text{FeCl}_3$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] in either acidic aqueous media (5) or certain nonaqueous solvents such as ethers (6), esters (6), alcohols

(7), or acetonitrile (8). In each case, the conducting polymer is invariably obtained as an insoluble bulk powder, with compressed pellet conductivities in the 1–200 S/cm range. It is well known that electronic mobility in conjugated organic polymers is greatly enhanced along a polymer molecule with conjugated bonds and also the delocalized electronic structure of these polymers is in part responsible for the stabilization of the various charge carriers (radical cations, dications, and their negative analogs) created upon doping (9, 10). In many cases, the conjugated electronic structure also involves a relatively small  $\pi\text{-}\pi^*$  band gap with strong absorption in the UV-visible range (11). Moreover, conjugated organic polymers have gained increasing interest in recent years as electrically conducting polymers (12–16). We now outline the synthesis and characterization of new conjugated polymer containing 4-phenylcyclohexanone moiety in the main chain. A major target of this work was to study the effect of phenyl ring as a rigid moiety upon the properties of polyconjugated polymers, including their solubility, thermal stability crystallinity, and conductivity.

## 2 Experimental

### 2.1 Measurement

Elemental analyses were performed with a Perkin–Elmer 240C Instrument. The IR spectra were recorded on a IR-200-91529 Shimadzu spectrophotometer using the KBr

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pellet technique.  $^1\text{H-NMR}$  spectra were run on a Bruker 11.1HO100-MHz NMR spectrometer at room temperature in dimethylsulfoxide (DMSO) using tetramethylsilane as the internal reference. The UV-visible spectra were scanned on a Shimadzu 2110 PC scanning spectrophotometer in dimethylformamide (DMF). Viscosity measurements were made with 0.5% (w/v) solution of polymers in DMSO at 25°C using an Ubbelohde suspended level viscometer. TGA was carried out in air with a Shimadzu TGA-50H thermal analyzers at a heating rate of 10°C/min. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 psi using an IR die to get pellets with a diameter of about 1.2 cm. Silver paste was used to make contacts between the pellets and two copper wires with a diameter of about 1.5 mm. The V-I characterization was taken to estimate the electrical conductivity at room temperature ( $\sim 25^\circ\text{C}$ ), using two digital multimeters for measuring V and I at normal atmosphere and the doping was done by the addition of 5% (w/w) to the polymer then pressing into a pellet. Joel-JSM—5610 LV scanning electron microscope together with carbon coating system were used to assess the particle size and the morphology of the produced polymer. A small amount from the powder of polymer speared on double adhesive sticker fixed on aluminum specimen holder, coated by carbon layer for about 10 nm thickness, and then examined by SEM.

## 2.2 Monomers and Reagents

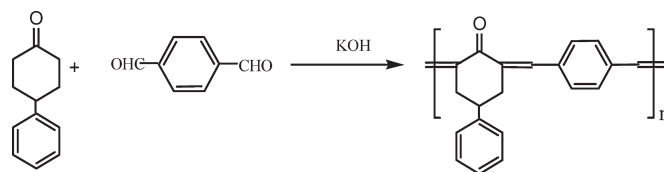
4-phenylcyclohexanone (Aldrich) was used without purification. Terephthalaldehyde was purchased from (Fluka) and recrystallized twice from water. Sodium hydroxide was analytical grade. All other chemicals and solvents were highly pure and purified by standard methods (17).

## 2.3 Polymerization

In a three-necked flask equipped with a condenser, a magnetic stirrer, and a dry nitrogen inlet and outlet, a mixture of 10 mmol (1.34 g) terephthalaldehyde and 10 mmol (1.74 g) 4-phenylcyclohexanone was dissolved in 50 mL of absolute ethanol and vigorously stirred at room temperature. Then a few drops of a 15% alcoholic solution of NaOH was added, the temperature was allowed to rise to 50°C over 45 min, and reflux was continued for 10 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. Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}$ : C, 88.23; H, 5.88% Found: C, 88.76; H, 5.96%.

