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Arylidene polymers

I. Synthesis, doping and electrical conductivity of poly(arylidenecycloalkanones)

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Summary

A new class of polyconjugated polymers namely poly(2,5-arylidenecyclopentanone) and poly(2,6-arylidenecyclohexanone) has been obtained by condensation of cyclopentanone or cyclohexanone with terephthaldehyde. Copolymerization of the corresponding monomers were also carried out. The model compounds were prepared from cyclopentanone or cyclohexanone with benzaldehyde and their structures were elucidated by IR, NMR, and elemental analyses. The polymers were charactrized by elemental analysis, IR, UV, viscometry, DSC measurements, thermogravimetric and X-ray analyses. Electrical conductivities in the insulating range 10^{-10} - 10^{-12} (ohm cm)$^{-1}$ were observed for the polymers 1,2, while the copolymers 3 gave 10^{-9} (ohm cm)$^{-1}$.

Doping with iodine increases the semiconducting values of the polymers 10^{-7} - 10^{-8} (ohm cm)$^{-1}$, whereas the increase in case of copolymer was more distinct 10^{-6} (ohm cm)$^{-1}$.

Introduction

Interest in the electrical properties of conjugated organic polymers is well established, and a great variaty of such materials have been recived attention (1-6). These materials are prepared by polymerization of simple monomers which are able to form a network of highly delocalized electrons. Such delocalization decreases the ionization potential and increases electron affinity to an extent such that the near molecule is easily attacked by an electron donor or acceptor (doping mechanism) (7) whereas, the undoped polymer is generally an insulator. The doped material shows conductivity values which may approach those of metals.

In this paper we wish to present a route for the synthesis of some new poly and copolyconjugated polymers containing cycloalkanone rings in the main chain. Influence of the monomer structure upon the polymer properties such as thermostability, solubility and conductivity was studied.

Experimental

The elemental analyses were done on a Perkin-Elmer 240 C Instrument. The IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer using KBr pellet technique. ^1H-NMR spectra were run on a Varian EM-390 90 MHz NMR spectrometer at room temperature in $CDCl_3$ using TMS as the internal reference. The UV, visible spectra were scanned on

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*To whom offprint requests should be sent a Varian CARY 219 spectrophotometer in sulfuric acid. The inherent viscosity of polymer solutions (0.5 g/100 ml) in sulfuric acid were determined at 30°C using a Ubbelohde Suspended Level Viscometer. The solubility of polymers were examined using 0.02 g of polymer in 3-5 ml of solvent at room temperature. X-Ray diffractographs were obtained with philips X-ray PW 1710 diffractometer, using Ni-filtered CuKα radiation. TGA and DSC were carried out in air with Du Pont, Model 951,910 and Du Pont 1090 thermal analyzers at heating rate of 10°C/min. Pellets for electrical conductivity measurments have been pressed at constant pressure 1000 psi using IR die. Silver paste was used to make contacts and sandwiched between two graphite electrodes. Conductivities have been measured at room temperature under air using 610 C Keithley Electrometer and Arrhenius plots were applied for calculations. Iodine doping was accomplished by vapour-phase doping technique (8).

Model Compounds

2,5-Dibenzylidenecyclopentanone(DBCp) and 2,6-dibenzylidnecyclohexanone (DBCh) were prepared as reported in literature (9,10).

Polymerization

In a three necked flask, a mixture of terephthaldehyde 0.1341 g (1 mmol) and cyclopentanone 0.0841 g (1 mmol) or cyclohexanone 0.0981 g (1 mmol) was dissolved in 50 ml ethanol and mechanically stirred under steam of dry nitrogen at room temperature (25°C). Then a few drops of 5% alcoholic solution of potassium hydroxide was added and the temperature was allowed to rise up to 45°C through 15 min. At the end of this time, a colored polymer was precipitated. The formed polymer was filtered off, washed with water, ethanol, acetone and dried.

Copolymerization

Similar procedure was applied as described above. The copolymer was synthesized by interaction of terephthaldehyde 0.1341 g (1 mmol) with a mixture of cyclopentanone 0.0425 g (0.5 mmol) and cyclohexanone 0.0495 g (0.5 mmol), yield 98.3%.

Results and Discussion

Literature survey revealed that interaction of dialdehyde (Terephthaldehyde) and diamines leads to polyimines as typically conjugated polymers by step growth polycondensation reaction (11). In continuation of our previous work concerning the synthesis and the chemistry of diarylidenecycloalkanone (with five, six, and seven membered rings) derivatives (9,10) and for the importance of polymers, we aimed in this work to prepare a new class of poly(arylidenecycloalkanone).

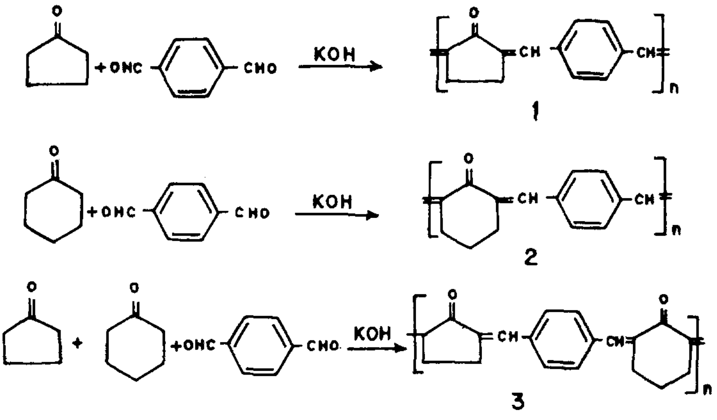
Condensation of terephthaldehyde with cyclopentanone and/or cyclohexanone in alcoholic potasium hydroxide afforded the poly-conjugated polymers namely poly(2,5-benzylidenecyclopentanone) PBCp 1 and poly(2,6-benzylidenecyclohexanone) PBCh 2. Copolycondensation of equinmolar quantities of terephthaldehyde with a mixture of cyclopentanone and cyclohexanone gave the copolymer 3 (Scheme 1).

The early precipitation of polymers within fifteen minutes after mixing the monomers indicated that the polymers were insoluble in the ethyl alcohol. This behaviour might be responsible for the low degree of polymerization as proved by their inherent viscosities (Table 1). These polymers were insoluble in almost organic solvents such as acetone, ethyl acetate, $CHCl_3$, CH_2Cl_2, CCl_4, CH_3CN, and partially soluble in polar aprotic solvent as DMF, NMP, DMSO and N,N-dimethylacetamide. In polar protic acids such as sulfuric acid, trifluoroacetic acid and methanesulfonic acid, the polymers were soluble at 30°C

To characterize these polymers, the model compounds of dibenzylidenecyclopentanone (DBCp) and dibenzylidenecylohexanone (DBCh) were synthesized by literature (9,10).

The IR spectra of polymers showed characteristic absorption bands at 1665-1695 cm^{-1} assigned to the (C=0 stretching), at 2950 cm^{-1} for C-H aromatic stretching and at 1620, 1580 cm^{-1} for aromatic in plane stretching of C=C.

UV visible spectra were obtained for model and polymers in H_2SO_4 at concentration 2.6×10^{-6}M and displayed two absorption bands at 245 nm due to π-π^* transition within the benzenoid system, and at 330 nm concerning π-π^* excitation of α,β-unsaturated ketone. The spectra of polymers showed absorption bands broadened and small bathochromically shifting of both bands, indicating the high conjugation in polymers.



Scheme 1

Table 1: Physical properties and conductivity of polymers.

Polymer No.	$^a\eta$.inh (dL/g)	Color	Yield %	Conductivity $(ohm\ cm)^{-1}$ Undoped	Doped
1	0.22	Yellow	97	2.1×10^{-10}	2.2×10^{-7}
2	0.23	Yellow	96	2.3×10^{-12}	2.1×10^{-8}
3	0.21	Yellowish	98	2.4×10^{-9}	2.5×10^{-6}

[a] Inherent viscosity in concentrated H_2SO_4 (0.5 g/100 ml) at 30°C.

Thermal characterization of polymers was carried out by DSC and TGA in air (Fig. 1) shows typical DSC traces of polymer 1,2 and copolymer 3. The large exotherms were attributed to thermal degradation because the TGA thermograms of these polymer showed considerable rate of weight loss in the respective temperature. Figure 1 shows that a broad exotherm appeared above 200°C. Since TGA traces did not show

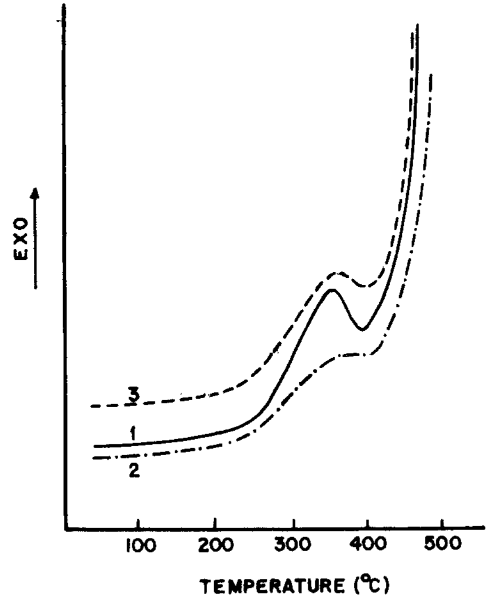


Fig.(1) DSC of polymers 1,2 and 3.