## 3 Results and Discussion

In this work, was prepared new polyconjugated polymer based on 4-phenylcyclohexanone moiety by condensation of terephthalaldehyde with 4-phenylcyclohexanone in alcoholic

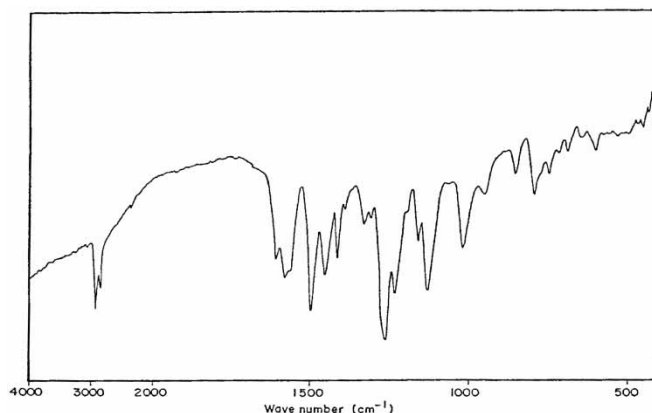


**Sch. 1.** Polymerization reaction of terephthalaldehyde with 4-phenylcyclohexanone.

sodium hydroxide gave the poly(2,6-dibenzyledene)-4-phenylcyclohexanone (Scheme 1).

The resulting polymer was characterized by elemental analysis, IR spectra,  $^1\text{H-NMR}$ , solubility, viscometry, TGA, X-ray analysis, conductivity measurements, and using the SEM. The elemental analysis of the polymer coincided with the characteristic repeating unit of the polymer. The spectral data support the structural assignments for the polymer and is in agreement with spectral data obtained for the polymer. IR data obtained in KBr disks for the polymer indicated the appearance of characteristic absorption bands at  $1695\text{ cm}^{-1}$  (C=O of 4-phenylcyclohexanone),  $1600\text{ cm}^{-1}$  for C=C groups,  $2985\text{--}2995\text{ cm}^{-1}$  for C-H aliphatic, and other characteristic absorption bands for the rest of the molecule (Fig. 1). The  $^1\text{H-NMR}$  (DMSO- $d_6$ ) showed peaks at 1.3 ppm (m, 4H, 2CH<sub>2</sub> of cyclohexanone), 2.6 ppm (pent, 1H, CH of cyclohexanone), 5.2 ppm (d, 2H of CH=C), and 7.0–8.2 ppm (9H of Ar-H) (Fig. 2).

The solubility of conjugated polymer synthesized in this study was determined for the powdery sample in various organic solvents including dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), tetrahydrofuran (THF), Dichloromethane (DMC) Tetrachloromethane (TCE),  $\text{CHCl}_3$ -acetone (1:1) and concentrated sulphuric acid at 3.0% (w/v). It was found that the polymer dissolved readily in concentrated  $\text{H}_2\text{SO}_4$  at room temperature giving deep red color due to the instability of the polymer. The polymer was soluble in various aprotic polar solvents such as DMSO, DMF, NMP and THF. The good solubility of the polymer may be elucidated by loose packing of the macromolecules because of pendent phenyl



**Fig. 1.** IR spectra of the conjugated polymer.

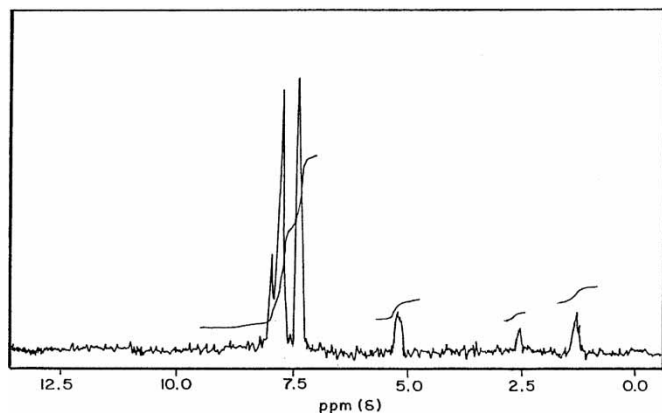


Fig. 2.  $^1\text{H-NMR}$  spectra of the conjugated polymer.

rings and low crystallinity (18). In common organic solvents and halogenated hydrocarbons the polymer was partly soluble. Therefore, the bulkiness of the pendent groups may play a more important role than rigidity in the improvement of the polymer solubility (19).

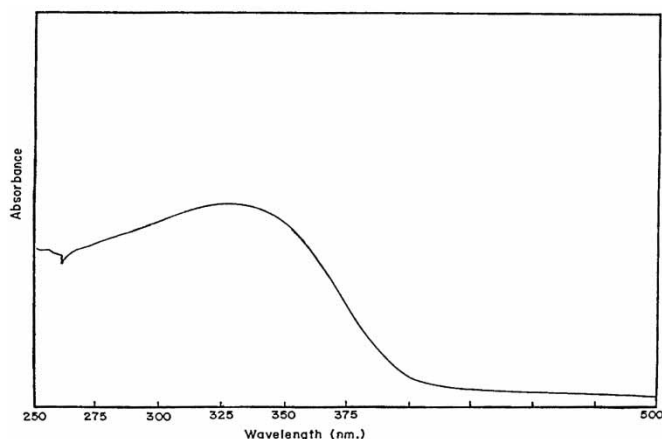


Fig. 3. UV-visible spectra of the conjugated polymer.

The inherent viscosity ( $\eta_{\text{inh}}$ ) of conjugated polymer was determined in DMSO at  $25^\circ\text{C}$  with an Ubbelohde suspended level viscometer. The inherent viscosity value is defined as:

$$\eta_{\text{inh}} = (2.3 \log t/t_0)/C$$

where  $t_0$  and  $t$  represent the viscometer flow periods for DMSO and the polymer solution, respectively; while solution concentration  $C$  is  $0.5 \text{ g}/100 \text{ ml}$ . The inherent viscosity was in the range of  $0.85 \text{ dl/g}$ .

The X-ray diffraction confirmed that the polymer was semi-crystalline because of a small portion of crystalline peaks in the region  $2\theta = 10\text{--}60^\circ$  or ( $d$  in  $\text{\AA}$ ) as shown in (Fig. 4). In spite of a small crystalline region in every case, amorphous patterns are due to a lower packing of the unsymmetrical polymer backbones. In particular, the bulky phenyl substituent, along the backbone most probably is the main reason for the amorphous nature of the present polymer, it is also evident that the presence of the phenyl substituent in the polymer main chain tends to destroy the polymers ability to form crystalline structure. It should be noted that the inclusion of 4-phenylcyclohexanone moiety as pendent group in the polymer main chain causes a slight decrease in the degree of crystallinity compared with those polymers based on diarylidencycloalkanones which were revealed in the literature (20).

The Ultraviolet and visible spectra of the polymer was measured in DMSO solution,  $1 \times 10^{-3} (\text{W/V})$ . The UV spectra of the polymer showed a broad absorption band at  $\lambda_{\text{max}}$ :  $375 \text{ nm}$  and  $250 \text{ nm}$ . The appearance of broad absorption band in the UV spectra is attributed to the excitation of  $(\pi - \pi^*)$  for  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  groups (Fig. 3).