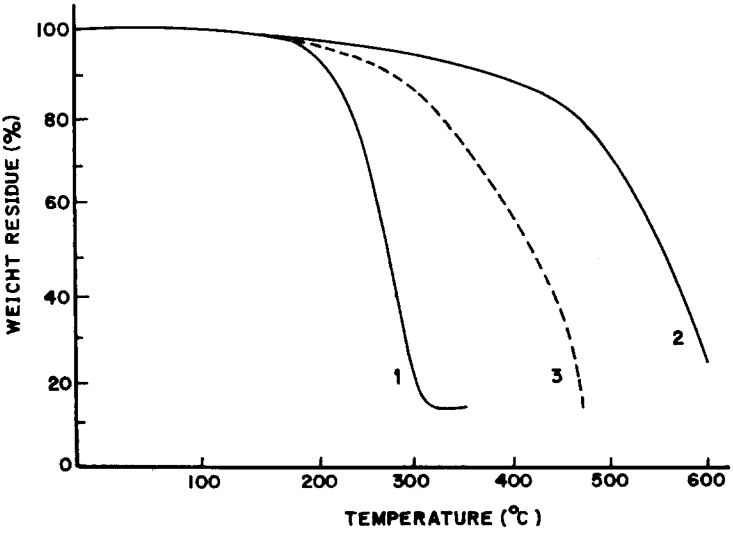


Fig.(2) TGA thermograms of polymers 1,2 and 3.

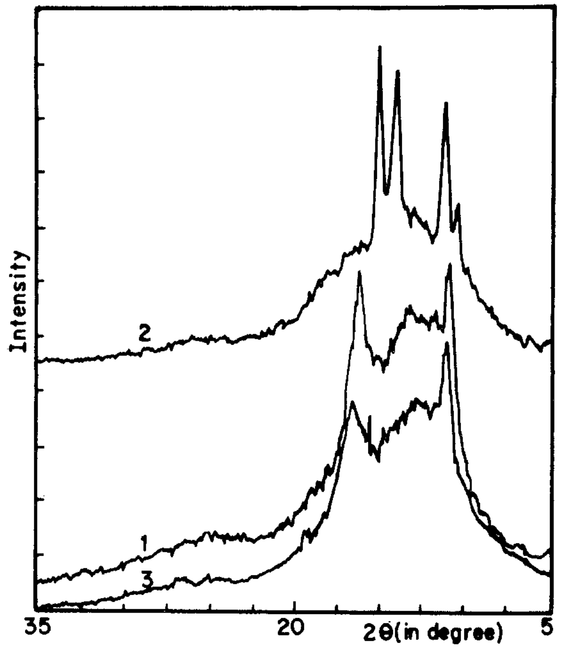


Fig.(3) X-ray diffraction patterns of polymer 1,2 and 3.

Table 2: Thermal properties of polymers.

Polymer No.	Mass Loss (%) 200°C	225°C	250°C	275°C	300°C	350°C	400°C
1	0	11.2	12	16	35	40	50
2	0	0	0	6.7	7	8	21
3	0	0	0	8.1	9	20	28

thermal degradation at this temperature, this exotherm should be attributed to curing reactions involving the olefinic bonds (12). The TGA thermograms of the polymers are shown in Figure 2 and the weight loss corresponding to temperatures are given in Table 2. The TGA data showed that the thermal stabilities of polymers were in the order 2>3>1.

Electrical conductivity measurment of undoped polymer 1 and 2 in the insulating range 10^{-10} - 10^{-12} (ohm cm)$^{-1}$, while undoped copolymer 3 gave 10^{-9} (ohm cm)$^{-1}$. Doping with iodine increases the semiconducting values of the polyconjugated polymers 10^{-7} - 10^{-8} (ohm cm)$^{-1}$, however the increase in case of copolymer was more distinct 10^{-6} (ohm cm)$^{-1}$.

X-Ray diffractogram of polymers 1,2 and copolymer 3 showed a few reflections of sharpness peaks intermediate between crystalline and amorphous interferences. This indicated that there is a large class of structures intermediate in ordered state between crystal with pronounced long range order and an isotropic liquid with short range order in the arrangement of its atoms and molecules (Fig. 3). Moreover, the presence of C=0 as a polar groups in addition to high C=C bonds induces some order between two adjacent chains in the polymer towards some extent of crystallinity (13). Also, the diffractogram indicated that PBCh 2 has high degree of crystallinity in comparison with PBCp 1 and the copolymer 3.

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