The thermal stability of the conjugated polymer was evaluated by TGA. In Figure 5, the TGA curve shows a small weight loss in the  $1.5\text{--}2\%$  range over a temperature range of  $50\text{--}100^\circ\text{C}$ , which may be attributed to the loss of absorbed moisture and entrapped solvents. The thermal decomposition result of the polymer shows that it undergoes

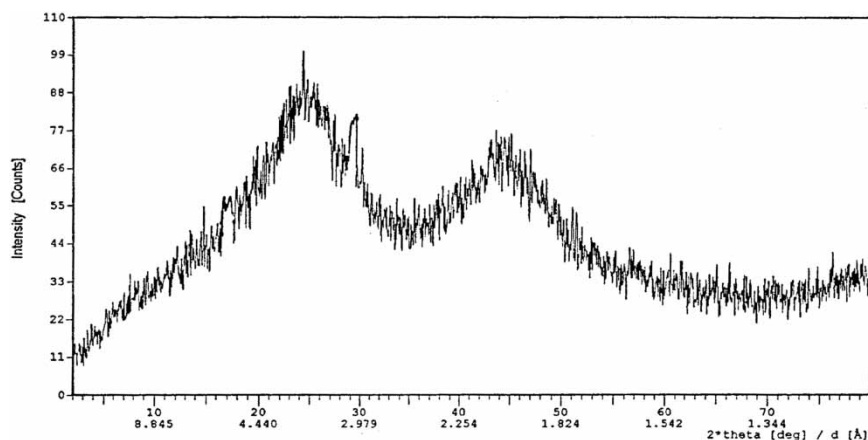


Fig. 4. X-ray diffraction patterns of the conjugated polymer.

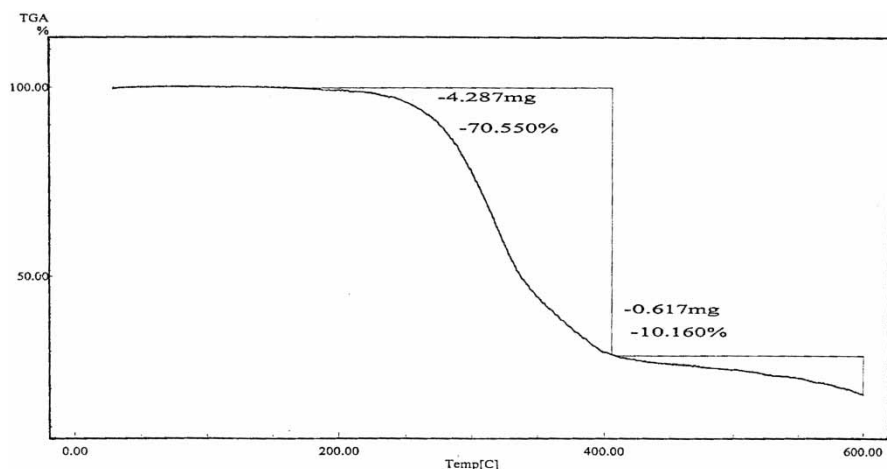


Fig. 5. TGA traces of the conjugated polymer in air at a heating rate of 10°C/min.

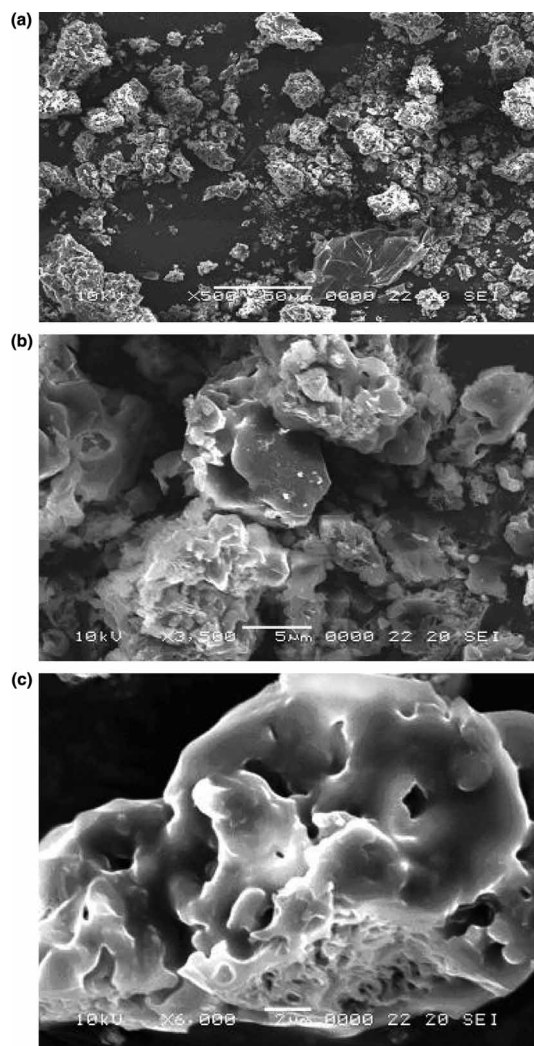


Fig. 6. (a) SEM micrograph showing some powder of produced polymer at low magnification, (b) SEM micrograph at magnification 3500X showing the morphology of the polymer particles, (c) SEM micrograph at 6000X showing the porous structure which has been recognized in the produced polymer.

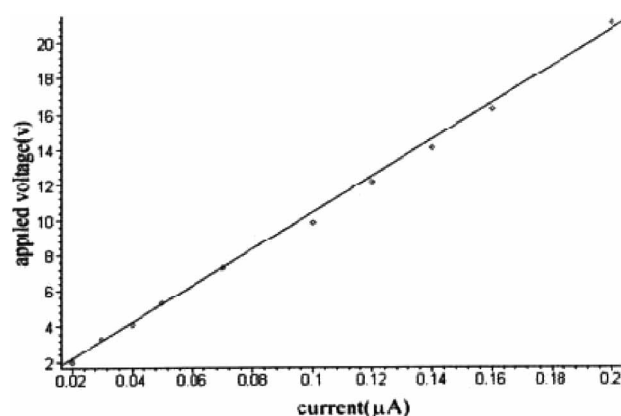


Fig. 7. Shows the relation between V and I for pressed sample of produced polymer.

50% wt. loss at 310°C. The expected nature of decomposition of the polymer is a pyrolytic oxidation of  $-C=C-$  scission of many bonds, in addition to the formation of char as an end product.

The observation by the SEM confirmed that the shape of most particles are irregular and porous, while some of them have flat surfaces. In addition, a wide range of particle size distribution was observed, the range is between a few microns up to about 10  $\mu\text{m}$ . The morphology and particle size distribution are shown in Figure 6 (a, b, and c). We expect that electrical conductivity in this sort of polymer is probably due to charge transport which occurs preferentially along the  $\pi$ -conjugated. The measurements showed a liner relation shape between V and I at room temperature and normal atmosphere. Figure 7 shows the relation of V and I, the electrical conductivity found to be within the range of  $8 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ , and this reflects that the value is in the region of the semiconductor. The results obtained in the present work could be compared with the values reported by Vasishta et al. (21), and higher than the values mentioned by Kamal (22) which were in

the range of  $10^{-9} - 10^{-10} \Omega^{-1} \text{cm}^{-1}$ . The novelty of this result is that the electrical conductivity of the new polymer was in the range of the semiconductor. The manifestation of electronic delocalization throughout the  $\pi$ -system requires that adjacent monomer units along the backbone to coplanar. This coplanarity tends to make the polymers inflexible. Phenyl ring as a pendent group and is believed to be due to the increased rigidity of the polymer chains and increase polar interactions between the polymeric chains. This is a direct result of the fact that the properties strengthen chain-chain interactions are also responsible for charge transport along the backbone of the polymer (23). In the case of the doped material ( $\text{I}_2$ ) the conductivity value of the polymer was found with in the range of  $2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ .

#### 4 Conclusions

A new conjugated polymer was synthesized by a solution of a polymerization technique. The conjugated polymer was soluble in aprotic polar solvents and  $\text{H}_2\text{SO}_4$ . X-ray diffraction analyses showed that the inclusion of pendant group in the polymer chain causes a decrease in the degree of crystallinity. The inherent viscosity was found to be 0.85 dl/g. The TGA of conjugated polymer showed good thermal stability, whereas the electrical conductivity was in the range of semiconducting properties at room temperature.

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